Max Planck Institute
for Solid State Research

TOPOLOGICAL MATERIALS AND SOLID STATE CHEMISTRY

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TOPOLOGICAL MATTER SCHOOL 2017

DONOSTIA-SAN SEBASTIAN

08/24/17

NEW MATERIALS

- Make materials that are of interest for PHYSICS
- Use CHEMSITRY knowledge to create them

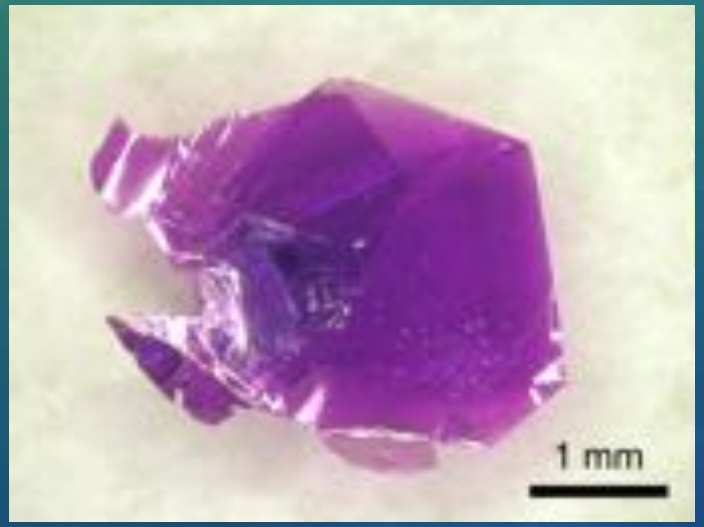


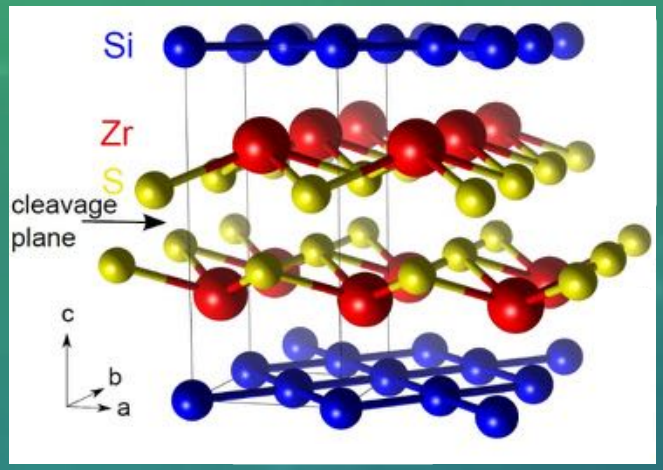
Image from https://epd.sutd.edu.sg

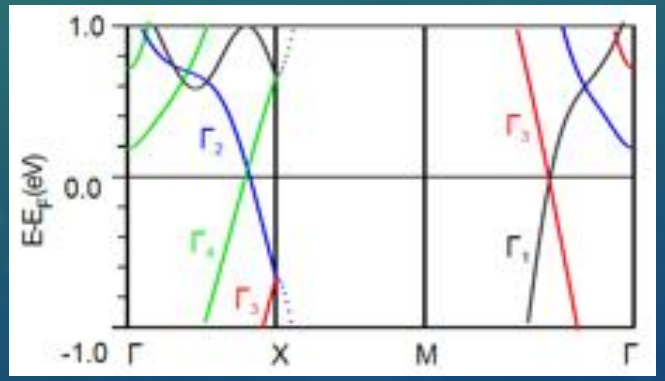
WHY MAKE NEW MATERIALS? EXAMPLE: QUANTUM COMPUTING

- Topological qubits still need to be invented
- This requires new materials

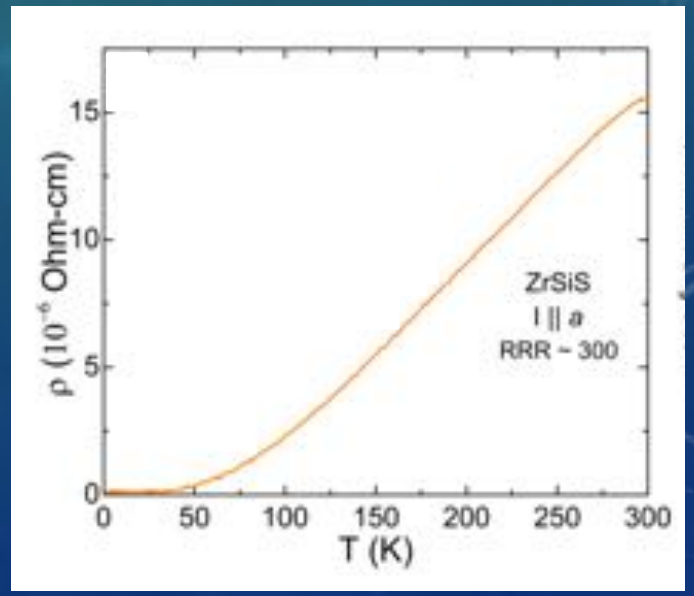
Science News, Dec 1st 2016

Crystal chemistry and structure



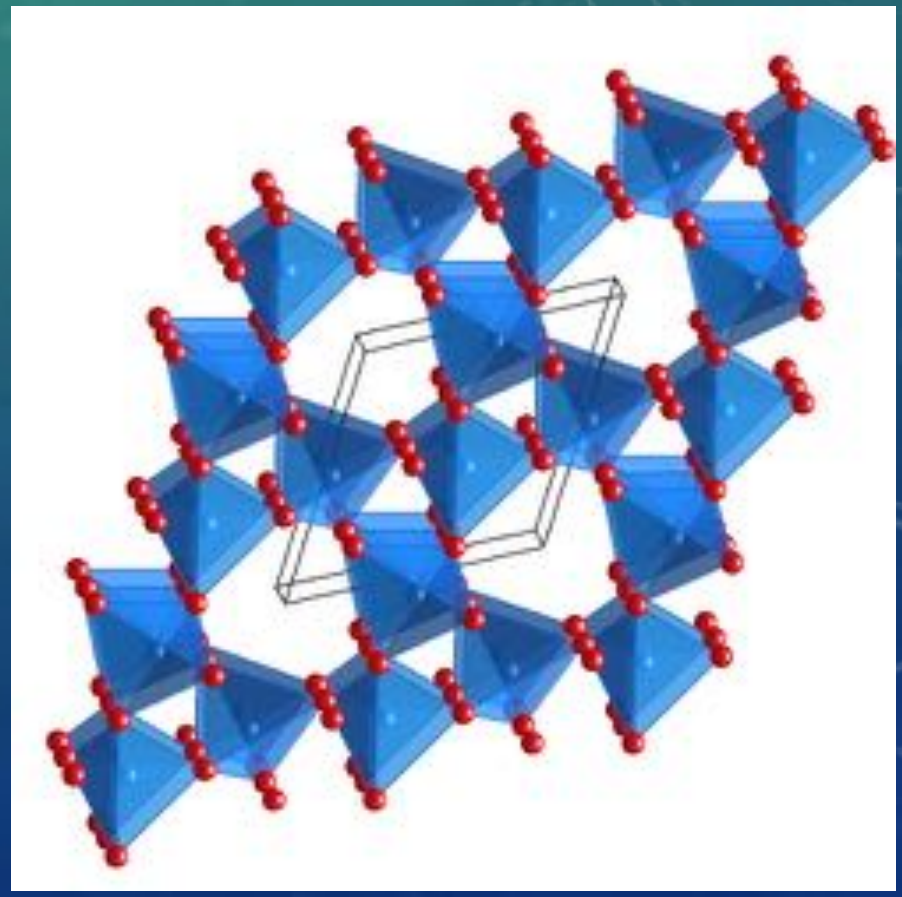


Electronic structure



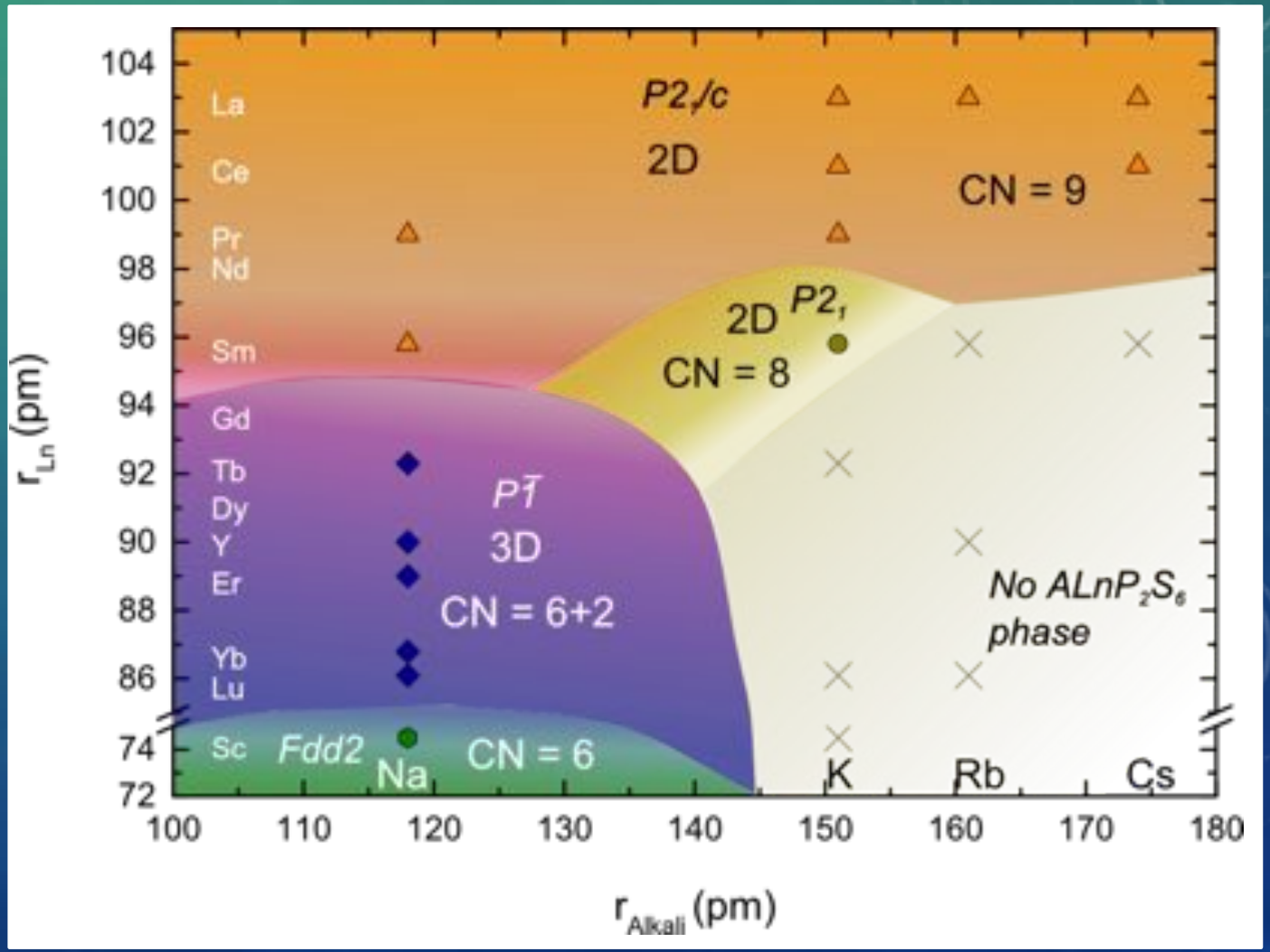
Properties

THE STRUCTURE OF MATTER



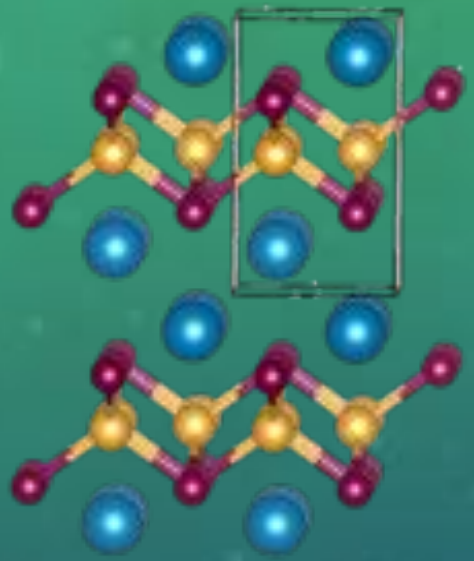
WHAT IS SOLID STATE CHEMISTRY ABOUT?

- Traditionally: The structure of matter
- Crystal structures
- Bonding
- What are stable structures for compositions?
- Electron counting
- Ionic and atomic radii

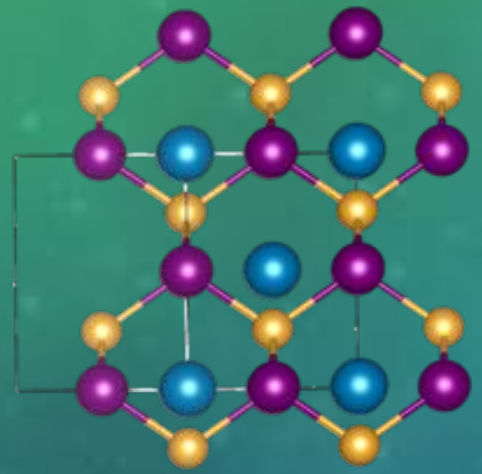


Schoop, Eger, Kuhn, Nuss, Kremer, Lotsch *inorganic chemistry,* 56 (3), 1121-1131 (2017)

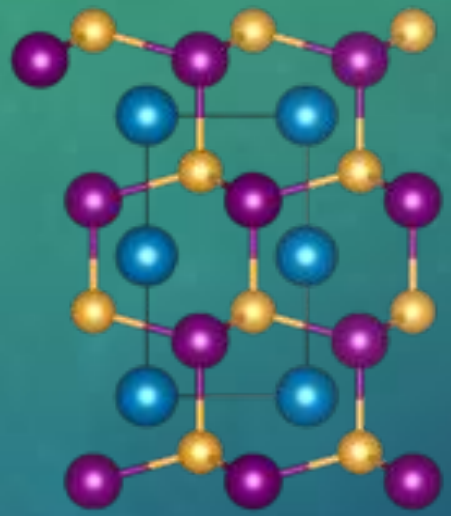
THE STRUCTURE OF MATTER - WHICH STRUCTURE IS STABLE?



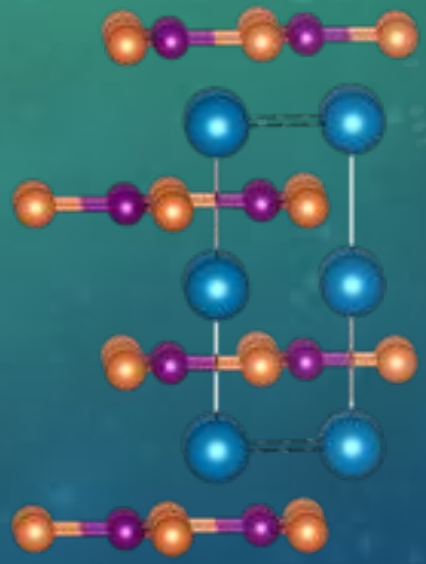
PbFCl



MgAgAs
(half Heusler)



LiGaGe



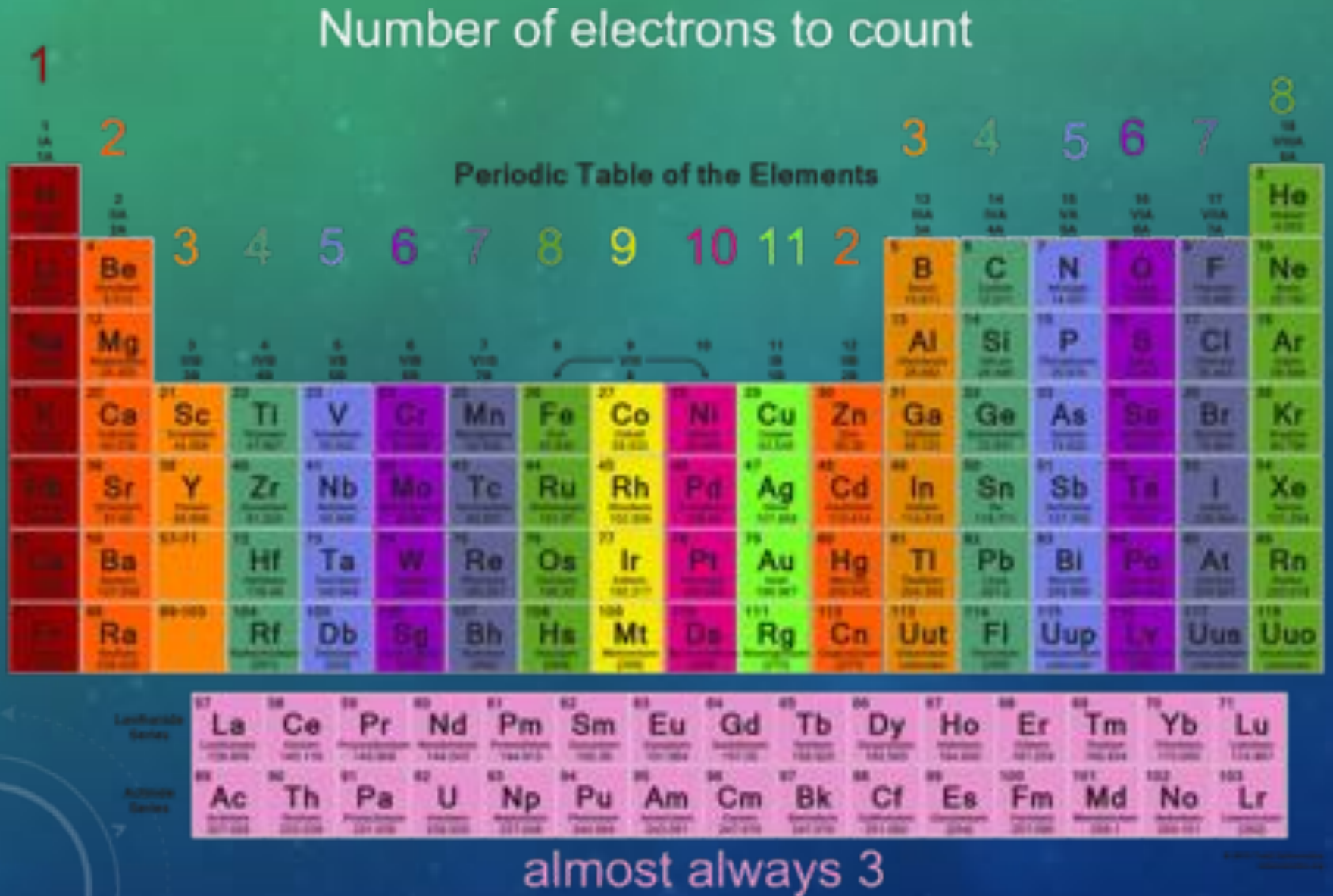
ZrBeSi

TiNiSi

Governed by:

- Electron count
- Sizes of the elements
- Type of bonding

ELECTRON COUNTING: A QUICK GUIDE



2

8

18

Number of electrons for filled shell

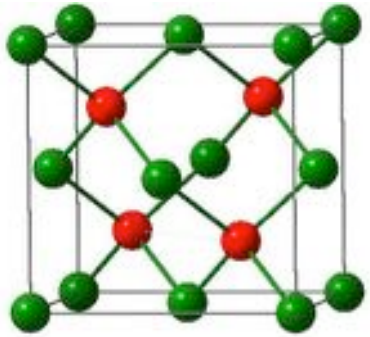
NaCl: 1+7 = 8

CaF_2: 2+2*7=16

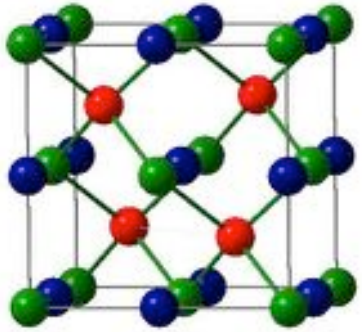
→ 8 per F

SOME EXAMPLES

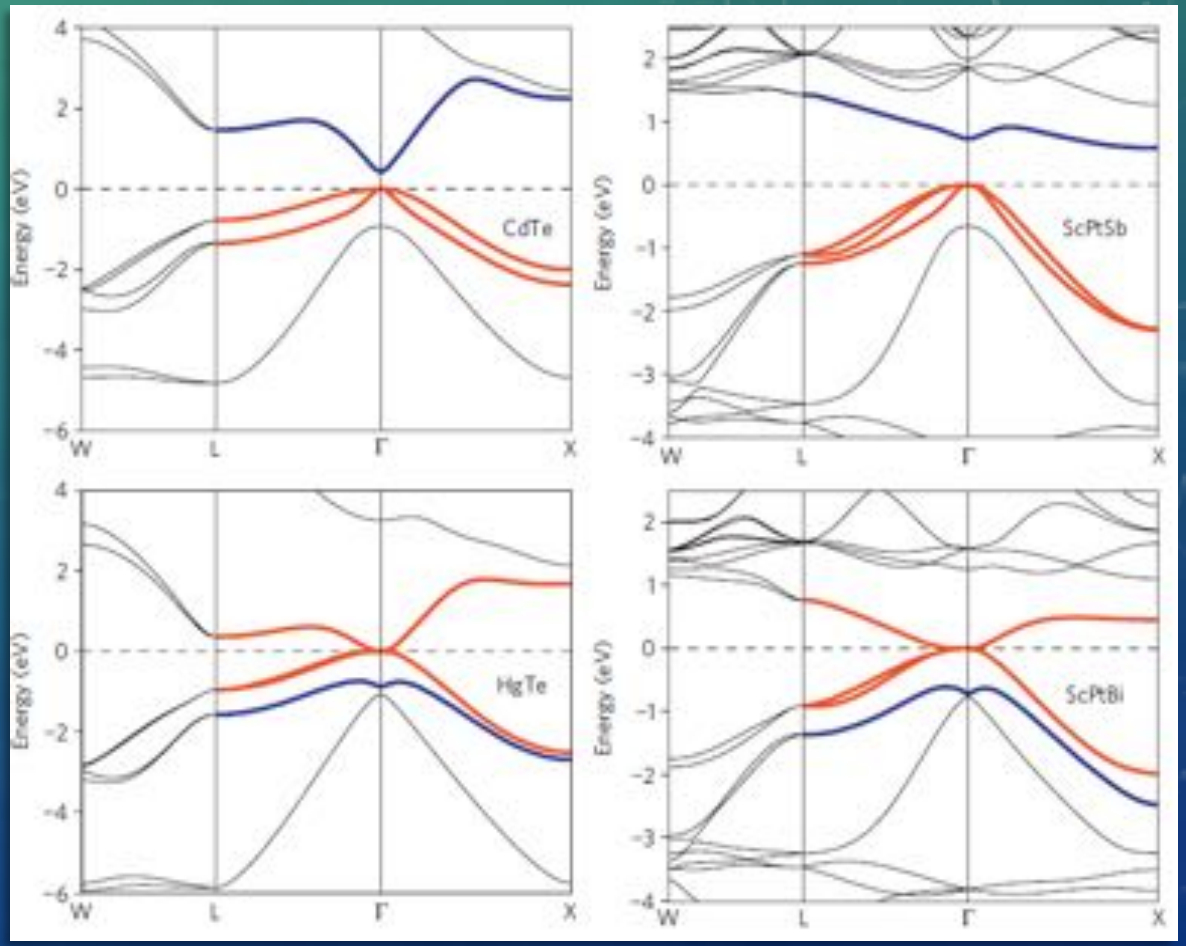
GaAs,CdTe, HgTe



Heusler XYZ



Ga	As		3 + 5 = 8
Li	Mg	As	1 + 2 + 5 = 8
Sc	Pt	Sb	3 + 10 + 5 = 18

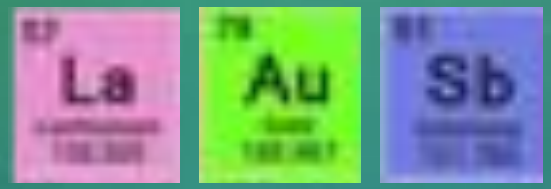


Graf, Felser, Parkin, Progress in Solid State Chemistry 39 (2011) 1.

