# Design and Synthesis of New Materials

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Department of Materials Science and Engineering
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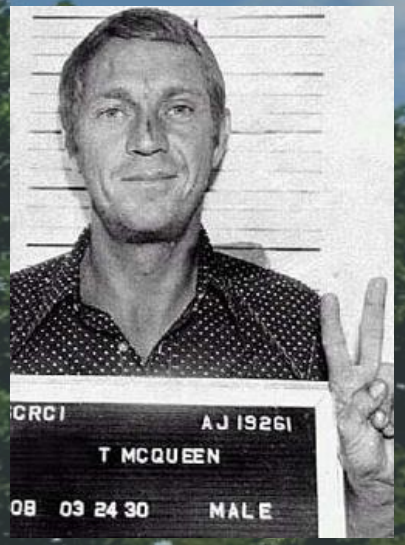
Institute for Quantum Matter




Discovery by Design

"Optimism Does Not Change the Laws of Physics [or Chemistry]"
- Science Officer T'Pol, Starship Enterprise

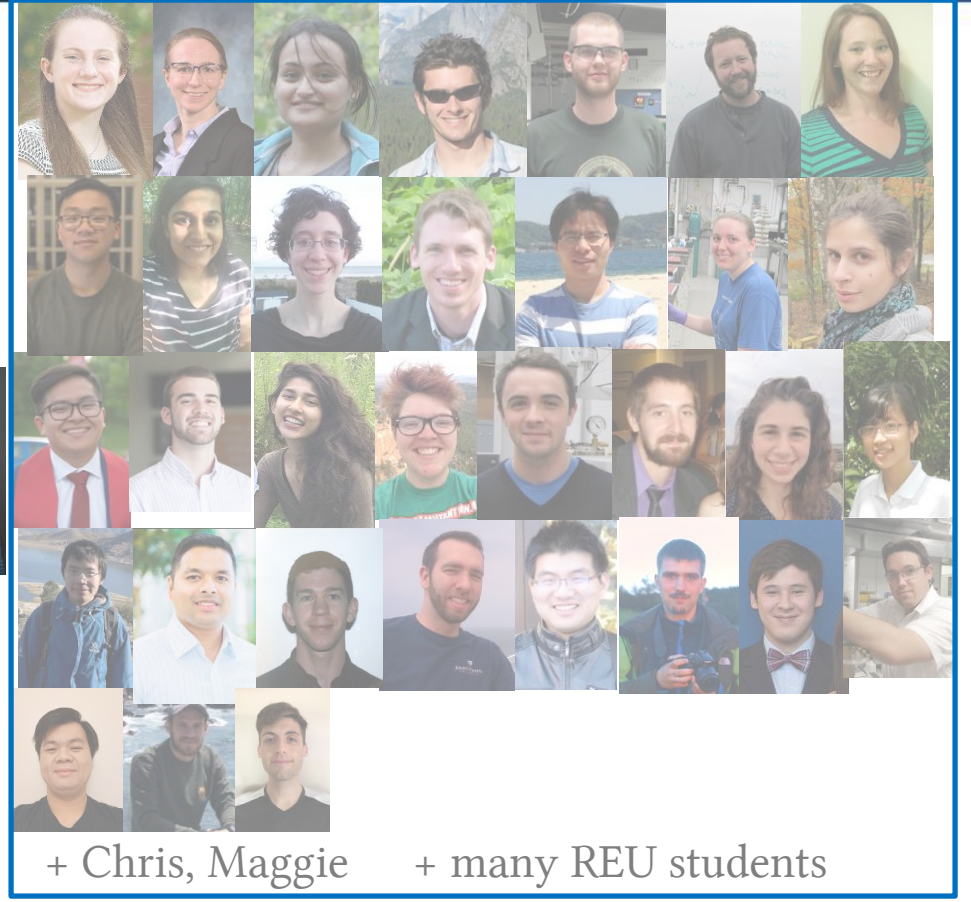
See also 9 years of summer school content at https://www.paradim.org/summer_schools_past

