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
THE STRUCTURE OF MATTER - WHICH STRUCTURE IS STABLE?

Governed by:

- Electron count
- Sizes of the elements
- Type of bonding
ELECTRON COUNTING: A QUICK GUIDE

<table>
<thead>
<tr>
<th>Number of electrons to count</th>
<th>Periodic Table of the Elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl: 1+7 = 8</td>
<td>CaF₂: 2+2*7=16</td>
</tr>
<tr>
<td></td>
<td>→ 8 per F</td>
</tr>
</tbody>
</table>

NaCl: 1+7 = 8
CaF₂: 2+2*7=16
→ 8 per F

- NaCl: 1+7 = 8
- CaF₂: 2+2*7=16
- 8 per F
SOME EXAMPLES

GaAs, CdTe, HgTe

Heusler XYZ

\[ 3 + 5 = 8 \]

\[ 1 + 2 + 5 = 8 \]

\[ 3 + 10 + 5 = 18 \]

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

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!

\[2 + 2 \times 4 = 10\]

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
- $VEC(X) > 8 \Rightarrow$ Polycations
- $VEC(X) < 8 \Rightarrow$ Polyanions
ZINTL PHASES: COUNT ELECTRONS TO FIND NUMBER OF BONDS

- Number of bonds in Polyanions:
  - $b(\text{xx}) = 8(\text{or}18) - \text{VEC}(x)$

\[
2 + 2 \times 4 = 10 \\
5 \text{ per Si} \\
\text{b(Si-Si)} = 8 - 5 = 3
\]
ZINTL PHASES: COUNT ELECTRONS TO FIND NUMBER OF BONDS

- Number of bonds in Polyanions:
- \( b_{(xx)} = 8 \) (or \( 18 \)) - VEC(x)

\[
4 + 4 + 6 = 14
\]

14 per Si
\[ b(\text{Si-Si}) = 18 - 14 = 4 \]
SIZE MATTERS!

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

\[
\frac{r_c}{r_a} > 0.732 \quad \text{cubic coordination} \\
\frac{r_c}{r_a} 0.424-0.732 \quad \text{octahedral coordination} \\
\frac{r_c}{r_a} <0.424 \quad \text{tetrahedral coordination}
\]

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!
CHEMICAL CONCEPTS: GIVE BASIC IDEAS ABOUT PROPERTIES

- Electron count (8 or 18)
- Electronegativity difference
- Heavy vs. light elements
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.
DISCOVERY OF TOPOLOGICAL MATERIALS: TIME LINE

- Kane - Mele model
- exp. confirmation (HgTe/CdTe)
- 3D TIs (Z2)
  - Bi2Se3, Bi2Te3, ...
- topological crystalline
  - insulators (Pb1-xSnxTe)
- 3D Dirac
  - Semimetals (Cd3As2, Na3Bi)
- Nodal line Semimetals
  - (Ca3P2, ZrSiS)

- Prediction of QSHE
  - (HgTe/CdTe quantum wells)
- First 3D Z2 TI
  - (Bi1-xSbx)
- New 3D TIs (Z2)
  - (TlBiSe2, PbBi2Te4 and many more)
- Correlated TI
  - SmB6
- Weyl Semimetals
  - (TaAs family, WTe2)
1) DIRAC MATERIALS

- Kane-Mele model
- exp. confirmation (HgTe/CdTe)
- 3D TIs (Z2)
  - Bi2Se3, Bi2Te3, ...
- Topological crystalline insulators (Pb1-xSnxTe)

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- Correlated TI SmB6
- Weyl Semimetals (TaAs family, WTe2)
- 3D Dirac Semimetals (Cd3As2, Na3Bi)
- Modal line Semimetals (Ca3P2, ZrS(S))
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

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

[Diagram showing band structure with labels X, Γ, Z, and normal insulator, gap closing, and 3D Dirac semi-metal]
### Example: Point Groups $\mathbf{C_{2V}}$ and $\mathbf{C_{4V}}$

<table>
<thead>
<tr>
<th></th>
<th>$E$</th>
<th>$C_{2}(z)$</th>
<th>$\sigma_{v}(xy)$</th>
<th>$\sigma_{v}(yz)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_1$</td>
<td>$A_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$\Gamma_2$</td>
<td>$B_2$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>$\Gamma_3$</td>
<td>$A_2$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>$\Gamma_4$</td>
<td>$B_1$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
</tbody>
</table>