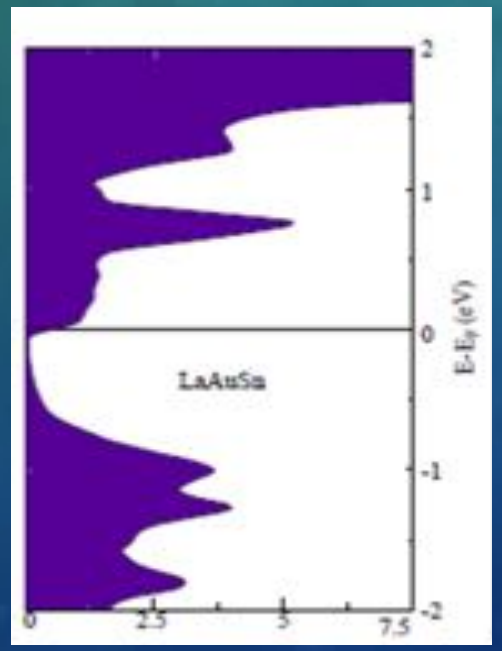
Credit: Claudia Felser and Binghai Yan

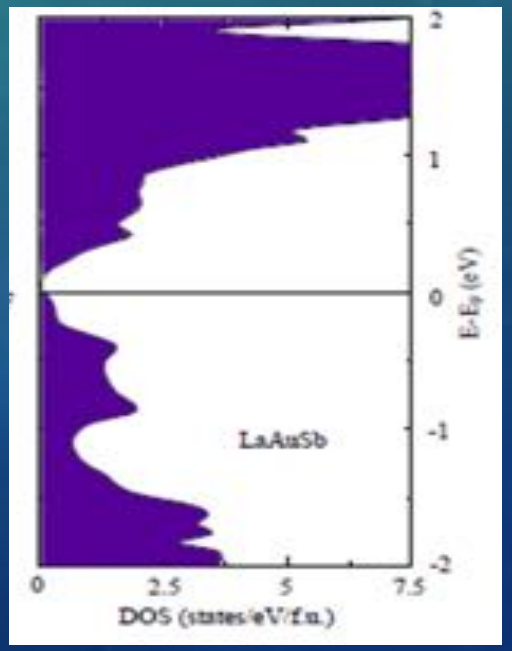
ELECTRON COUNTING AND BONDING

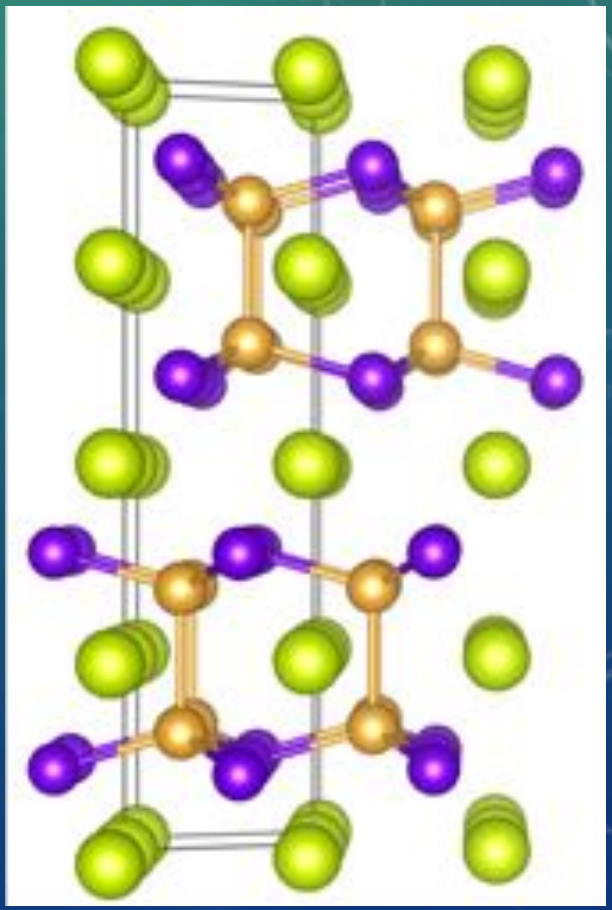
- Found new phases LnAuSb
- Known related phases: 18 electrons and charge balanced
- Why are our phases stable too?
- Au-Au bond!
- One electron localized in Au-Au bond



3+11+ 5 = 19





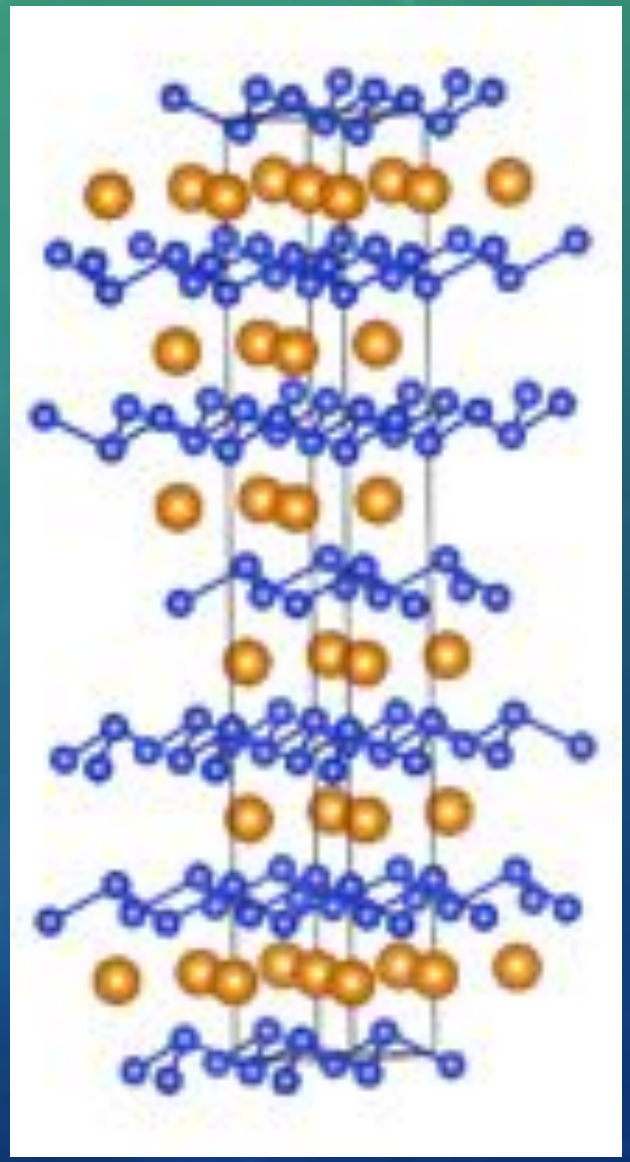


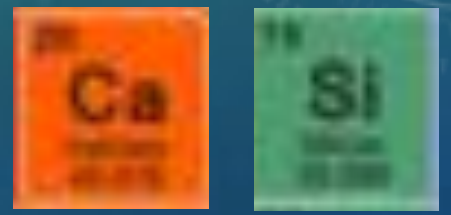
Seibel, Schoop, et al . Gold-Gold Bonding: The Key to Stabilizing the 19-Electron Ternary Phases LnAuSb (Ln= La-Nd and Sm). Journal of the American Chemical Society, 2014.

ZINTL PHASES

- Zintl Ions can make electron counting complicated
- Polyanions or Polycations

- Example: $CaSi_2$: Ca^{2+} and Si_2^{2-}
- Si_2^{2-} is polyanion
- You need to look at the crystals structure to know how to count electrons!



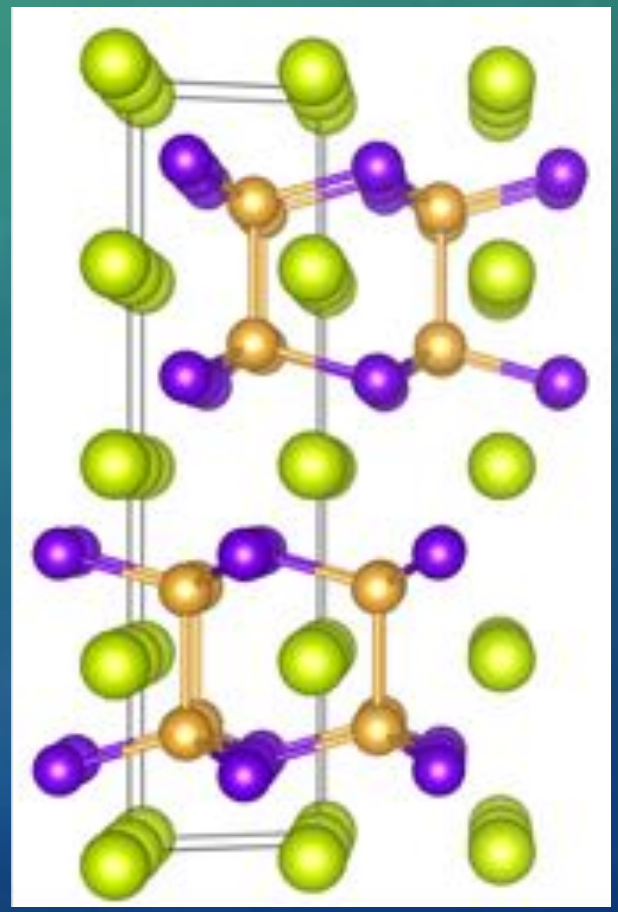


2+2*4 = 10

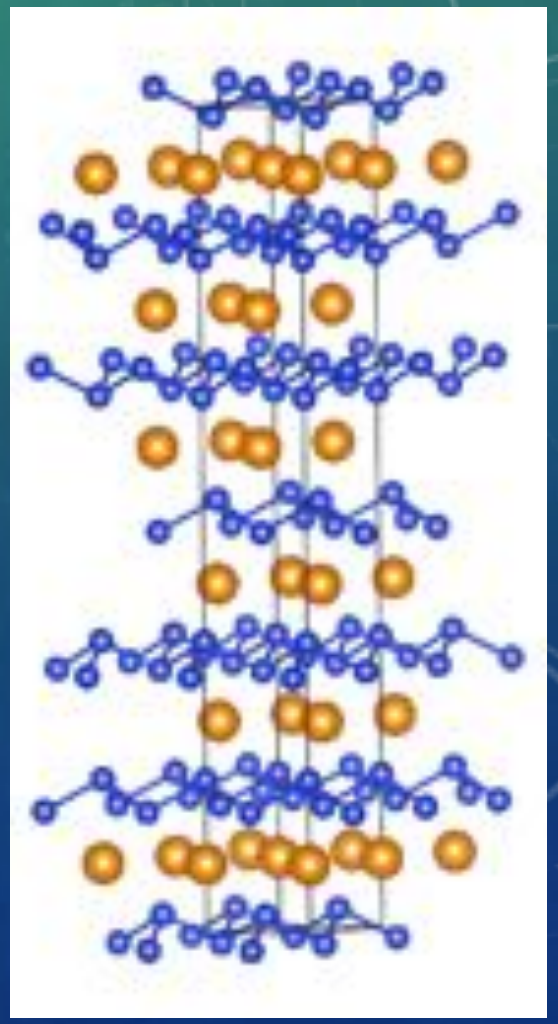
5 per Si

WHY SOMETIMES MORE AND SOMETIMES LESS ELECTRONS?

- Polycations: bonding electrons don't count towards valence electron count
- Polyanions: Anions need less electrons to be closed shell. They SHARE electrons. Add number of bonds to electron count
- VEC(X) > 8 → Polycations
- VEC(X) < 8 → Polyanions



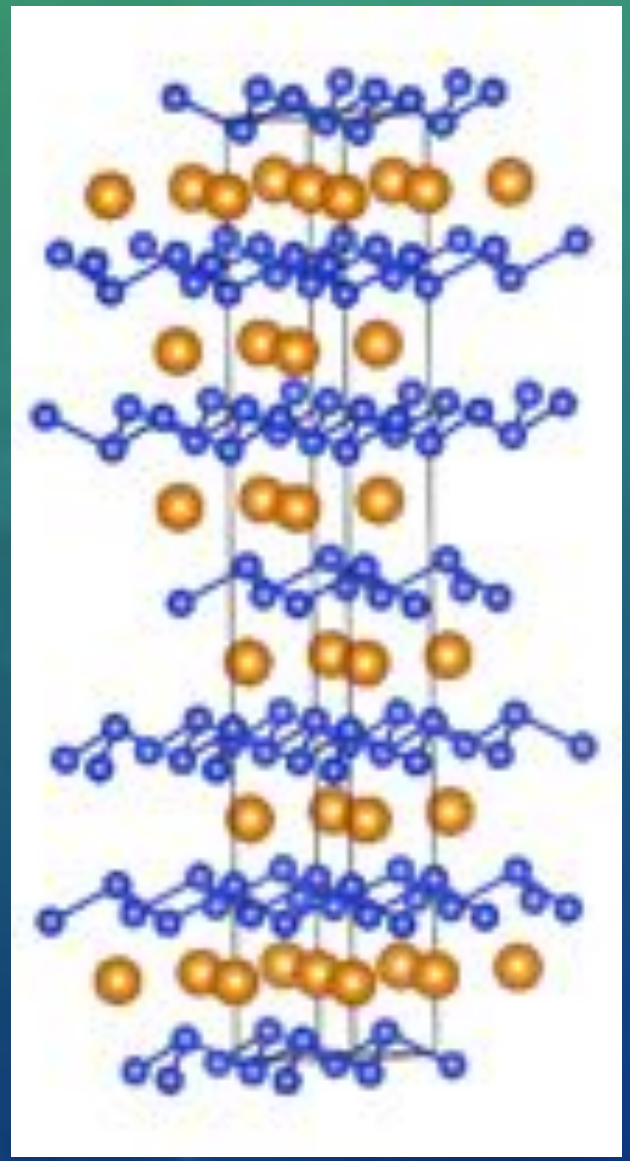
Polycation

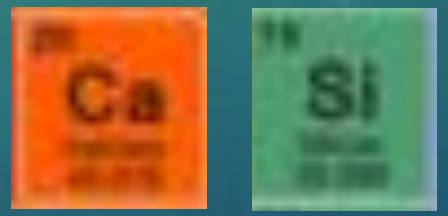


Polyanion

ZINTL PHASES: COUNT ELECTRONS TO FIND NUMBER OF BONDS

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





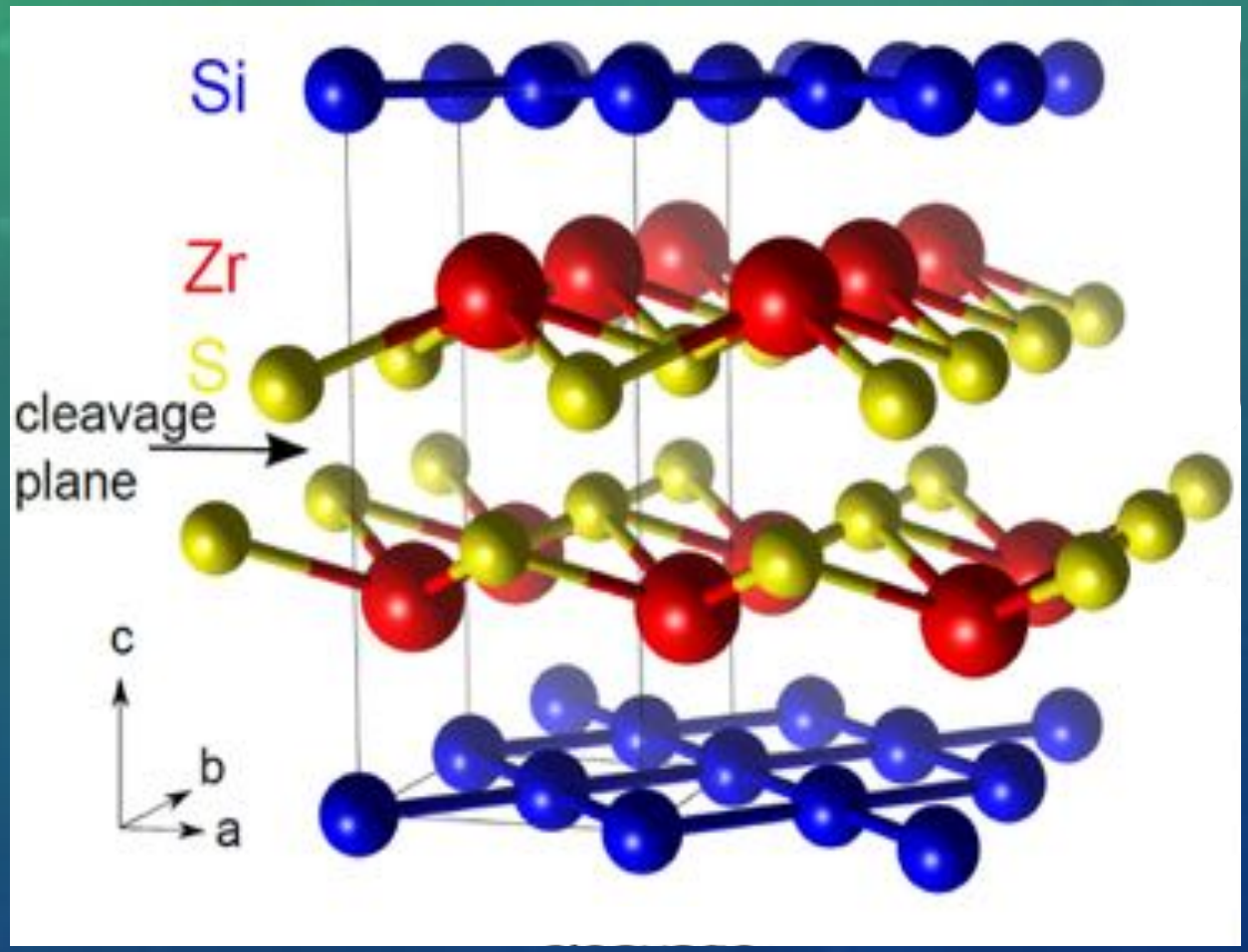
2+2*4 = 10

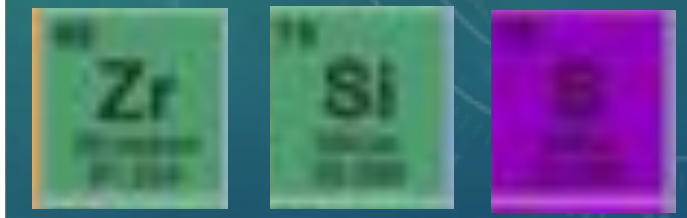
5 per Si

b(Si-Si)=8-5=3

ZINTL PHASES: COUNT ELECTRONS TO FIND NUMBER OF BONDS

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



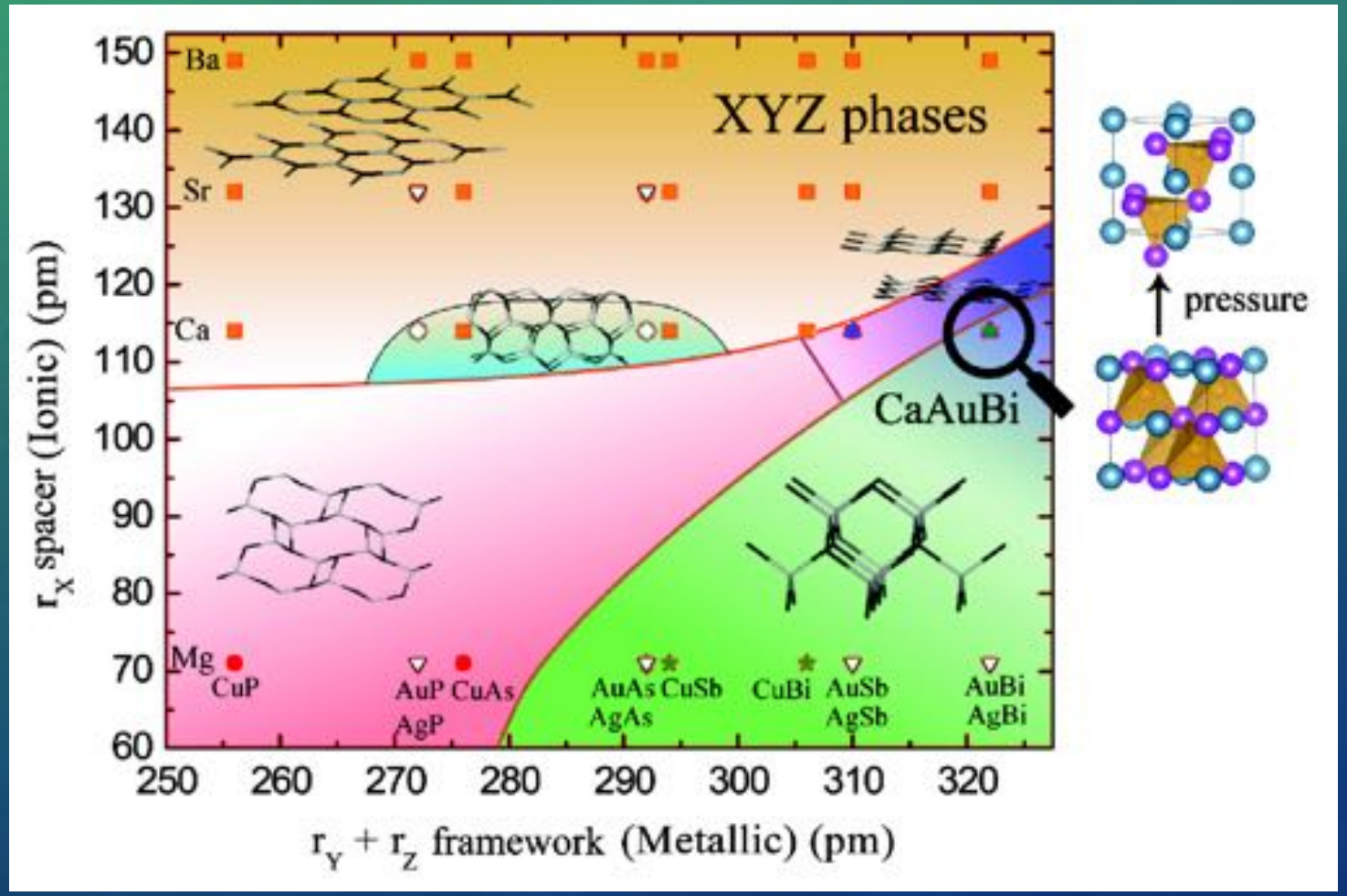


4+4+6 = 14

14 per Si

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

SIZE MATTERS!