# The Team

PARADIM

IQM

+Noah, James, Josh



+ Chris, Maggie + many REU students

APEX
A Center for Power Electronics Materials and Manufacturing Exploration

Office of Naval Research — Science & Technology

NSF

DR, MPMS
CAREER
PARADIM

PARADIM
PLATFORM FOR THE ACCELERATED REALIZATION, ANALYSIS & DISCOVERY OF INTERFACE MATERIALS

Alfred P. Sloan Foundation 1934

the David & Lucile Packard FOUNDATION

https://occamy.chemistry.jhu.edu

C²QA
Co-design Center for Quantum Advantage

APL JOHNS HOPKINS APPLIED PHYSICS LABORATORY

JOHNS HOPKINS UNIVERSITY

INSTITUTE FOR QUANTUM MATTER
A collaboration between JOHNS HOPKINS UNIVERSITY and PRINCETON UNIVERSITY

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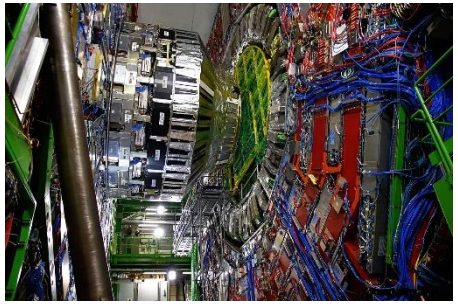
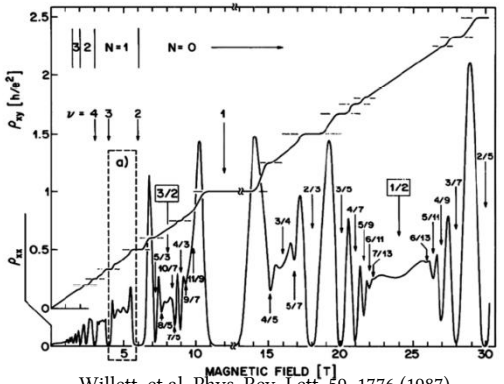
# Outline

- Materials Lifecycle and Defining Quantum Materials
- The Importance of Design
- Synthesis Preliminaries
- Characterization and “Defects, Defects, Defects!”
- Advancing Materials Synthesis
- Role of AI/ML Methods
- The Future

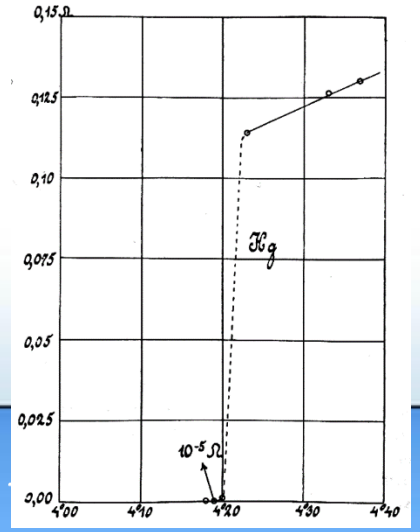
# [Materials] underlie…

## …basic science

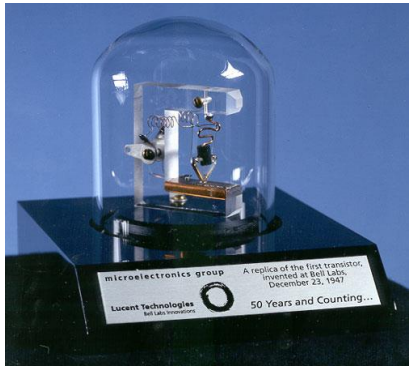



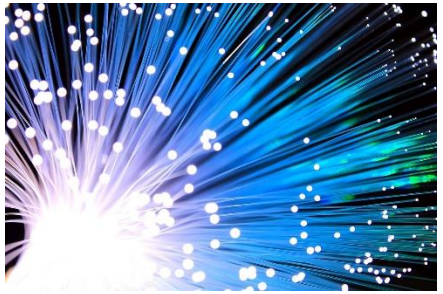


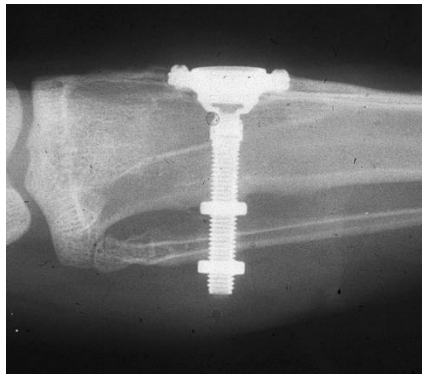

Willett, et al. Phys. Rev. Lett. 59, 1776 (1987)

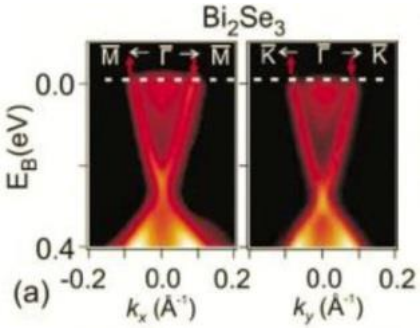



## …practical technologies








A NON-RUSTING STEEL.