**Without SOC**

| $\Gamma_5$ | $E_{1/2}$ | 2 | 0 | 2 | 0 |

**With SOC**

| $\Gamma_6$ | $E_{1/2}$ | 2 | $/2$ | 0 | 0 | 0 |
| $\Gamma_7$ | $E_{3/2}$ | 2 | $/-2$ | 0 | 0 | 0 |

### Higher symmetry allows for more irreps

**But crossings are still coincidental!**

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*To find Dirac Semimetals:*

*Look for highly symmetric charge balanced compounds with not too high electronegativity difference and some SOC*
EXAMPLE: $\text{Cd}_3\text{As}_2$

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

$3 \times 2 + 2 \times 5 = 16$
8 per As
KNOWN DIRAC SEMIMETALS : Na$_3$Bi

- Hexagonal: cone along ΓA, C$_6$ rotation
- $E_N$ (Bi) = 2.0 $E_N$ (Na) = 0.9
- SOC much higher than in Cd$_3$As$_2$

$3*1+5 = 8$

MORE EXAMPLES FOR CHARGE BALANCED COMPOUNDS

- BaAgBi family of compounds
- Crystalize in the ZrBeSi structure (hexagonal)
- Crossing along ΓA, C₆ 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

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:

- **Kane - Mele model**
- **exp. confirmation** (HgTe/CdTe)
- **3D TIs (Z2)** (Bi2Se3, Bi2Te3, ...)
- **topological crystalline insulators** (Pb1-xSnxTe)
- **3D Dirac Semimetals** (Ca3P2, ZrSiS)
- **Nodal line Semimetals**
- **Prediction of QSHE** (HgTe/CdTe quantum wells)
- **First 3D Z2 TI** (Bi1-xSbx)
- **New 3D TIs (Z2)** (Ti3BiSe2, PbBi2Te4 and many more)
- **Correlated TI SmB6**
- **Weyl Semimetals** (TaAs family, WTe2)
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!
3) LINE NODE MATERIALS

Kane - Mele model
exp. confirmation (HgTe/CdTe)

3D TIs (Z2)
Bi2Se3, Bi2Te3, ...

topological crystalline insulators
(Pb1-xSnxTe)

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SmB6

Weyl Semimetals
(TaAs family, WTe2)
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

AND WHAT NOW???
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

NON SYMMORPHIC SYMMETRY ⇒ NEW FERMIONS?

Example: New Fermions in Non-symmorphic materials

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

EXPERIMENTAL CHALLENGES FOR REALIZING NON-SYMMORPHIC SEMIMETALS

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

Cd$_3$As$_2$

3*2 + 2*5 = 16
8 per As

Na$_3$Bi

3*3 + 5 = 8

“conventional DSM”

“non-symmorphic DSM”

Trivial insulator (even e⁻/site)
Non-trivial Dirac metal (odd e⁻/site)

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 (antiferromagnetism)
FIRST PREDICTION: BiO$_2$

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

$r_{\text{Oxygen}} = 1.4$
$r_{\text{Si}}/r_O < 0.414$
$r_{\text{Bi}}/r_O = \text{at least } 0.53 > 0.414$

http://abulafia.mt.ic.ac.uk/shannon/ptable.php  
WHY NO BiO₂? - THE INERT PAIR EFFECT

• Bi⁴⁺ 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 Bi⁴⁺ → Bi³⁺ + Bi⁵⁺
“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 $\rightarrow$ 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!

$2 + 2 \times 4 = 10$
5 per Si
EXAMPLES FOR COMPOUNDS WITH HALF FILLED BANDS

- SrIrO$_3$: Orthorhombic form predicted to be non-symmorphic line node material
- $2 + 9 + 3 \times 6 = 29$ electrons $\rightarrow$ 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
SrIrO$_3$: PREDICTION VS. EXPERIMENT

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

Experiment on a thin film
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$_6$S$_8$
Mo$_6$ cluster, 12 edges
Cluster is filled with 24 electrons

PbMo$_6$S$_8$: Cluster has only 22 electrons
(=3.66 electrons per Molybdenum)
superconducting
NON SYMMORPHIC CLUSTER COMPOUNDS?

BAND STRUCTURE OF Tl$_2$Mo$_6$Se$_6$