X YZ

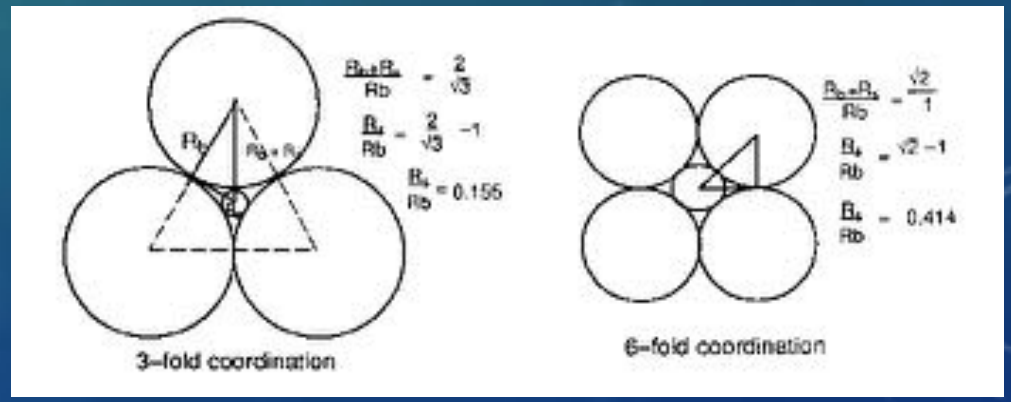
Ca CuP
Ba AgBi

Schoop, Xie, Medvedev, Felser, Cava *Solid State Sciences* 30 (2014): 6-10.

IONIC RADII – PAULING RULES

- A coordination polyhedron of anions is formed around each cation, wherein:
- The cation-anion distance is determined by the sum of the ionic radii, and
- The coordination polyhedron is determined by the cation/anion radius ratio

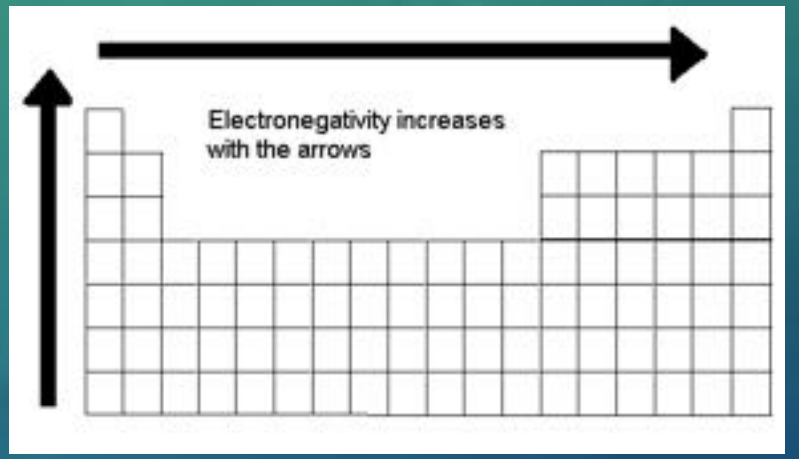
$r_k/r_a > 0.732$ cubic coordination
r_k/r_a 0.424-0.732 octahedral coordination
$r_k/r_a < 0.424$ tetrahedral coordination

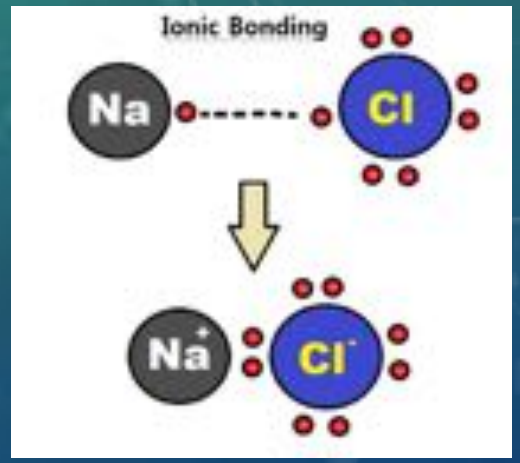


http://abulafia.mt.ic.ac.uk/shannon/ptable.php

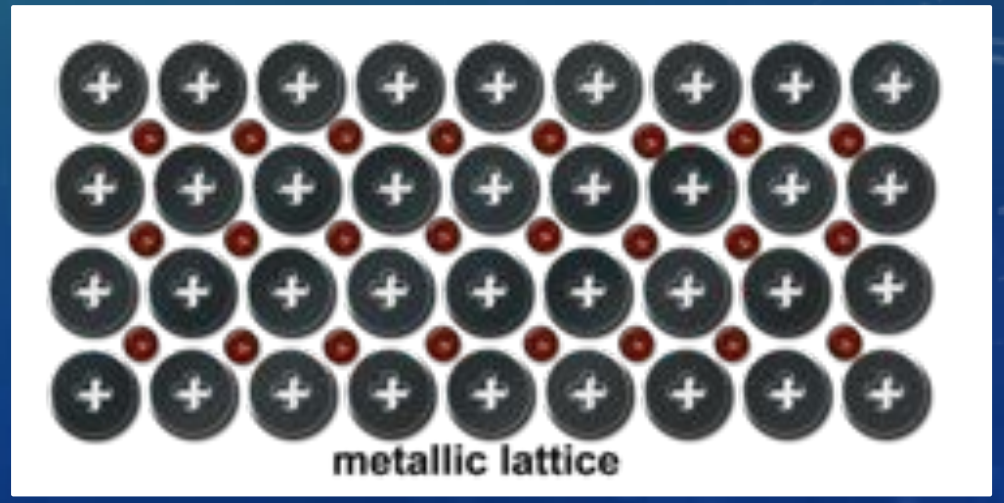
ELECTRONEGATIVITY DIFFERENCE – IONIC VS COVALENT BONDING

- Large difference in electronegativity: ionic bonding. Only charge balance (salt like) compounds possible



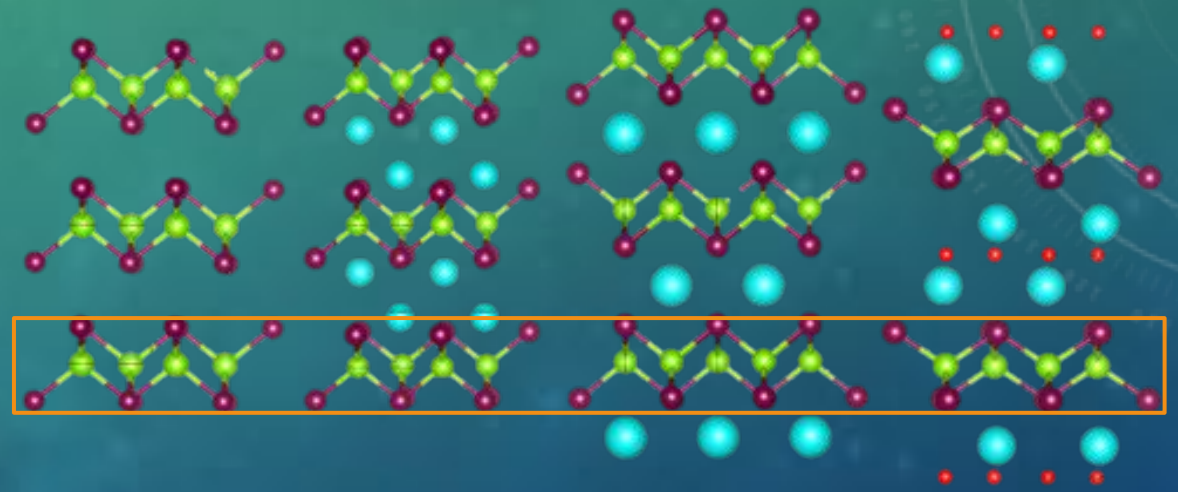


- Small electronegativity difference : covalent bonding. Also metallic compounds possible



CONNECT KNOWLEDGE ABOUT STRUCTURE AND COMPOSITION WITH PROPERTIES

- Properties often run in certain structure types
- Famous example: Superconductors



- Knowledge about structural stability is very important!

Frustrated magnets
Honeycomb, kagome…

Dirac Materials
High symmetry

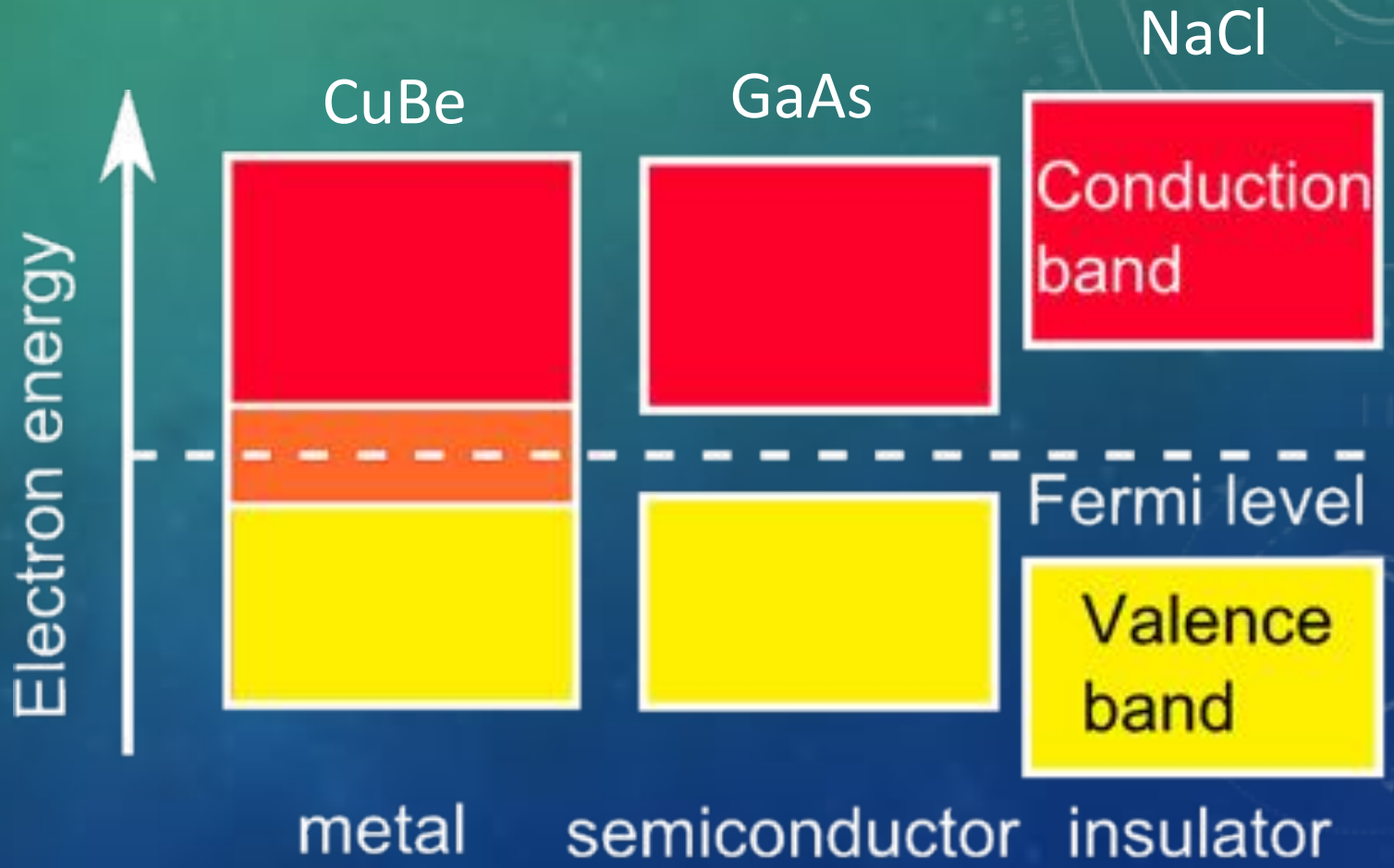
Quantum criticality
Borderline to magnetism

Superconductors
Structural families

Topological insulators
Heavy elements

CHEMICAL CONCEPTS: GIVE BASIC IDEAS ABOUT PROPERTIES

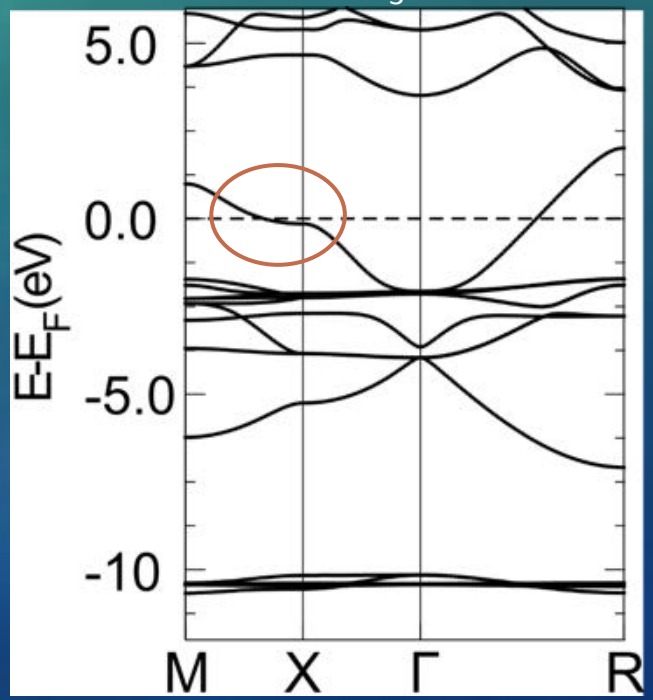
- Electron count (8 or 18)
- Electronegativity difference
- Heavy vs. light elements



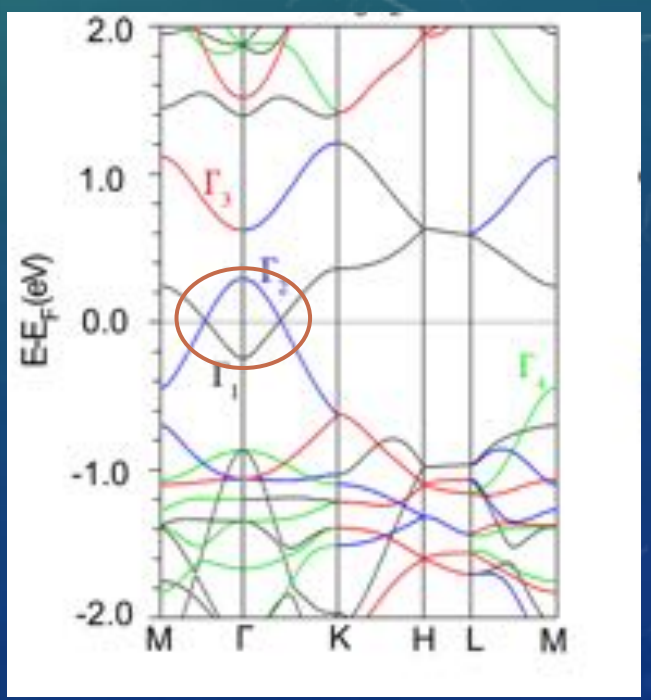
ELECTRONIC STRUCTURE CALCULATIONS

- The electronic structure can give important hints for a materials property
  - Topological materials: Clearly defined by their electronic structure
  - Superconductivity: van Hove singularity, steep DOS

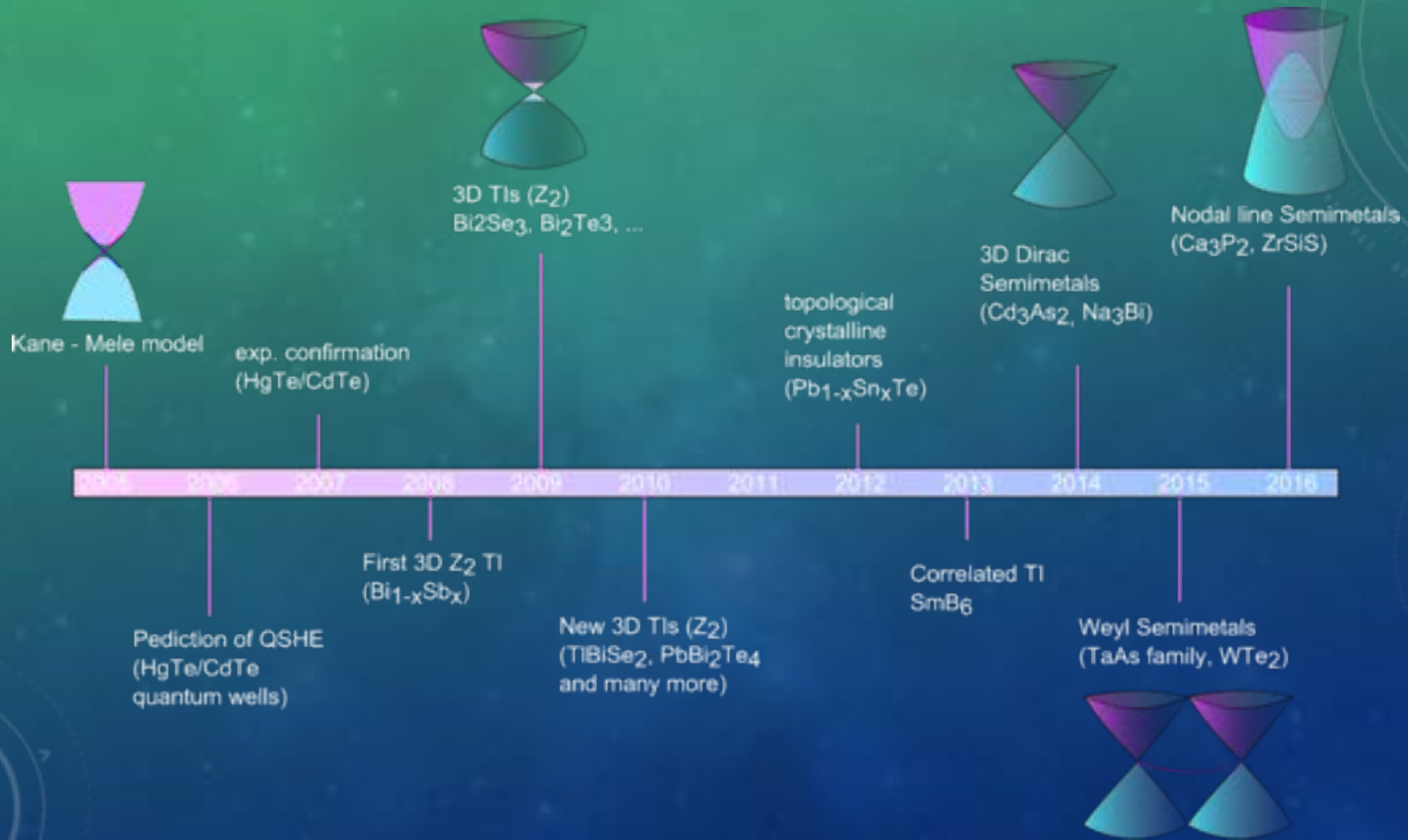
$RbTlCl_3$



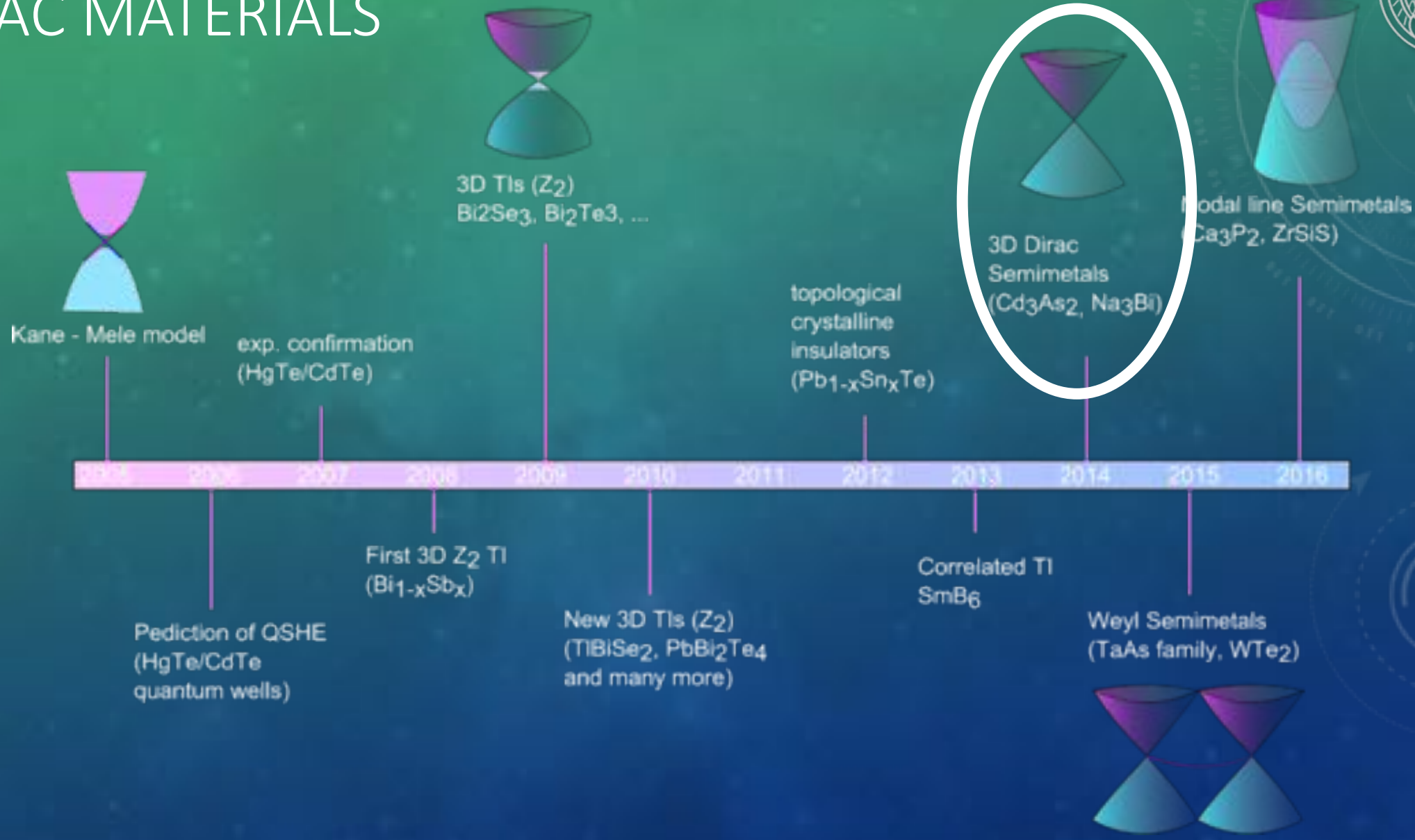
Ca_3P_2



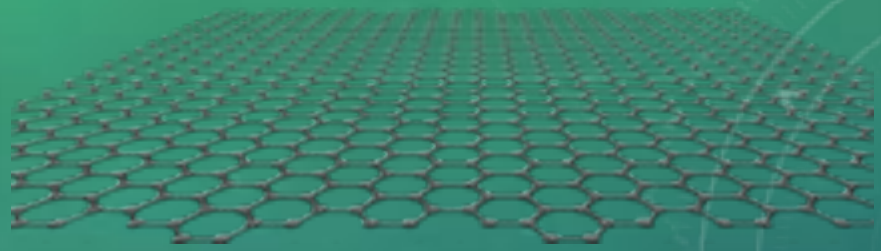
DISCOVERY OF TOPOLOGICAL MATERIALS: TIME LINE



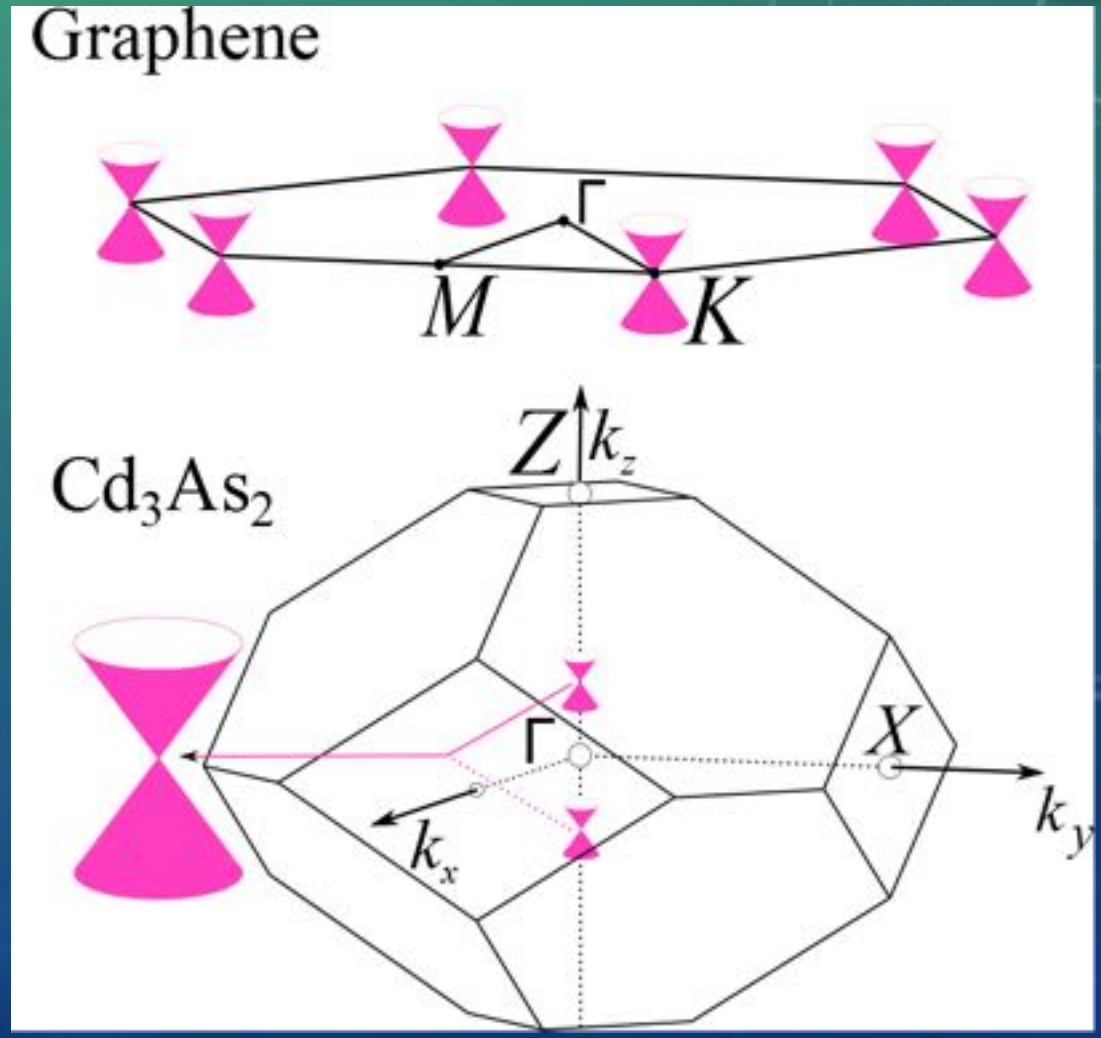
1) DIRAC MATERIALS



3D DIRAC SEMIMETALS



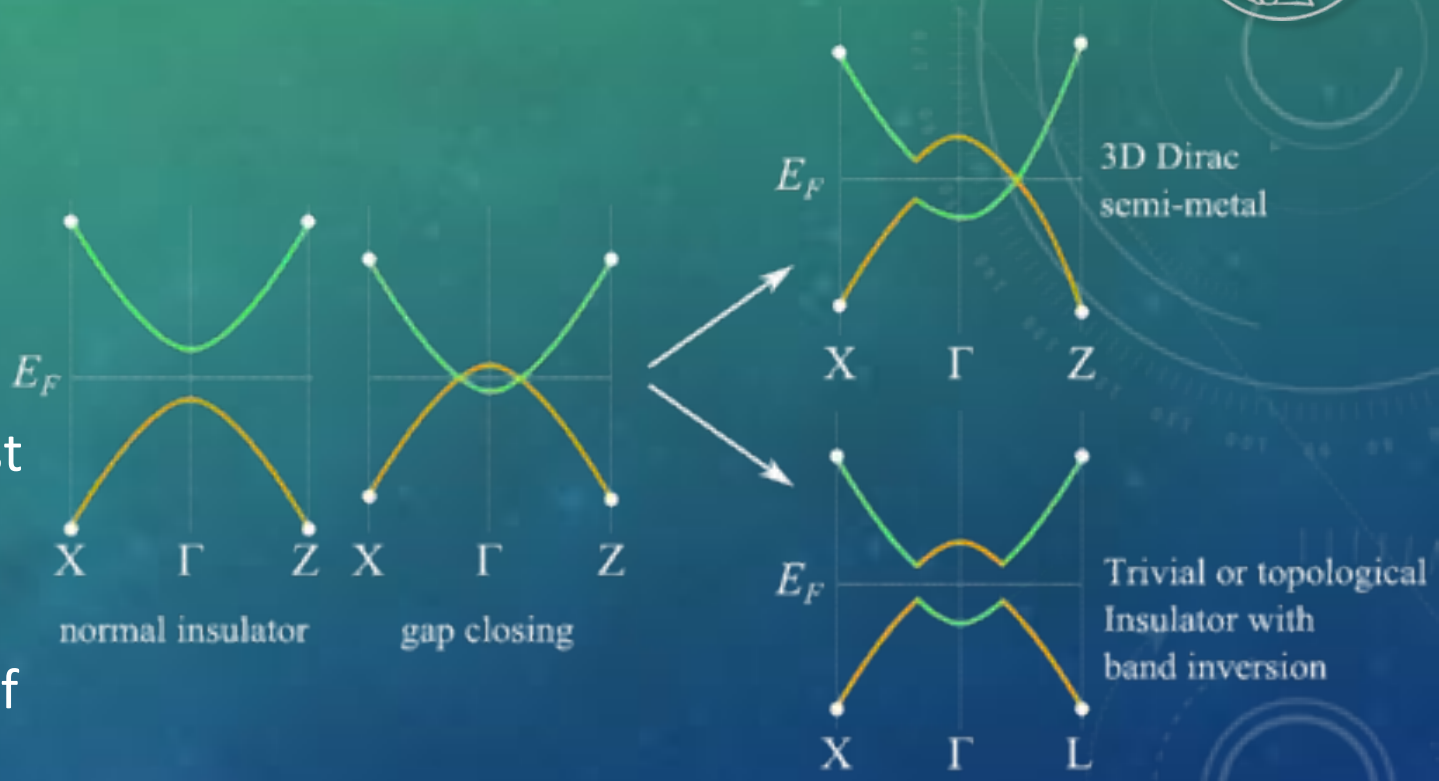
- 3D analogue of graphene
- Linear dispersed bands result in mass-less electrons
- Exceptional properties such a very high carrier mobility and extreme magnetoresistance
- Could find application in electronics
  - ultrahigh frequency transistors
  - novel electronics
  - qubits for quantum computing

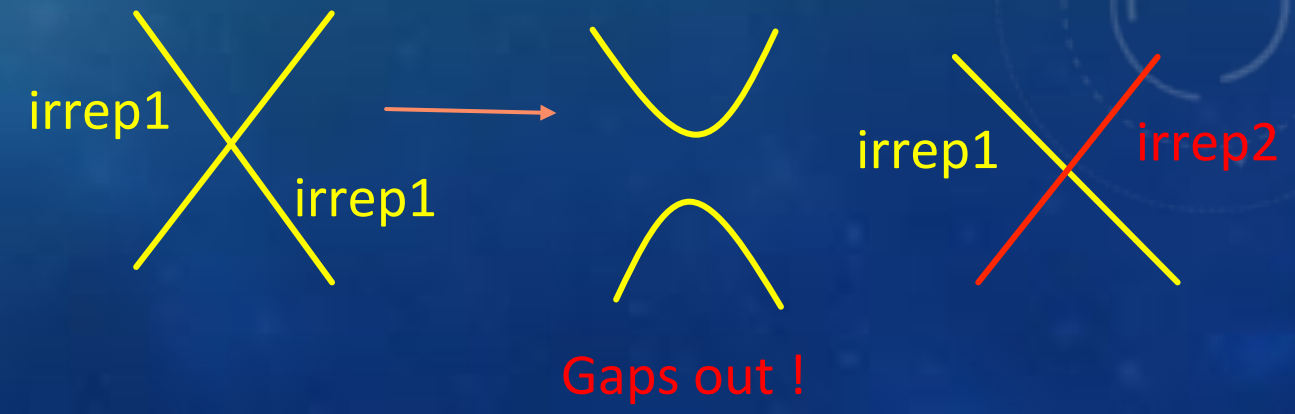


Gibson, Schoop, Muechler, Xie, Hirschberger, Ong, Car, Cava Phys. Rev. B 91 (20), 205128 (2015)

SCHEMATIC BAND STRUCTURE OF 3D DIRAC SEMIMETALS

- Band inversion needed
- In order to not gap, the crossing bands must have different irreps (group theory)
- In the presence of SOC double group is needed not point group (reduces number of irreps)
- Only C_3, C_4 or C_6 symmetry allow enough irreps





EXAMPLE: POINT GROUPS C_{2V} AND C_{4V}

Without SOC

		E	$C_2(z)$	$\sigma_v(xy)$	$\sigma_v(yz)$
Γ_1	A_1	1	1	1	1
Γ_2	B_2	1	-1	1	-1
Γ_3	A_2	1	1	-1	-1
Γ_4	B_1	1	-1	-1	1
With SOC					
Γ_5	$E_{1/2}$	2	0	2	0

Without SOC

		E	$2C_4(z)$	C_2	$2\sigma_v$	$2\sigma_d$
Γ_1	A_1	1	1	1	1	1
Γ_2	A_2	1	1	1	-1	-1
Γ_3	B_1	1	-1	1	1	-1
Γ_4	B_2	1	-1	1	-1	1
Γ_5	E	2	0	-2	0	0
With SOC						
Γ_6	$E_{1/2}$	2	/2	0	0	0
Γ_7	$E_{3/2}$	2	-/2	0	0	0

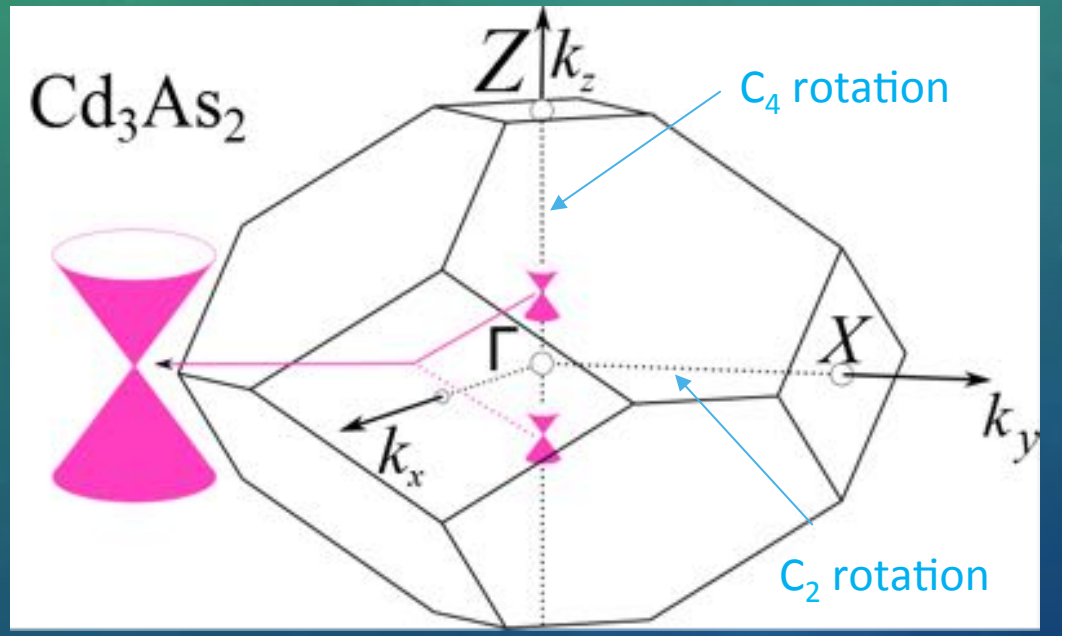
Higher symmetry allows for more irreps
But crossings are still coincidental!

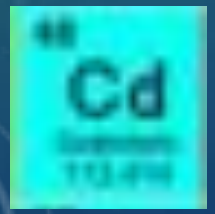
To find Dirac Semimetals:
Look for highly symmetric charge balanced compounds with not too high electronegativity difference and some SOC

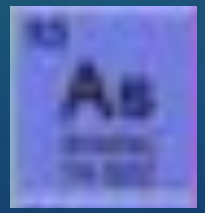
EXAMPLE: Cd_3As_2

- Look for high symmetry materials
- Need band inversion
- Charge balanced: count electrons

Tetragonal: a = b ≠ c



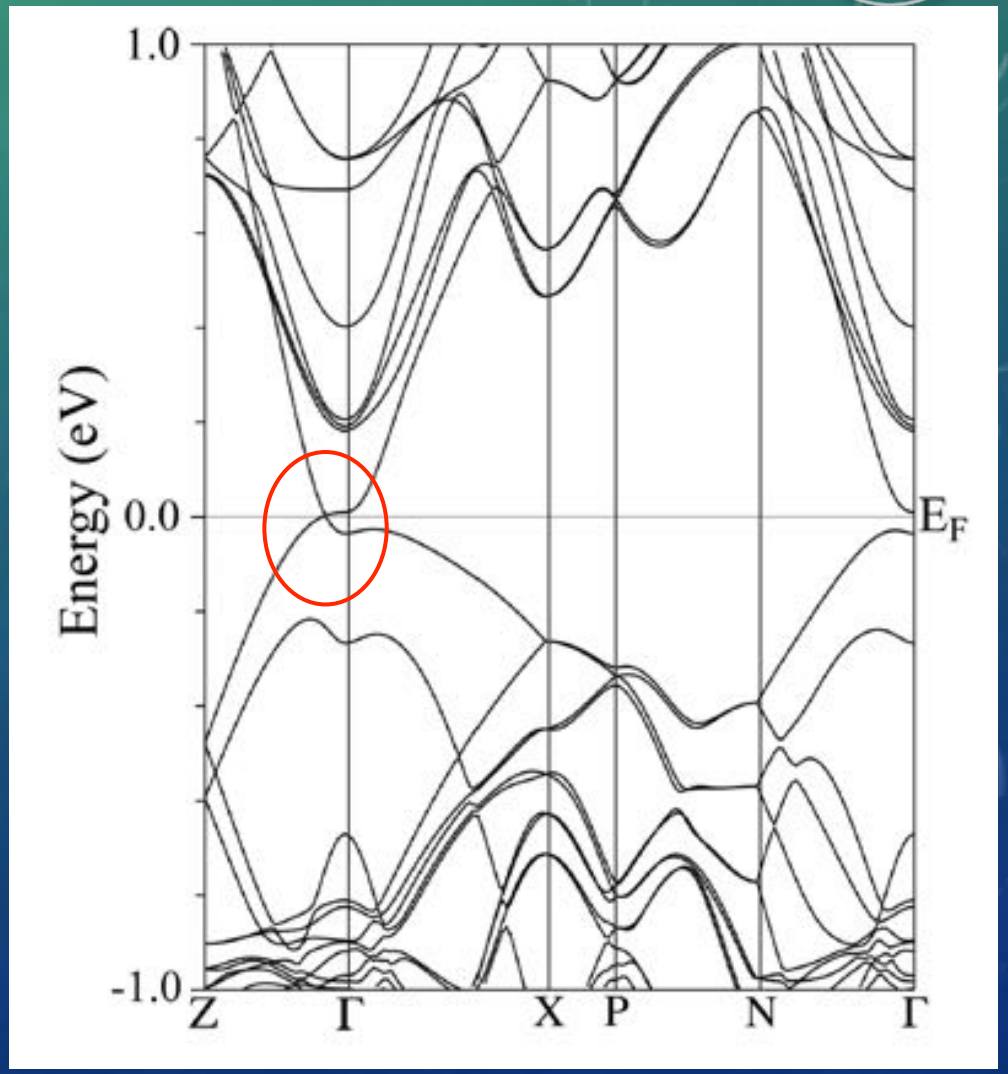




3*2+2*5 = 16

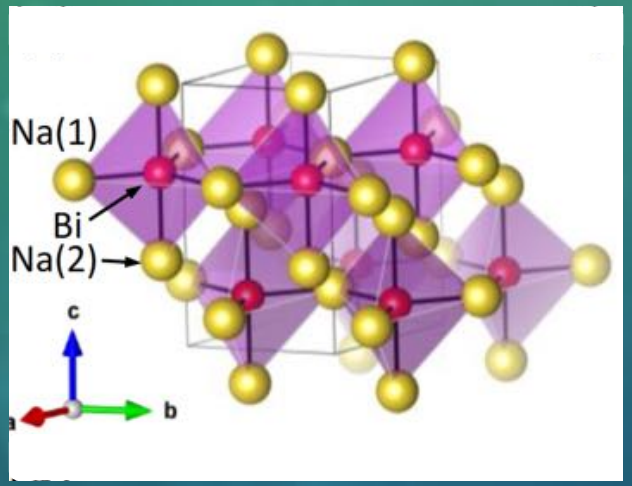
8 per As

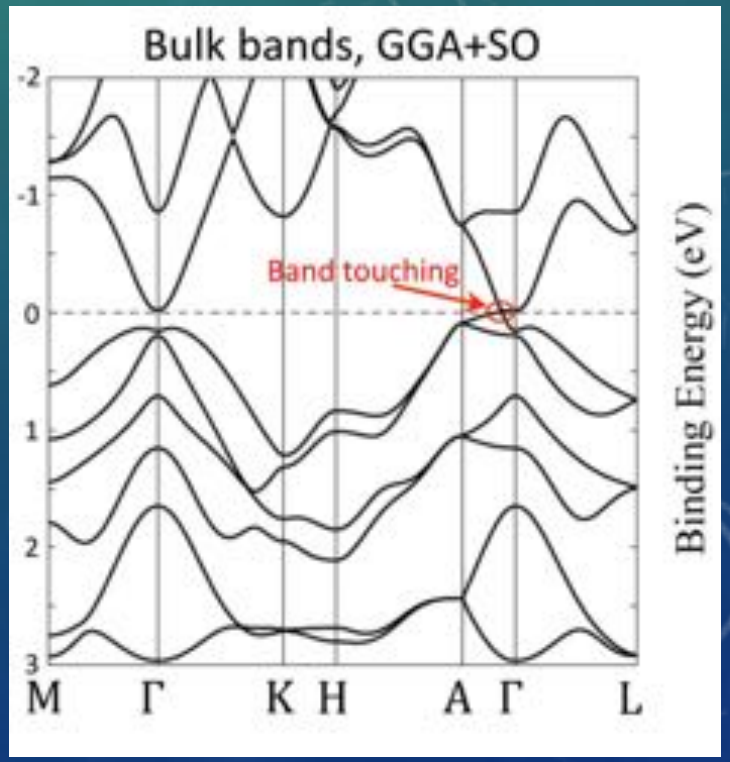
Cd_3As_2

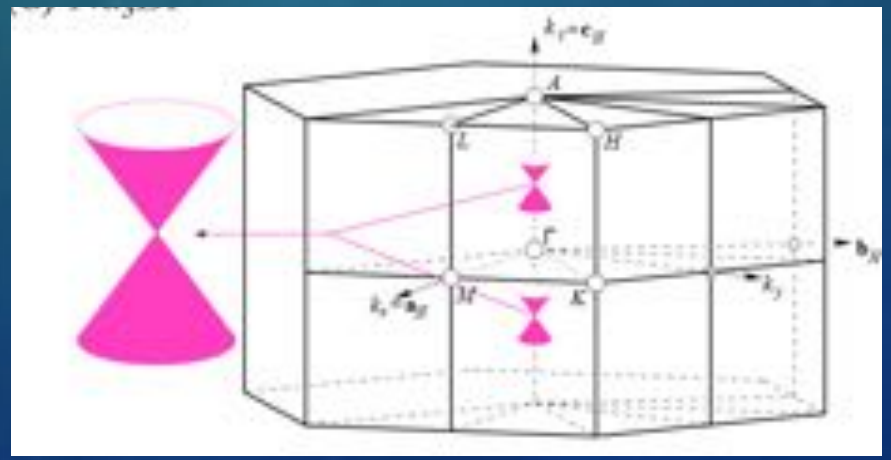


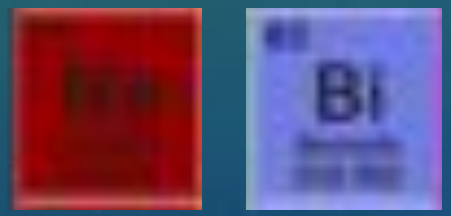
KNOWN DIRAC SEMIMETALS : Na_3Bi

- Hexagonal: cone along ΓA, C_6 rotation
- E_N (Bi) = 2.0 E_N (Na) = 0.9
- SOC much higher than in Cd_3As_2









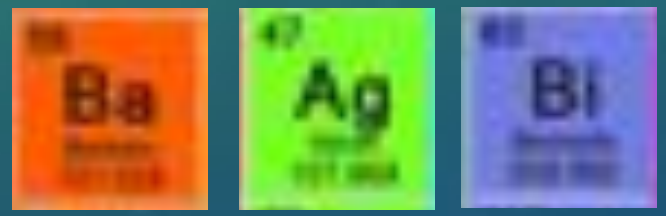
3*1+5 = 8

Kurshwaha et al. APL Mater. 3, 041504 (2015)

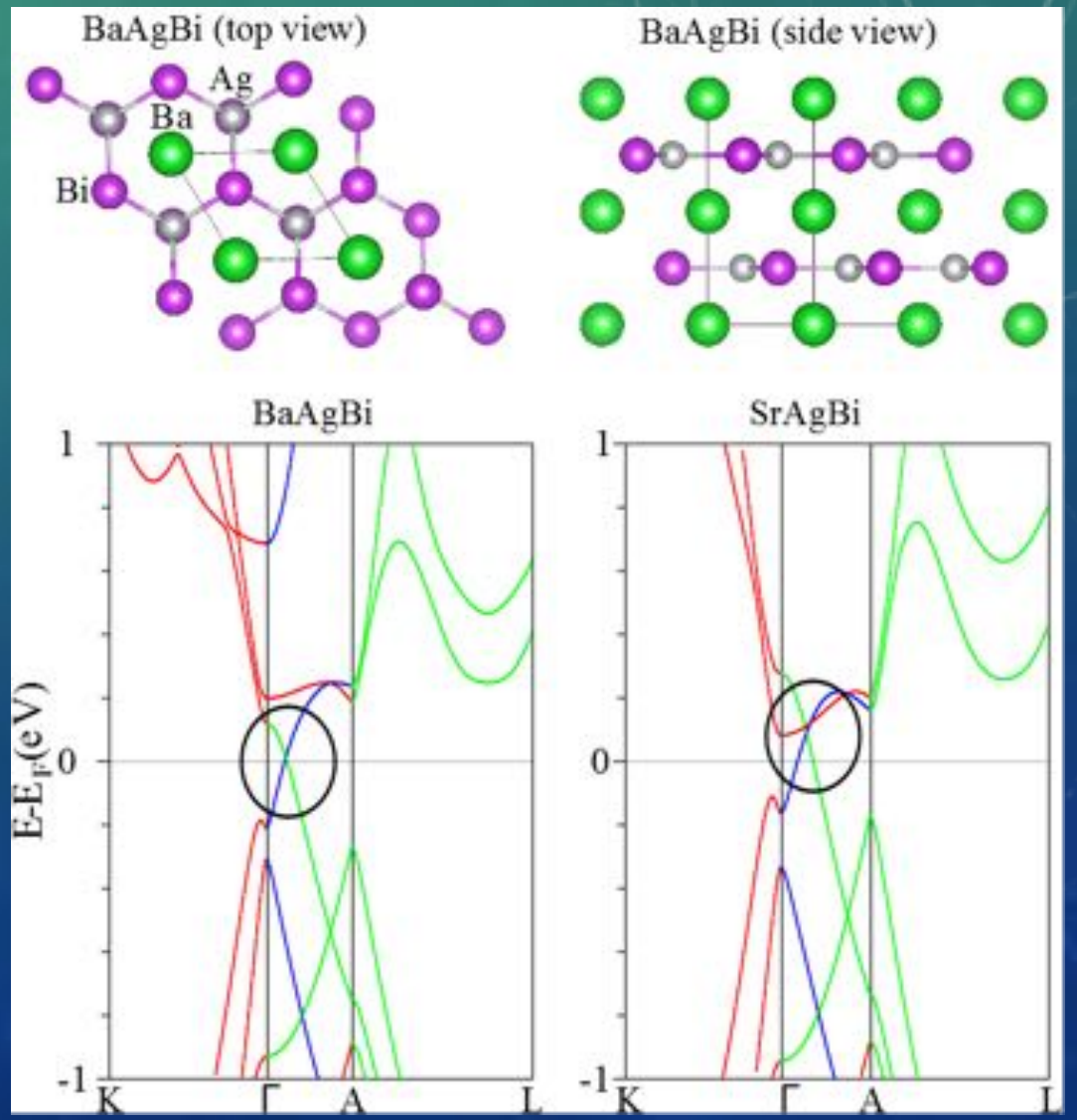
Xu, Su-Yang, et al. *Science* 347.6219 (2015): 294-298.

MORE EXAMPLES FOR CHARGE BALANCED COMPOUNDS

- BaAgBi family of compounds
- Crystalize in the ZrBeSi structure (hexagonal)
- Crossing along ΓA, C_6 rotation



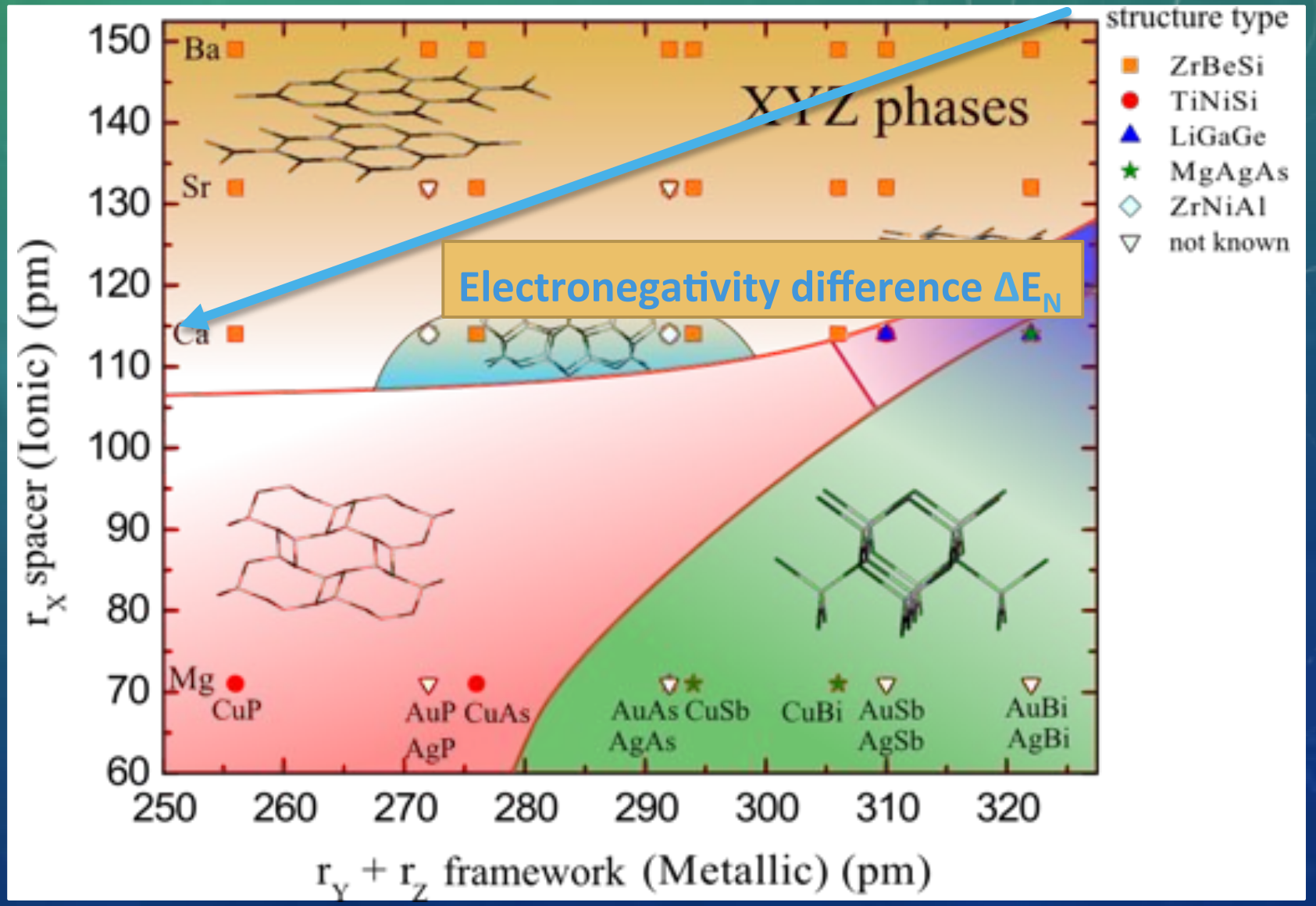
2 + 11 + 5 = 18



Gibson, Schoop, Muechler, Xie, Hirschberger, Ong, Car, Cava Physical Review B 91 (20), 205128 (2015)

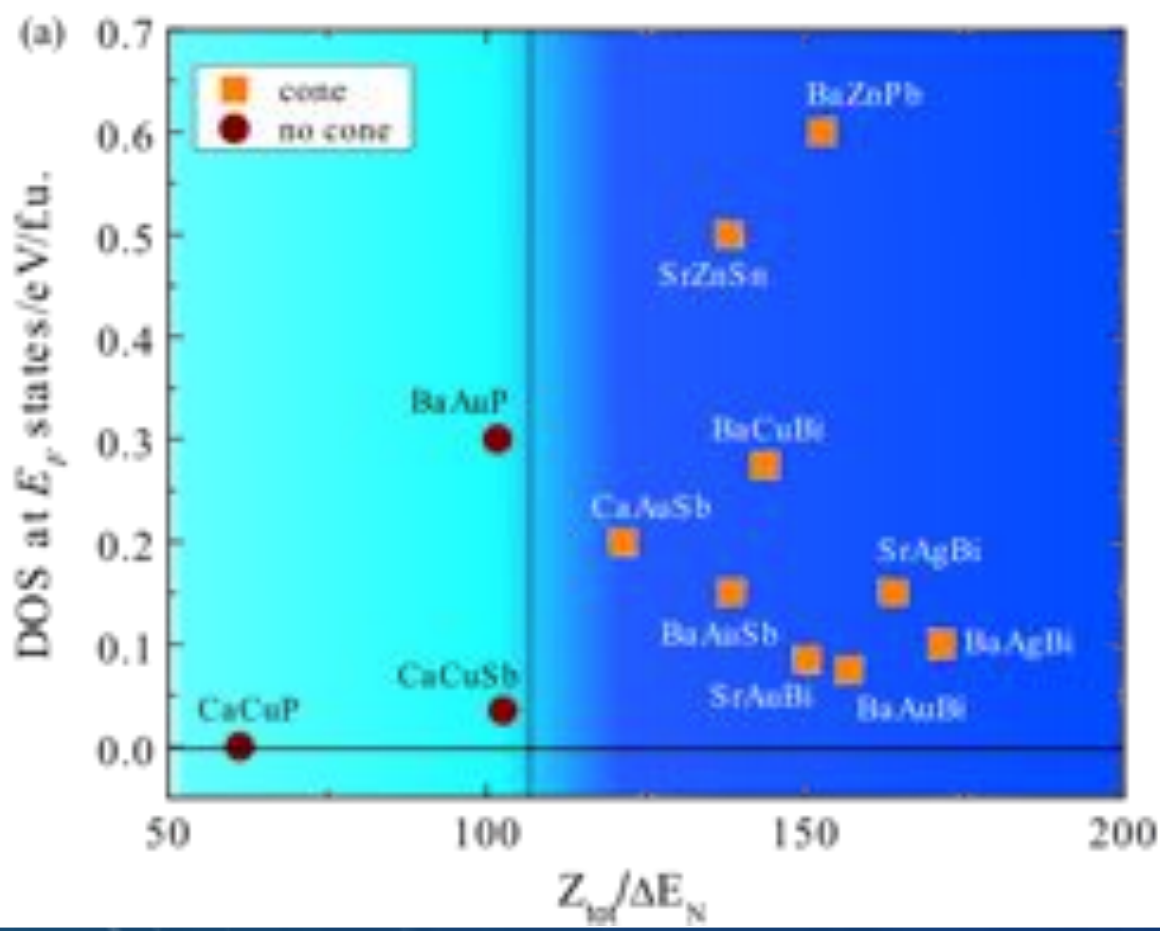
THE XYZ FAMILY OF COMPOUNDS WITH 18 ELECTRONS

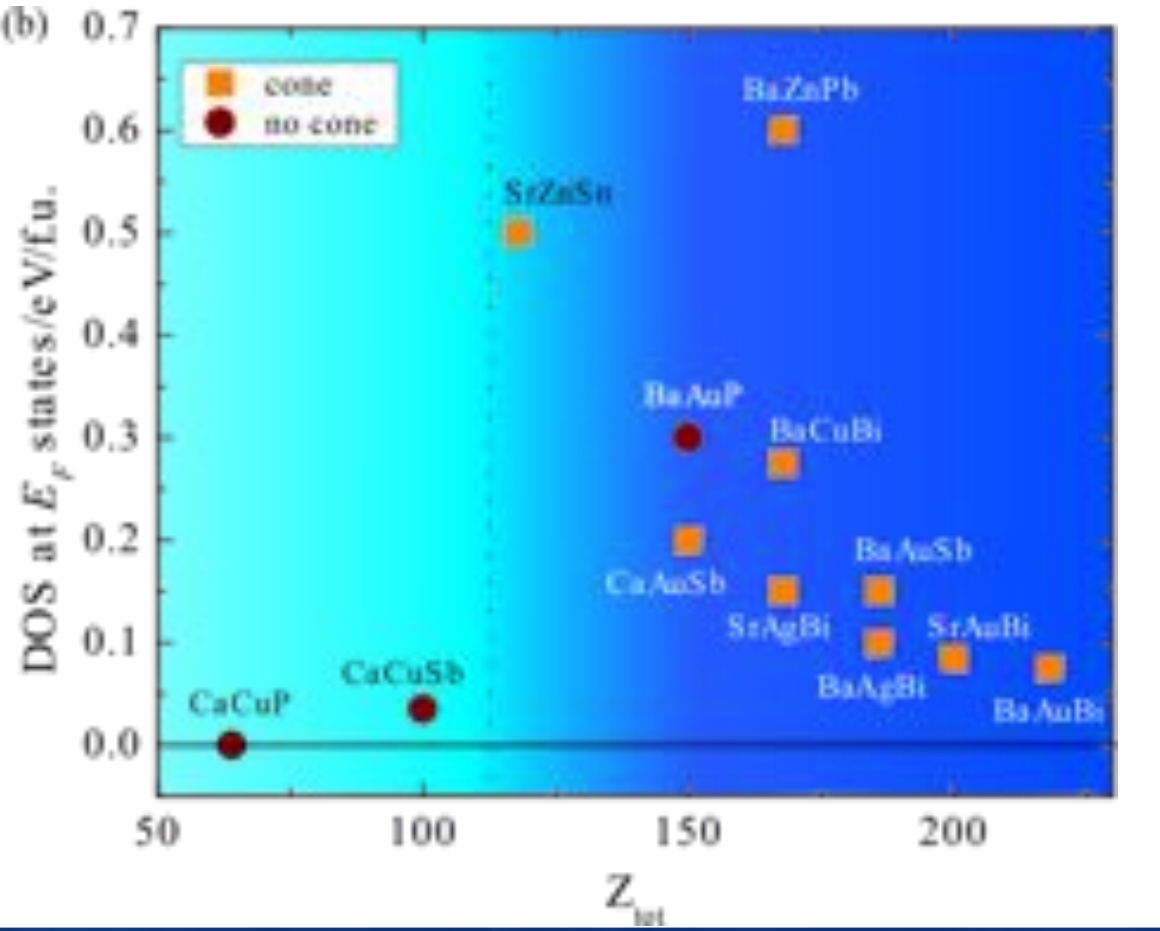
- ZrBeSi structure is preferred for large alkaline earth elements
- Electronegativity difference can be tuned



Schoop, Xie, Medvedev, Felser, Cava *Solid State Sciences* 30 (2014): 6-10.

HOW DOES ELECTRONEGATIVITY EFFECT THE BAND STRUCTURE?



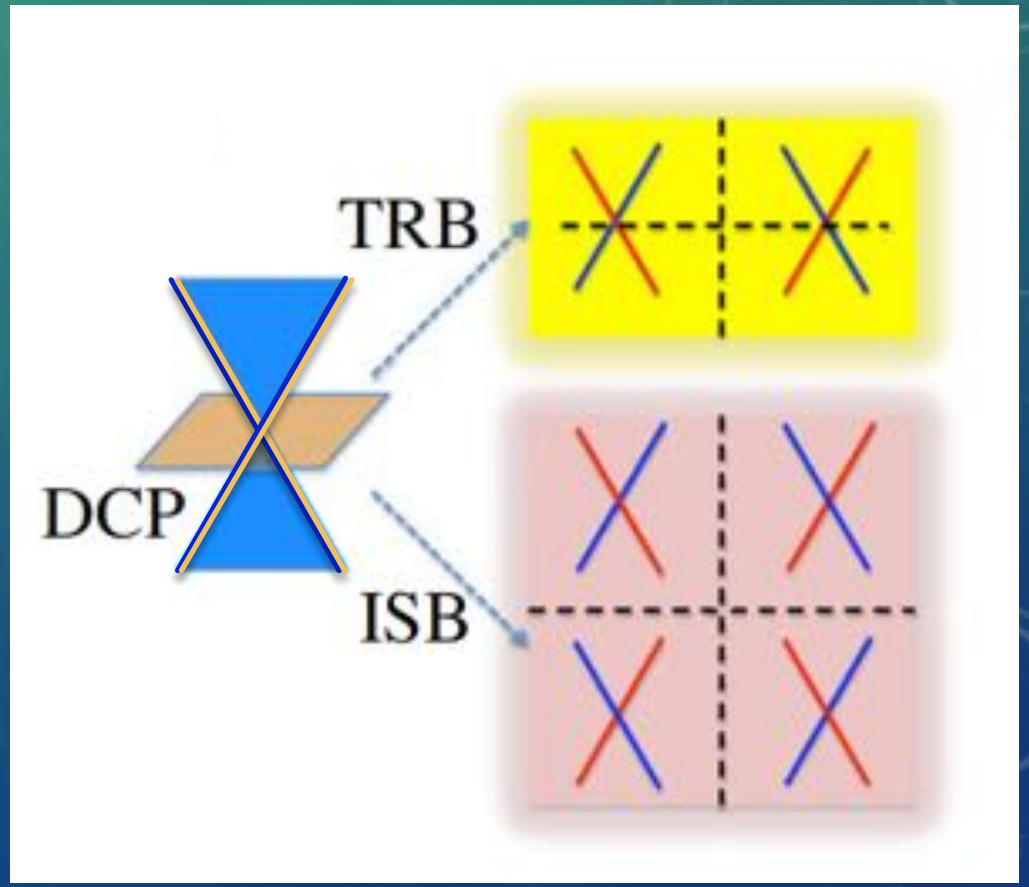


Gibson, Schoop, Muechler, Xie, Hirschberger, Ong, Car, Cava Physical Review B 91 (20), 205128 (2015)

2) WEYL MATERIALS

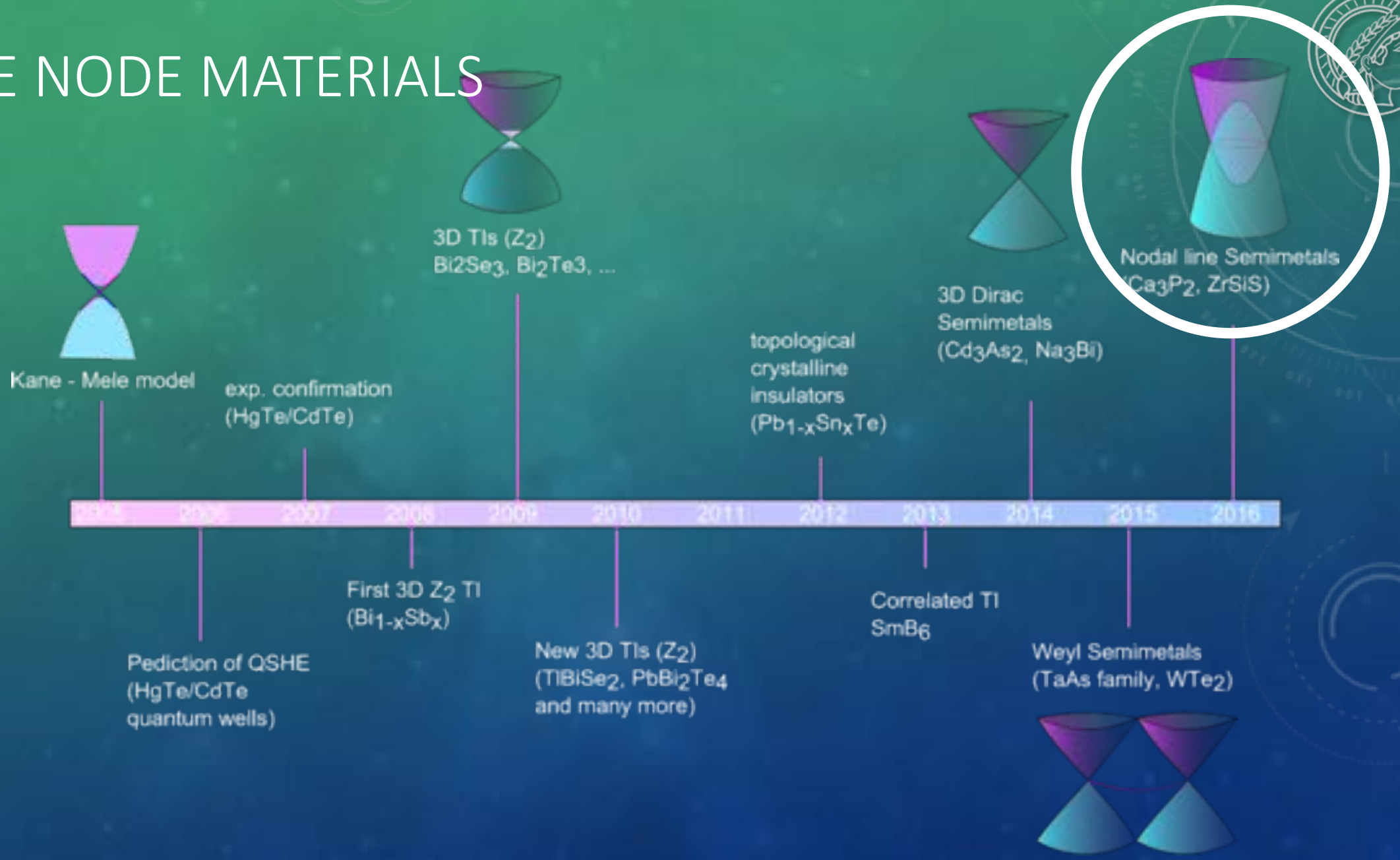
3D DIRAC vs. WEYL

- Only 2 fold degeneracy
- Weyl points appear much more easily
- But are often off the high symmetry lines and hard to find
- Chemistry not so helpful here
- Except: break time reversal symmetry!



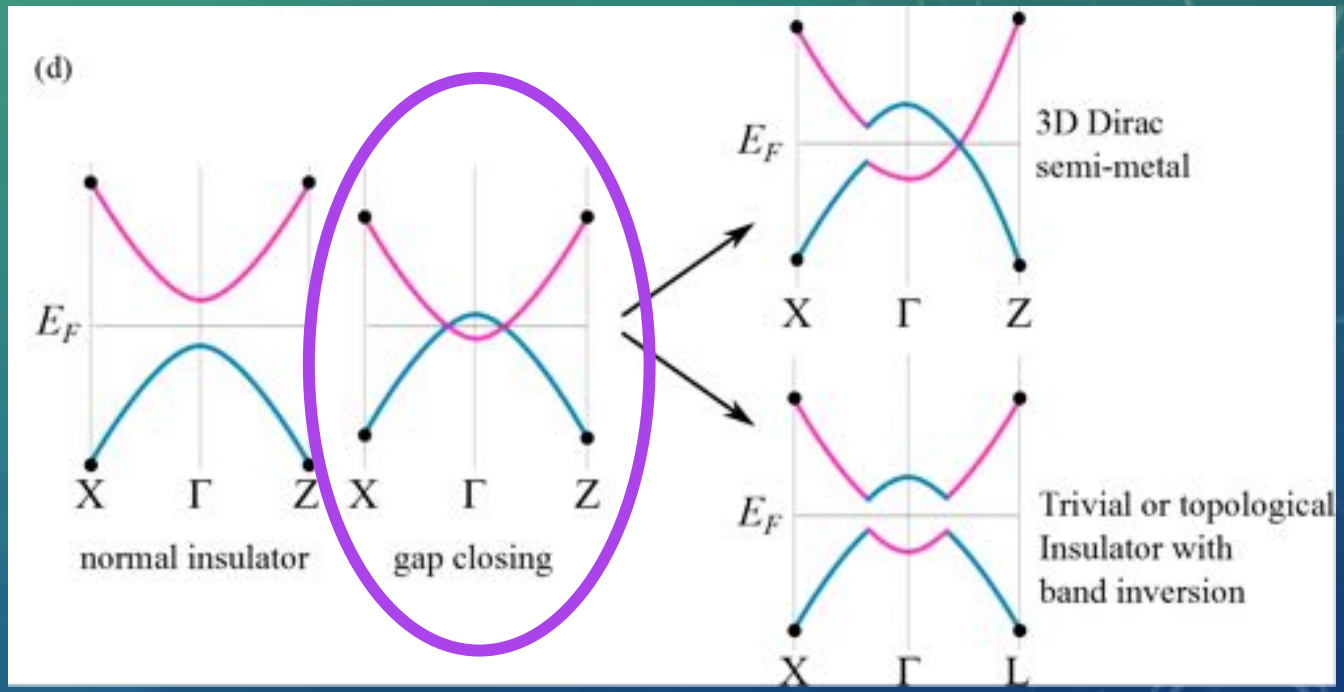
Lv, Ding PHYSICAL REVIEW X 5, 031013 (2015)

3) LINE NODE MATERIALS

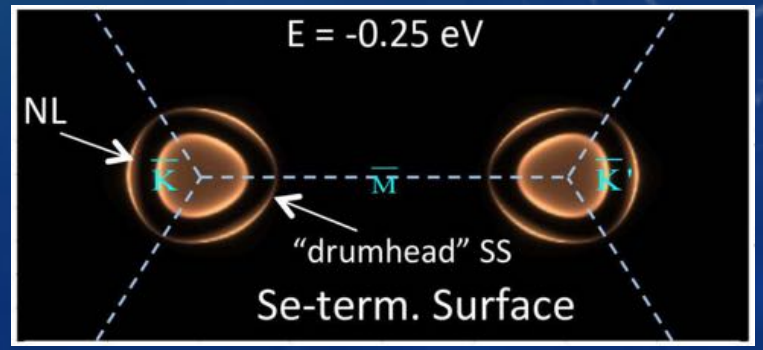


3D DIRAC LINE NODES

- If two bands cross and no crossing gaps
- 3D Dirac line nodes that are stable towards SOC are rare
- Need very highly symmetric materials with low SOC

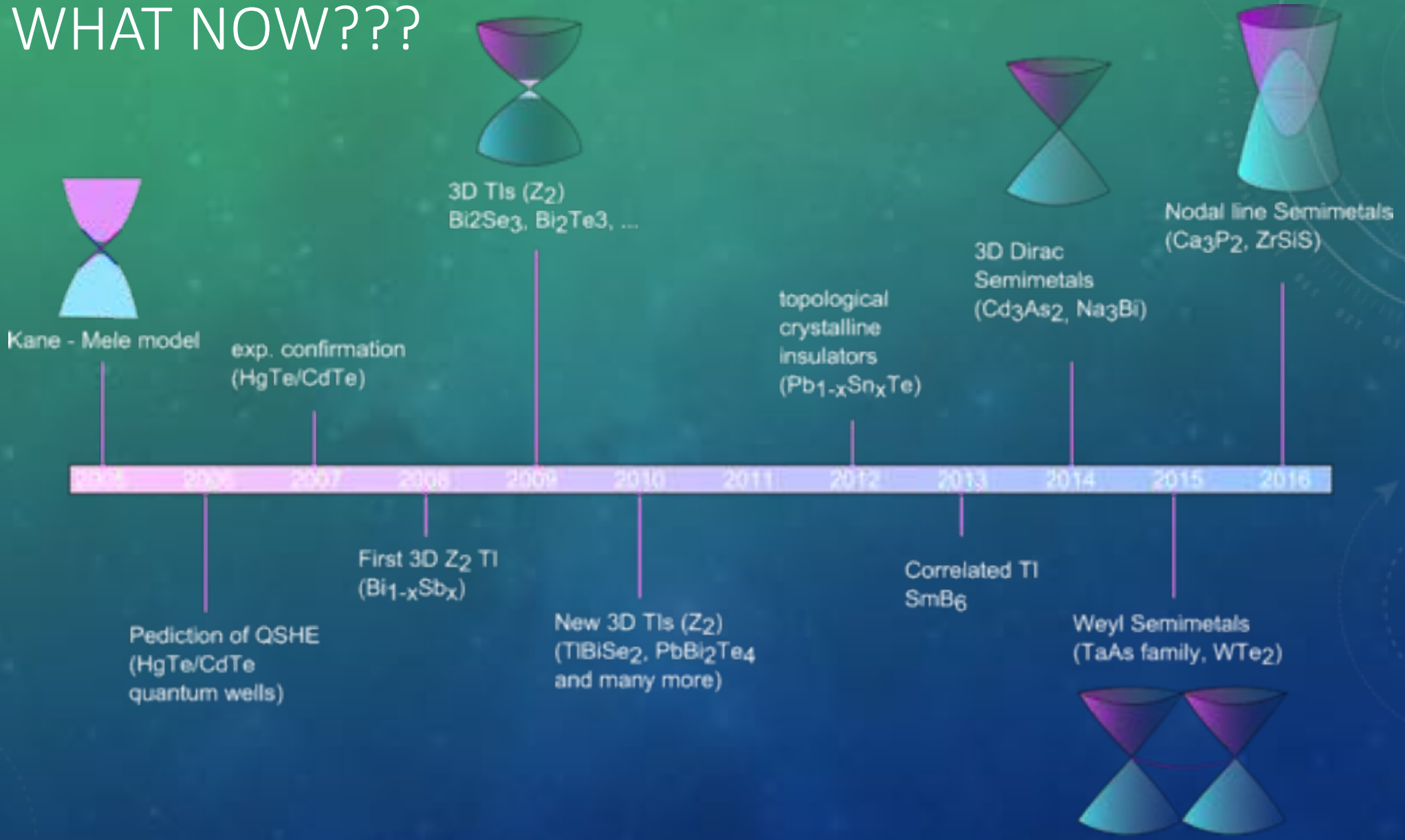


Line node!

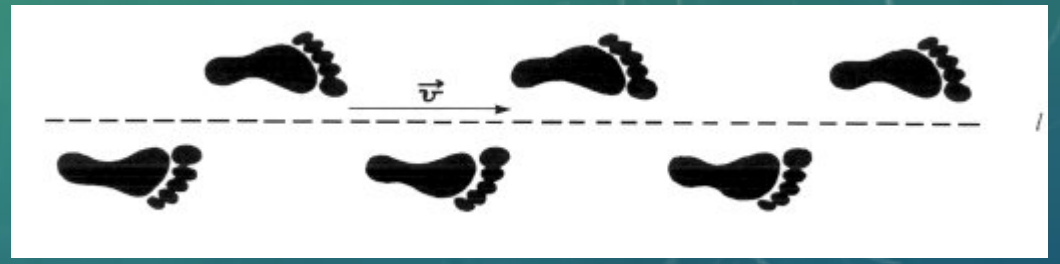


Bian, Guang, et al. *Nature communications* 7 (2016).
Chan, Chio, Chou, Schnyder *Physical Review B* 93.20 (2016): 205132.

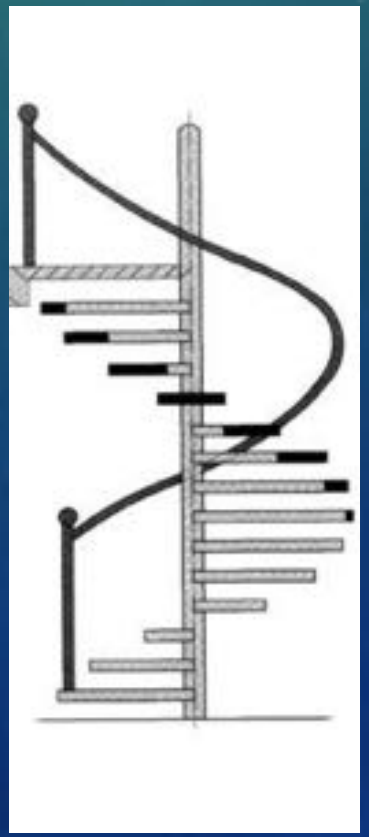
AND WHAT NOW???


Kane - Mele model
Pediction of QSHE (HgTe/CdTe quantum wells)
exp. confirmation (HgTe/CdTe)
First 3D Z_2 TI ($Bi_{1-x}Sb_x$)
3D TIs (Z_2) Bi_2Se_3, Bi_2Te_3, ...
New 3D TIs (Z_2) ($TlBiSe_2$, $PbBi_2Te_4$ and many more)
topological crystalline insulators ($Pb_{1-x}Sn_xTe$)
Correlated TI SmB_6
3D Dirac Semimetals (Cd_3As_2, Na_3Bi)
Weyl Semimetals (TaAs family, WTe_2)
Nodal line Semimetals (Ca_3P_2, ZrSiS)

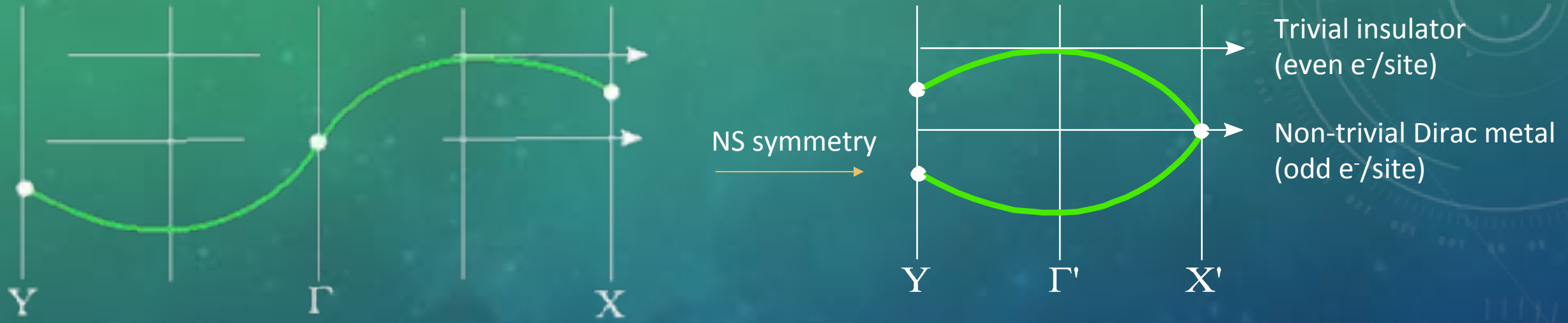
DIRAC SEMIMETALS FROM NON-SYMMORPHIC SYMMETRY



- Non-symmorphic space groups contain glide mirrors or screw axis
- Symmetry elements do not conserve spatial origin
- Causes enlargement of the unit cell in comparison to symmorphic space groups



NON-SYMMORPHIC 3D DIRAC SEMIMETALS



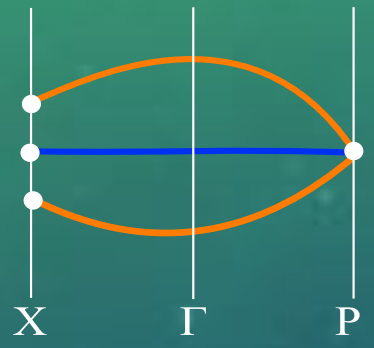
- Enlargement of unit cell causes folding of k-space
- Forced band touching, SOC has no effect
- Can result in Dirac semimetals

Young, Zaheer, Teo, Kane, Mele, Rappe Phys. Rev. Lett. 108, 140405 (2012)

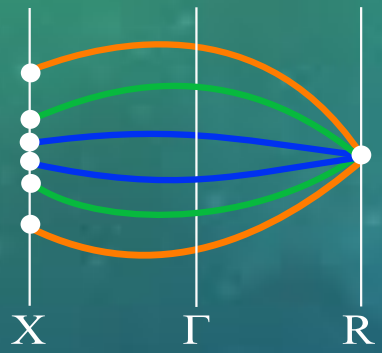
NON SYMMORPHIC SYMMETRY → NEW FERMIONS?

Example: New Fermions in Non-symmorphic materials

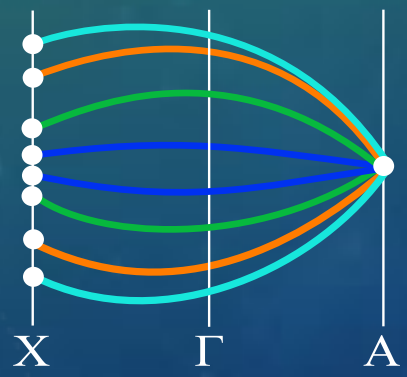
- 3-fold, 6-fold, 8-fold → New Fermions?



e.g. space group
199 and 214



e.g. space group
198 and 212



e.g. space group
130 and 135

RESEARCH ARTICLE

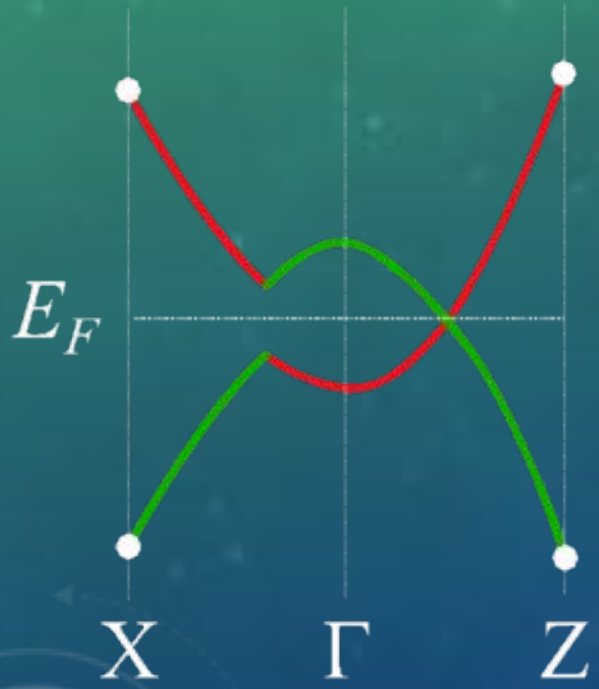
Beyond Dirac and Weyl fermions: Unconventional quasiparticles in conventional crystals

Barry Bradlyn, Jennifer Cano, Zhijun Wang, M. G. Vergniory, C. Felser, R. J. Cava, B. Andrei Bernevig

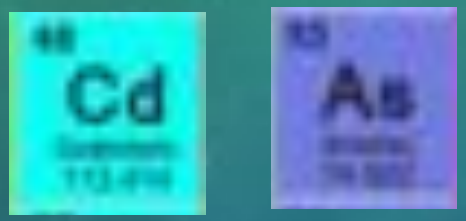
Bradlyn, Cano, Wang, Vergniory, Felser, Cava, Bernevig. *Science*, *353*(6299), aaf5037. (2016)

EXPERIMENTAL CHALLENGES FOR REALIZING NON-SYMMORPHIC SEMIMETALS

"conventional DSM"



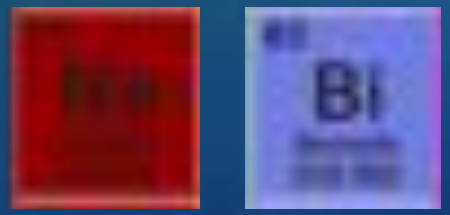
Cd_3As_2



3*2+2*5 = 16

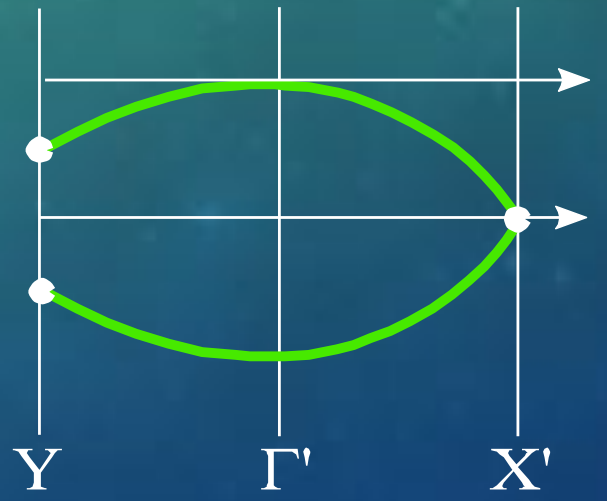
8 per As

Na_3Bi



3*1+5 = 8

"non-symmorphic DSM"



Trivial insulator (even e^-/site)

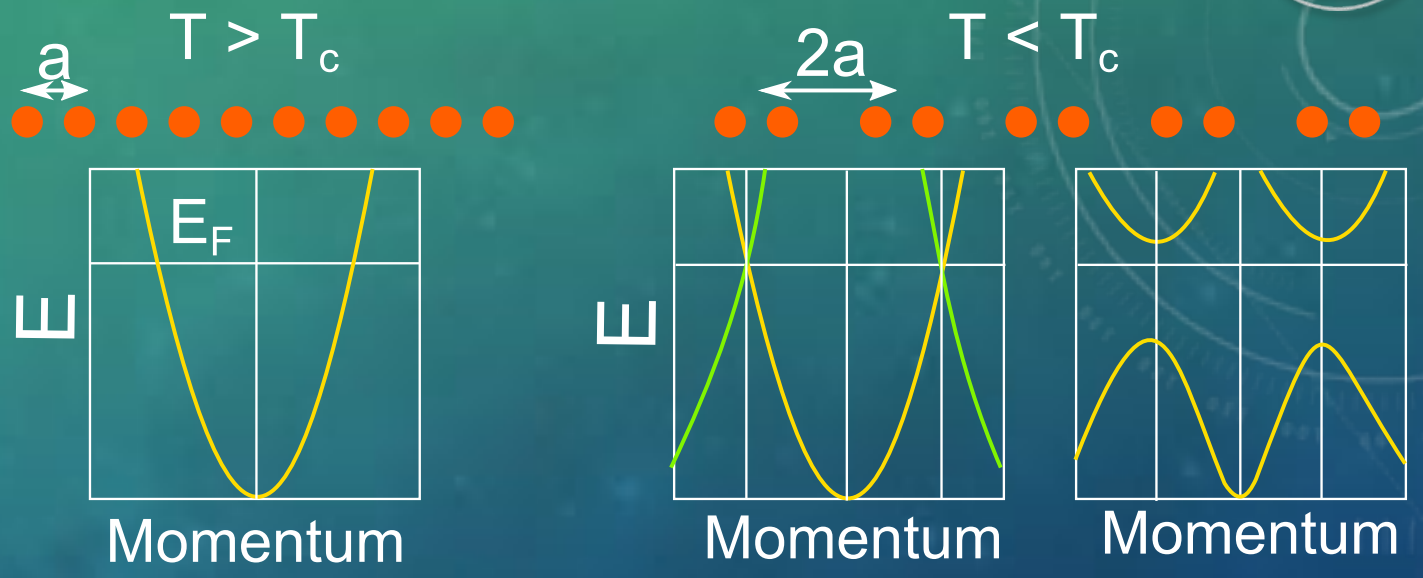
Non-trivial Dirac metal (odd e^-/site)

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

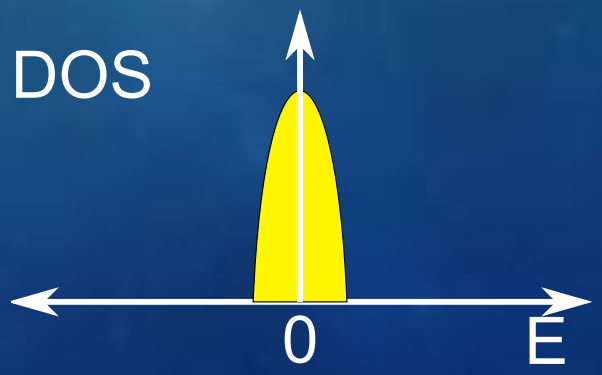
Gibson et al. Physical Review B 91 (20), 205128 (2015)

THE PROBLEM WITH THE HALF-FILLED BAND:

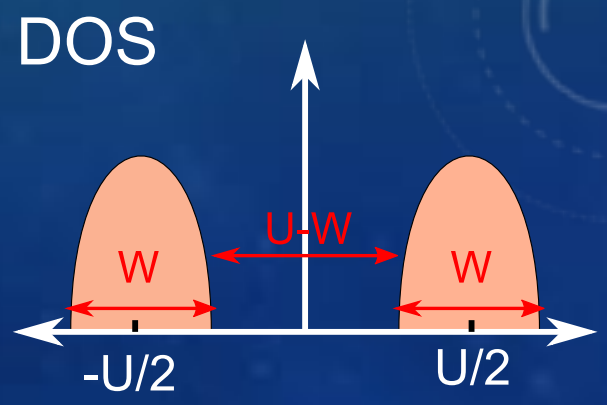
- Isolated half-filled bands often unstable
- Peierls distortion (i.e. $TaSe_2$)
- Charge density wave
- Mott insulators (i.e. NiO, CoO…)
- Electron localization (antiferromagentism)



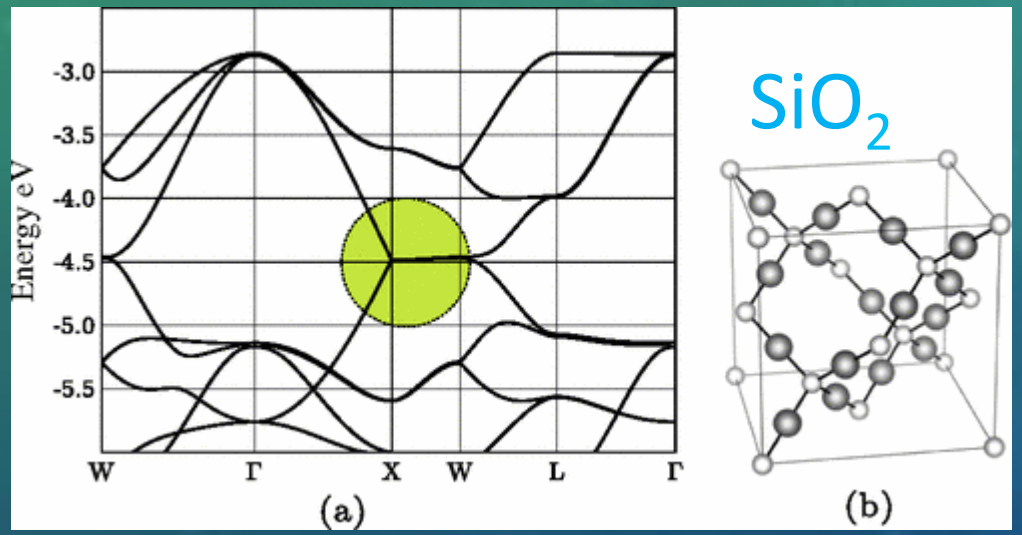
Metal U=0



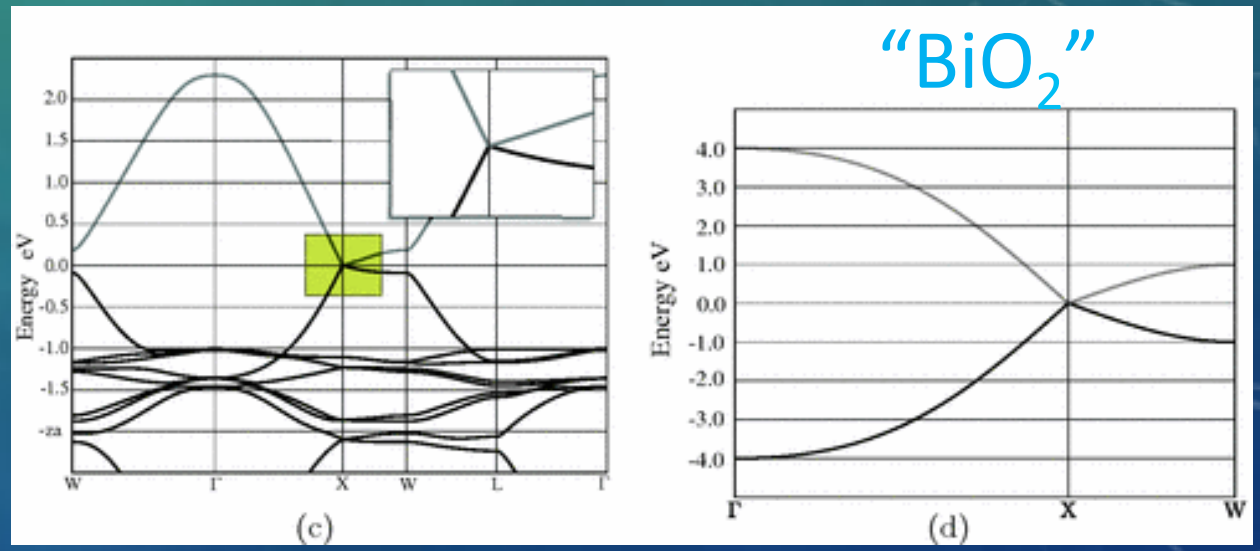
Mott Insulation U >> W



FIRST PREDICTION: BiO_2



SiO_2

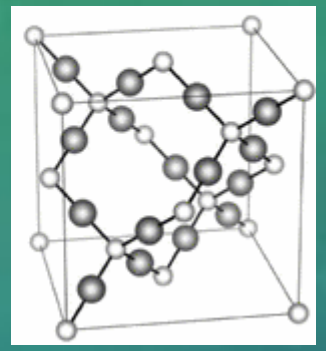


"BiO_2"

Young, Zaheer, Teo, Kane, Mele, Rappe Phys. Rev. Lett. 108, 140405 (2012)

WHY NO BIO_2 ? IONIC RADII

$r_M/r_X > 0.732$ cubic coordination
r_M/r_X 0.424-0.732 octahedral coordination
$r_M/r_X < 0.424$ tetrahedral coordination



$r_{Oxygen} = 1.4$

$r_{Si}/r_O < 0.414$

r_{Bi}/r_O = at least 0.53 > 0.414

Radii for Si

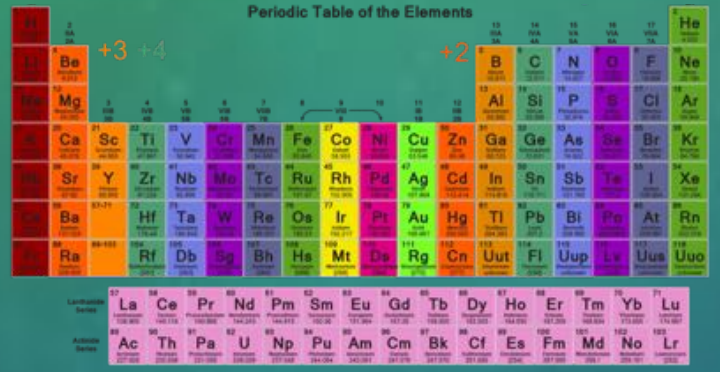
Ion	Charge	Coordination	Spin State	Crystal Radius	Ionic Radius	Key
Si	4	IV		0.4	0.26	*
		VI		0.54	0.4	R*

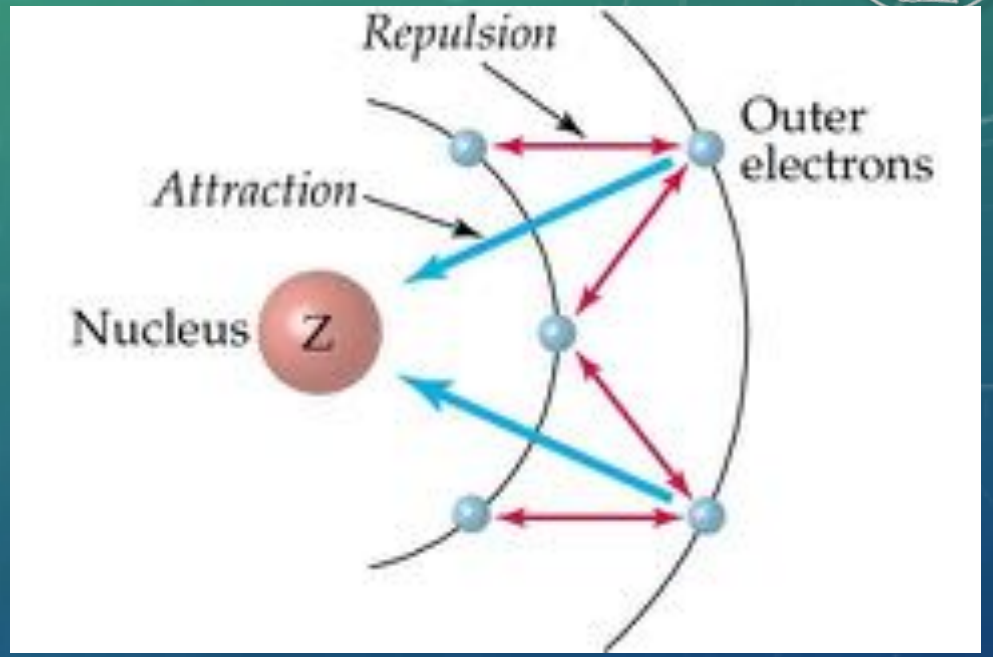
Radii for Bi

Ion	Charge	Coordination	Spin State	Crystal Radius	Ionic Radius	Key
Bi	3	V		1.1	0.96	C
		VI		1.17	1.03	R*
		VIII		1.31	1.17	R
	5	VI		0.9	0.76	E

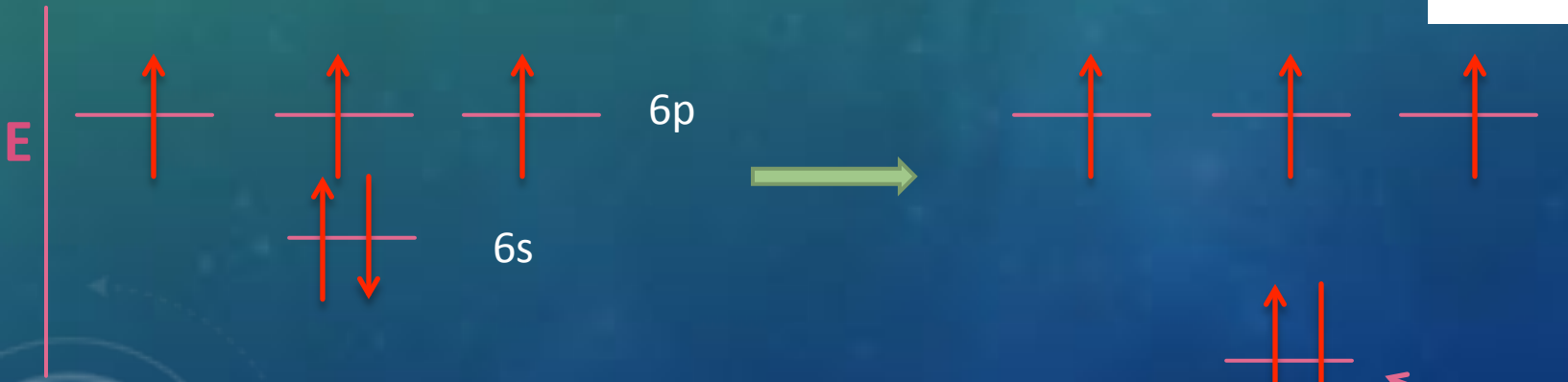
http://abulafia.mt.ic.ac.uk/shannon/ptable.php R. D. Shannon Acta Crystallographica. (1976). A32, Pages 751-767

WHY NO BiO_2? - THE INERT PAIR EFFECT





- Bi^{4+} does not exist:
- 6s Orbital very low in energy!
- In general: watch out for preferred oxidation states



Electron shielding: s > p > d > f

Easy to oxidize

Hard to oxidize

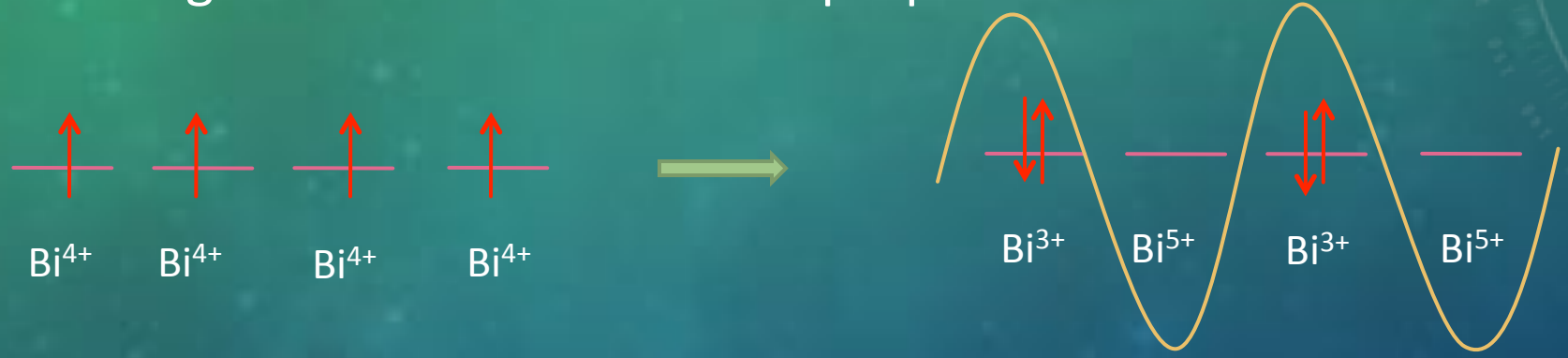
Inert pair effect: Tl > Pb > Bi

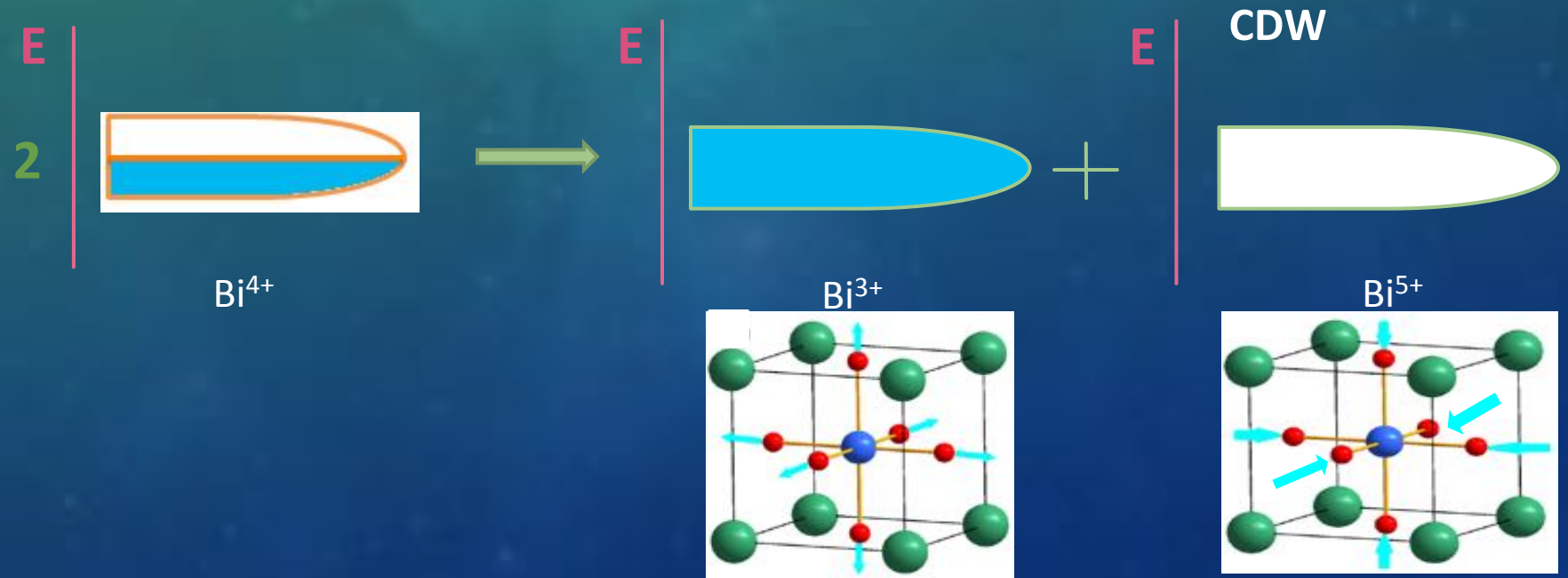
$2\ Bi^{4+} \rightarrow Bi^{3+} + Bi^{5+}$

“FAKE” HALF FILLED BANDS: EXAMPLE: $BaBiO_3$

Appears to have half filled s band by simple electron counting

Bi^{4+}: $6s^1$ configuration is unstable → disproportionation Bi^{3+} and Bi^{5+}

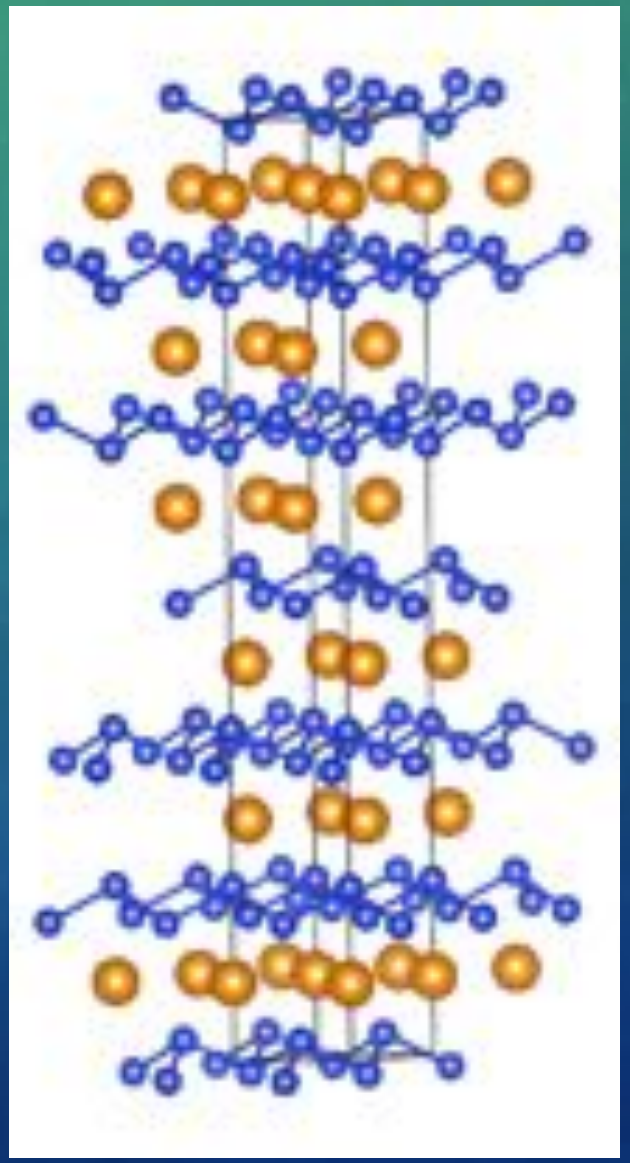


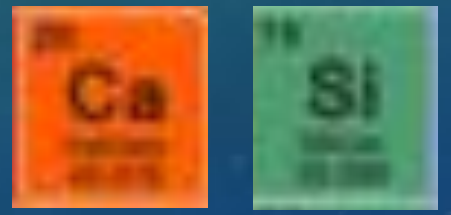


“FAKE” HALF FILLED BANDS: ZINTL COMPOUNDS

- Zintl Ions can make electron counting complicated
- Polyanions or Polycations

- Example: $CaSi_2$: Ca^{2+} and Si_2^{2-}
- Si_2^{2-} is polyanion
- All bands are filled!



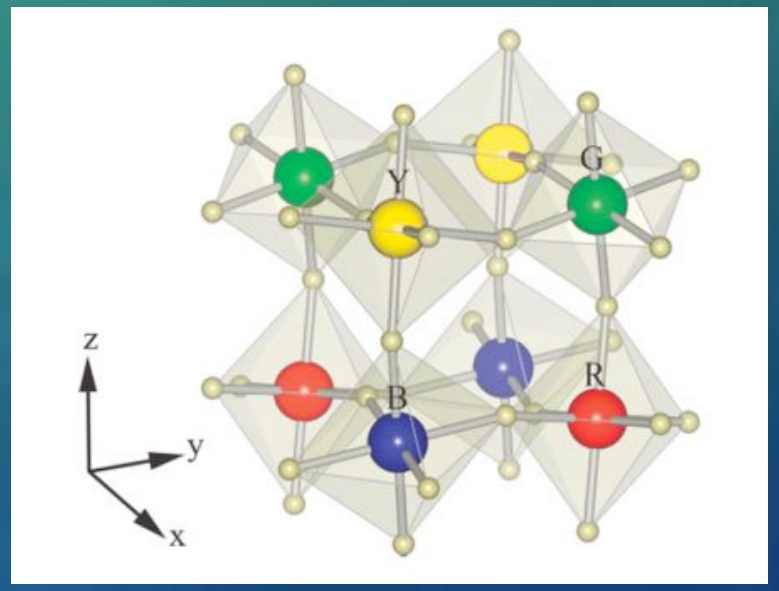


2+2*4 = 10

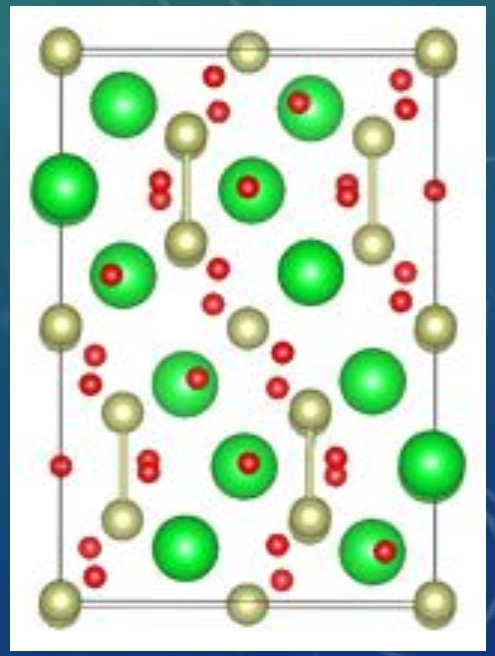
5 per Si

EXAMPLES FOR COMPOUNDS WITH HALF FILLED BANDS

- $SrIrO_3$: Orthorhombic form predicted to be non-symmorphic line node material
- 2 + 9+ 3x6 = 29 electrons → half filled Ir d band
- Stable from however is monoclinic and has Ir-Ir dimers
- Orthorhombic form can only be made as thin film or as powder with high pressure synthesis

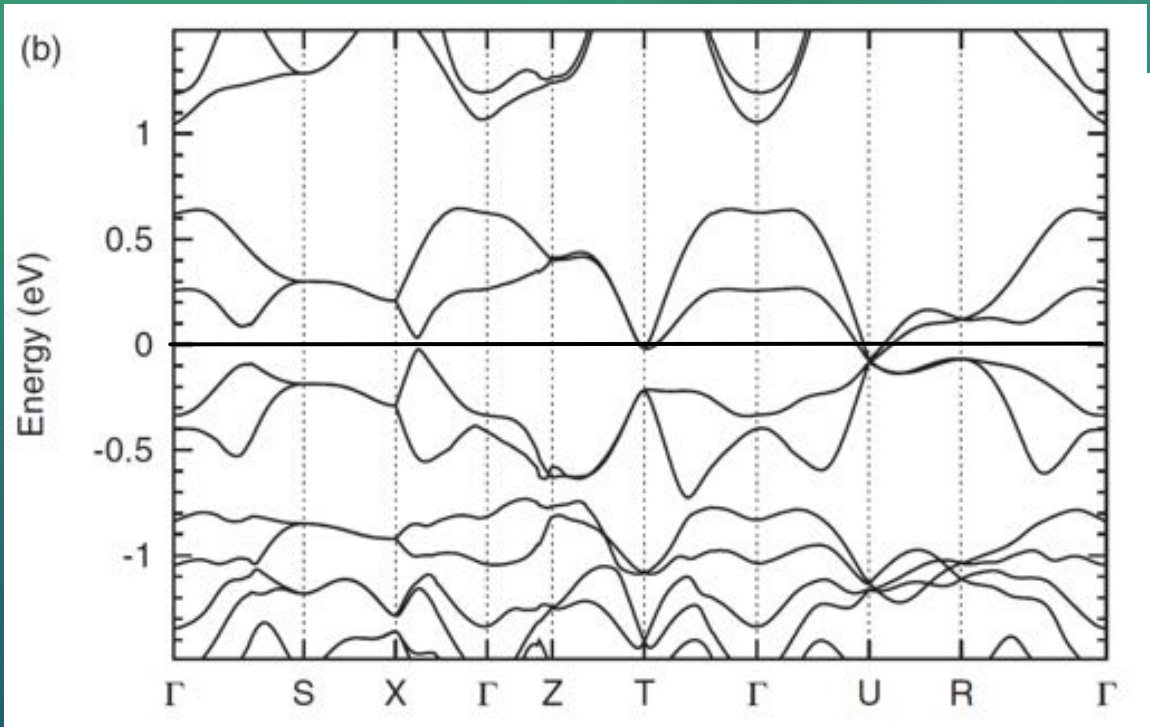


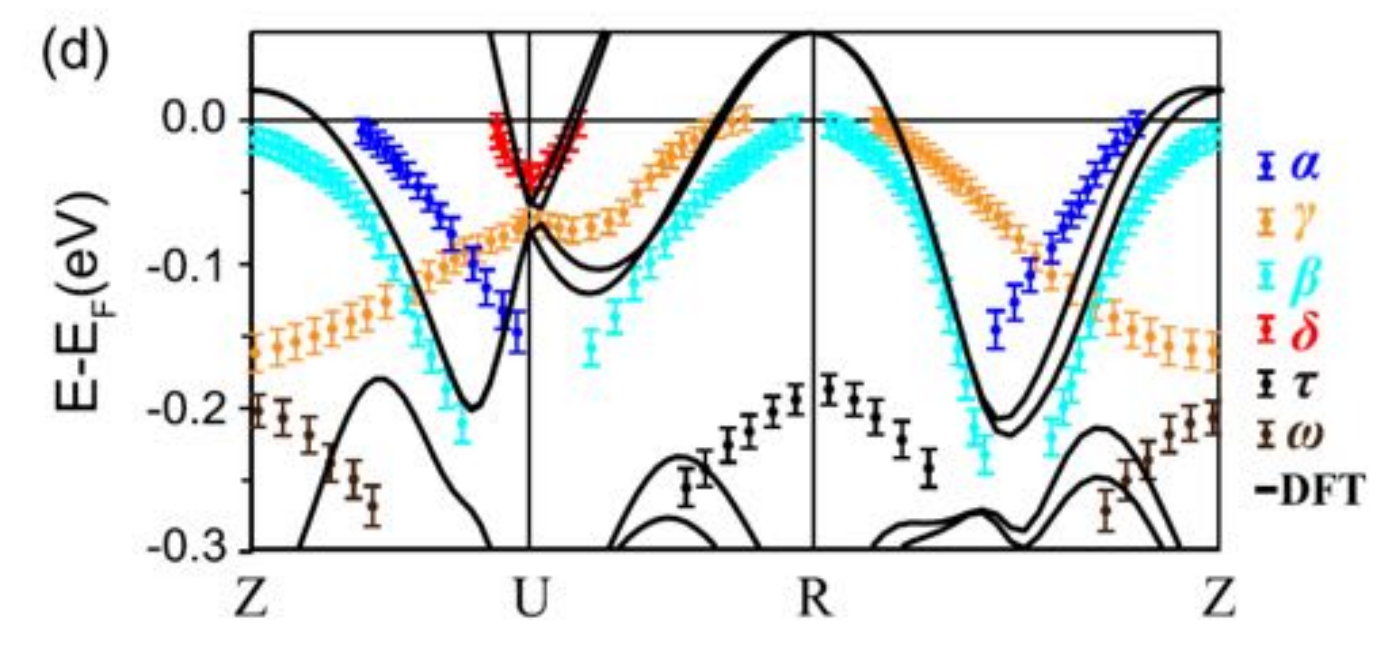
Orthorhombic



monoclinic

$SrIrO_3$: PREDICTION VS. EXPERIMENT





Prediction (DFT)

Experiment on a thin film

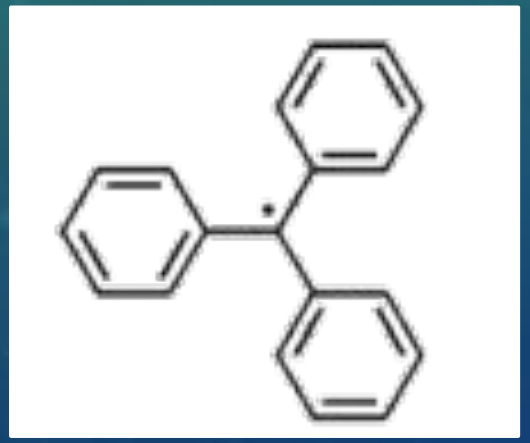
Carter, Shankar, Zeb, Kee PRB 85 115105 (2012)

Liu, Li, Shen et al scientific reports 6:30309 (2015)

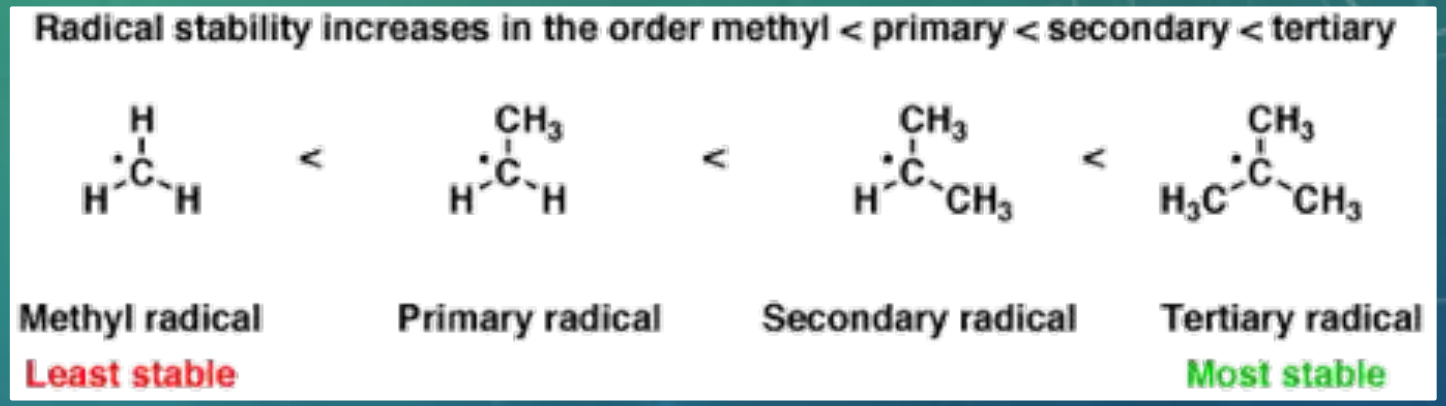
CAN CHEMISTRY HELP US HERE?

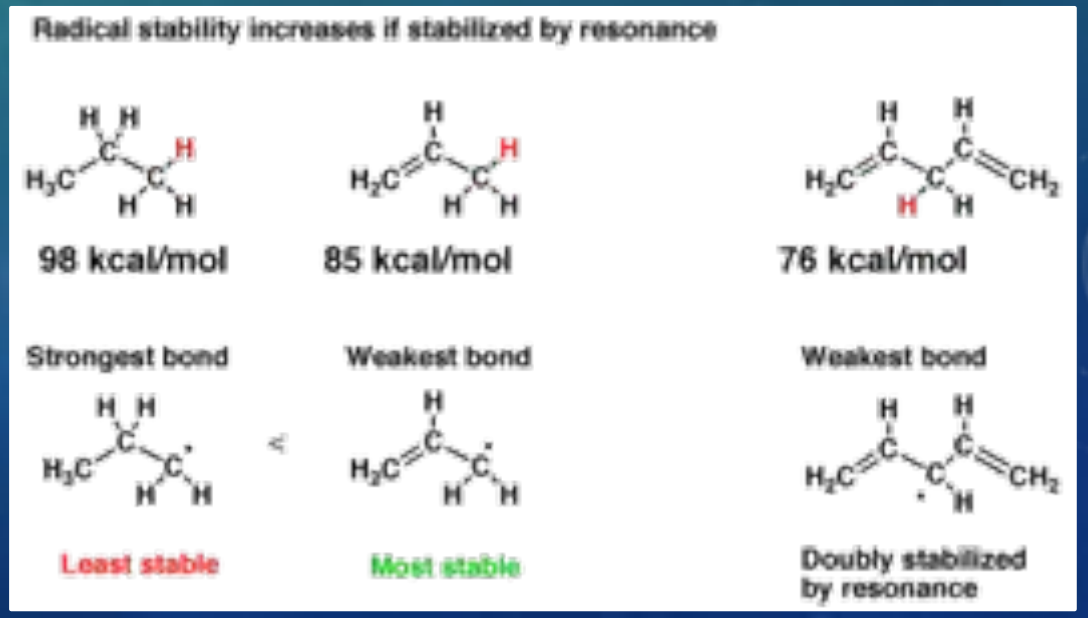
A WAY OUT WITH LESSONS FORM ORGANIC CHEMISTRY?

- Molecules with Half filled orbitals are called radicals
- Highly reactive
- But: stable radicals do exist!



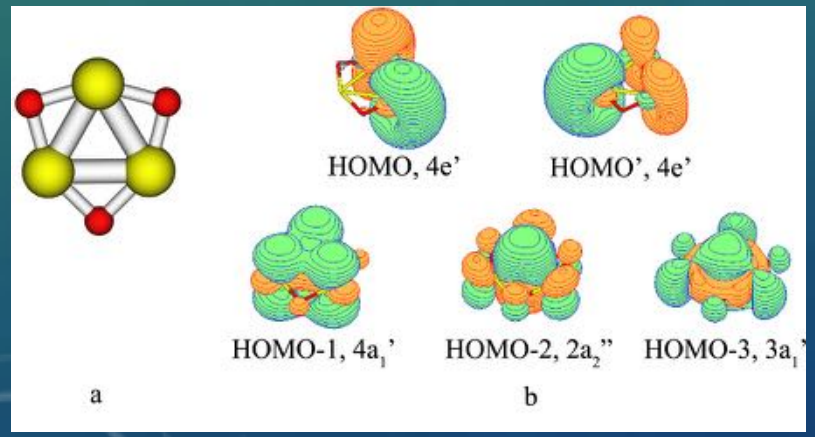
Stable at room temperature

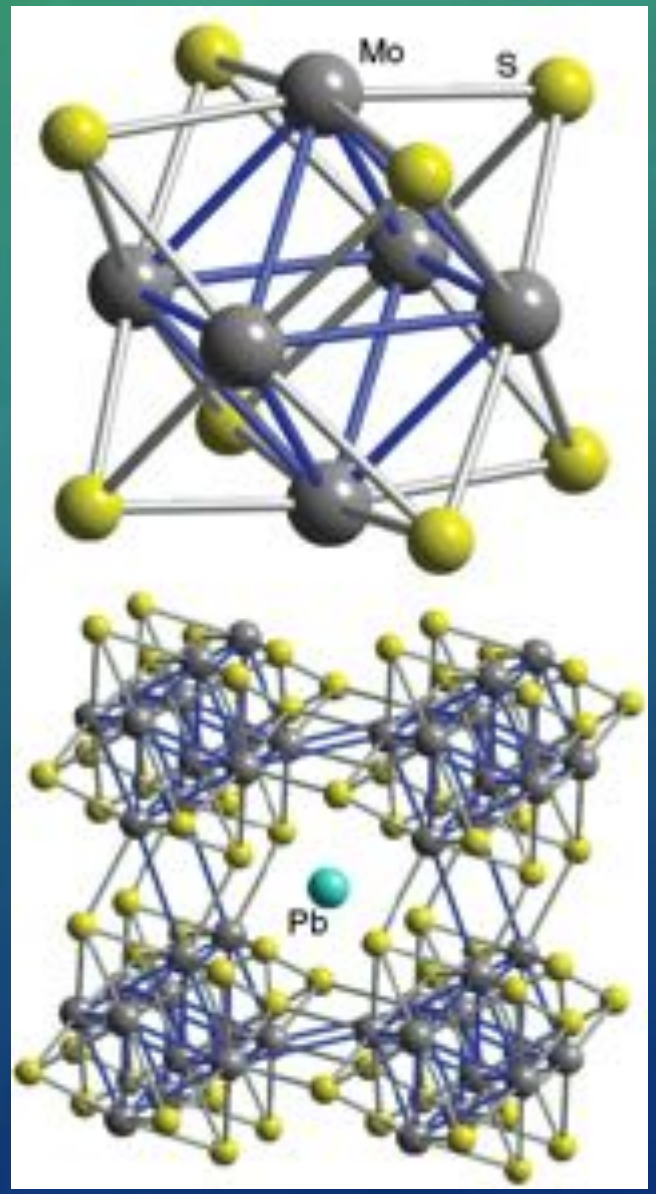




USE SIMILAR CONCEPT IN INORGANIC CHEMISTRY?

- Cluster compounds
- Have molecular orbitals
- Can delocalize an electron
- Partially filled bands!



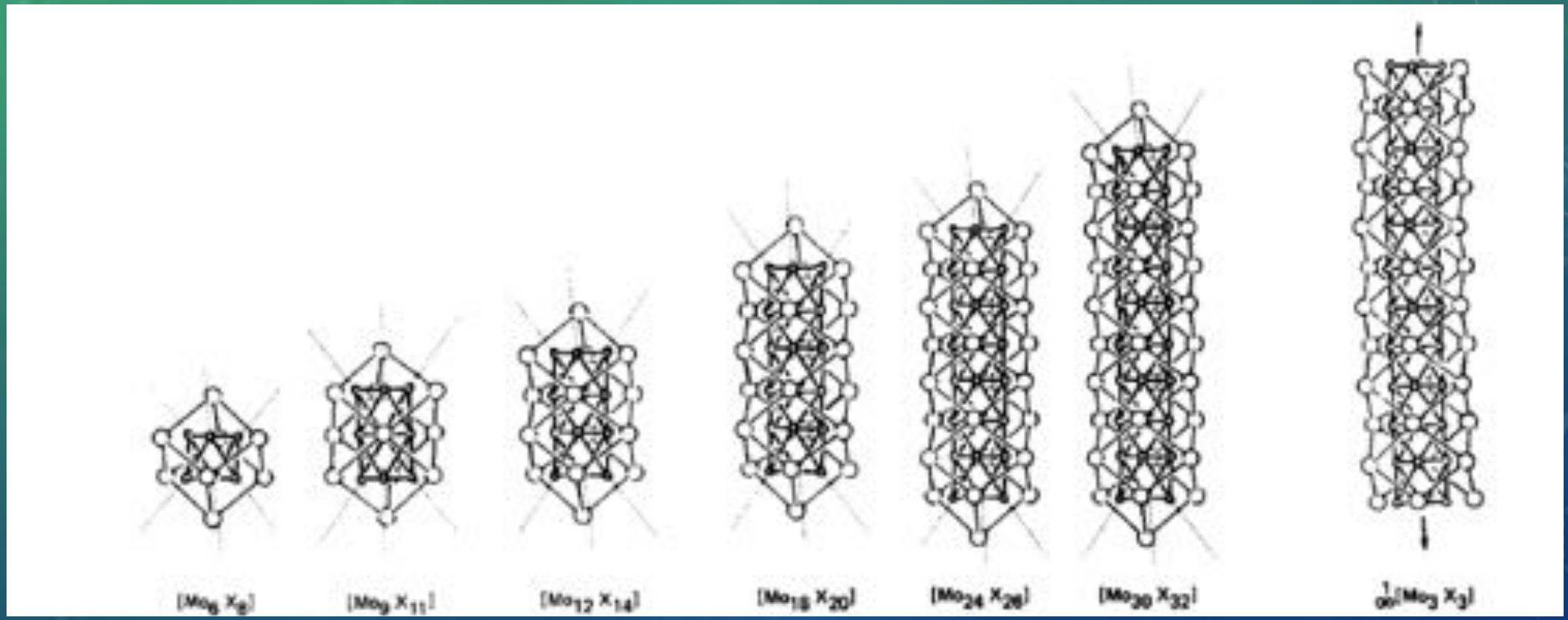


Example: Chevrel phase $PbMo_6S_8$
Mo_6 cluster, 12 edges
Cluster is filled with 24 electrons

$PbMo_6S_8$: Cluster has only 22 electrons
(=3.66 electrons per Molybdenum)

superconducting

NON SYMMORPHIC CLUSTER COMPOUNDS?



$P6_3/m$

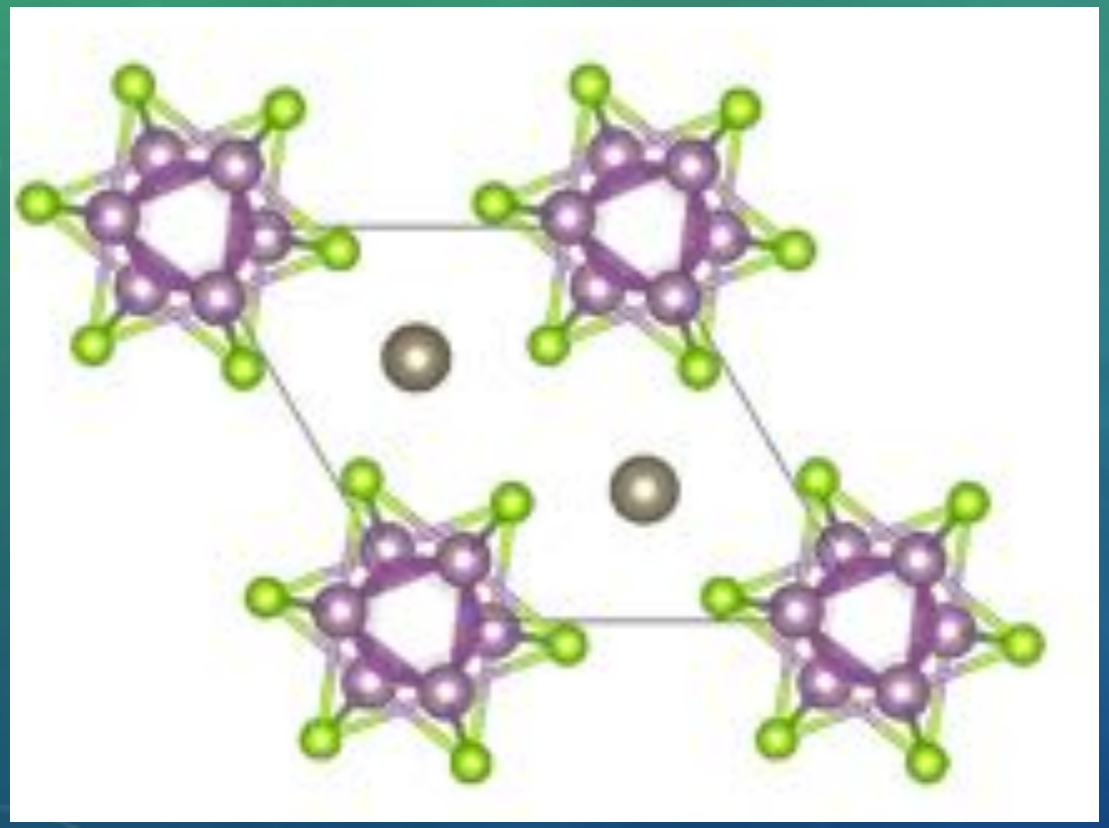
Chevrel, Gougeon, Potel, Sergent, Ternary molybdenum chalcogenides: A route to new extended clusters. *Journal of Solid State Chemistry*, *57*(1), 25-33 (1985).

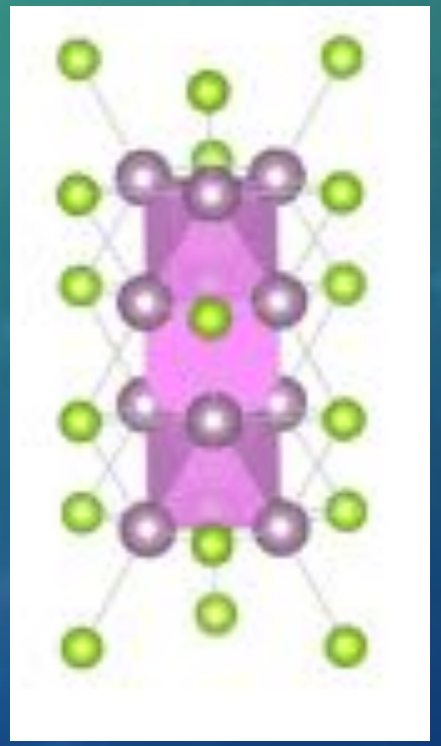
NON SYMMORPHIC CLUSTER COMPOUNDS?

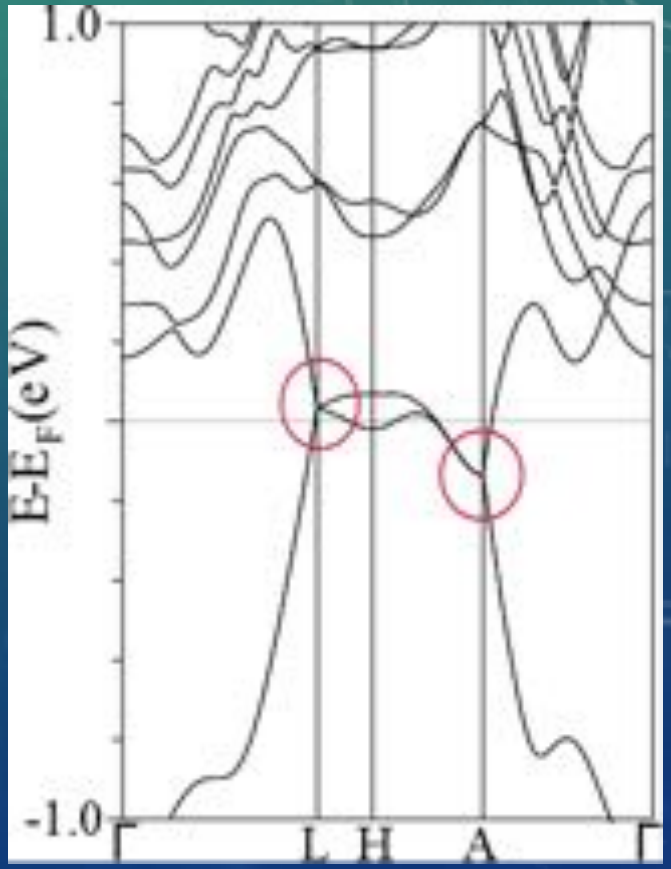
X/Mo_6	X/Mo	Compound	Cluster units	VEC/cluster	VEC/Mo	Formal oxidation number = 6 − VEC
8	1.33	$M_xMo_6X_8$	$\|Mo_6X_8\|^{0\to4-}$ M_x^{x+} $^{1+\to4+}_{0\to-4}$	20–24 e^-	3.33–4	2.66–2
7.6	1.26_7	$In_{\sim3}Mo_{15}Se_{19}$				
		$2\ In^{+1} \sim 1\ In^{3+}$	$(Mo_6X_8)(Mo_9X_{11})$			
		$In_2^+Mo_{15}Se_{19}$	$= (Mo_6X_8)^{0\to4-} + (Mo_9X_{11})^{2+\to4+}$	20–24 e^-	3.33–4	2.66–2
		$Ba_2^{2+}Mo_{15}Se_{19}$		30–36 e^-	3.33–4	2.66–2
7.33	1.22_2	$Ag_{3.6}^+Mo_9Se_{11}$	$\|Mo_9X_{11}\|$			
			$(Mo_9Se_{11})^{3.6-}$	35.6 e^-	3.95_5	2.04
		$Tl_2^+Mo_9S_{11}$	$(Mo_6X_8)(Mo_{12}X_{14})$			
			$= (Mo_6X_8)^{0\to4-} + (Mo_{12}X_{14})^{4-\to0}$	20–24 e^-	3.33–4	2.66–2
				44–48 e^-	3.66–4	2.33–2
7	1.16_7	$Cs_2Mo_{12}Se_{14}$	$\|Mo_{12}Se_{14}\|^{2-}$	46 e^-	3.83_3	2.16_7
6.66	1.11_1	$Rb_4Mo_{18}Se_{20}$	$\|Mo_{18}Se_{20}\|^{4-}$	72 e^-	4	2
6.50	1.08_3	$Cs_6Mo_{24}Se_{26}$	$\|Mo_{24}Se_{26}\|^{6-}$	98 e^-	4.08	1.92
6.40	1.06_6	$Cs_8Mo_{30}Se_{32}$	$\|Mo_{30}Se_{32}\|^{8-}$	124 e^-	4.13	1.87
6	1	$Tl_2Mo_6Se_6$	$\|Mo_{6/2}Se_{6/2}\|_\infty^{1-}$	13 e^-/Mo_3	4.33_3	1.66_6

Chevrel, Gougeon, Potel, Sergent, Ternary molybdenum chalcogenides: A route to new extended clusters. *Journal of Solid State Chemistry*, *57*(1), 25-33 (1985).

BAND STRUCTURE OF $Tl_2Mo_6Se_6$







$Tl_2Mo_6Se_6$

Gibson, Schoop, Muechler, Xie, Hirschberger, Ong, Car, Cava Physical Review B 91 (20), 205128 (2015)