Sheffield Invention Especially Good for Table Cutlery.

The New York Times

Published: January 31, 1915

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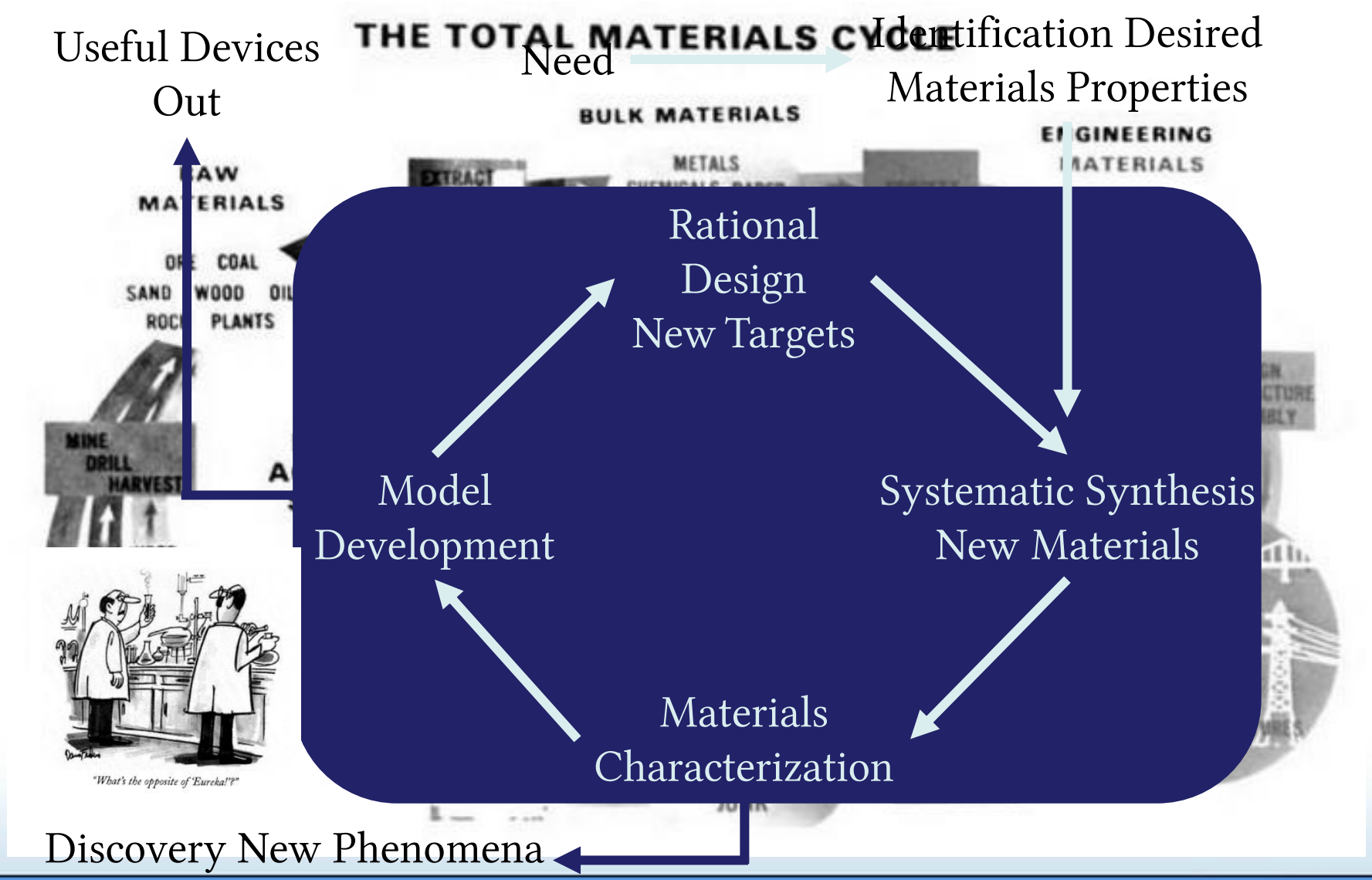
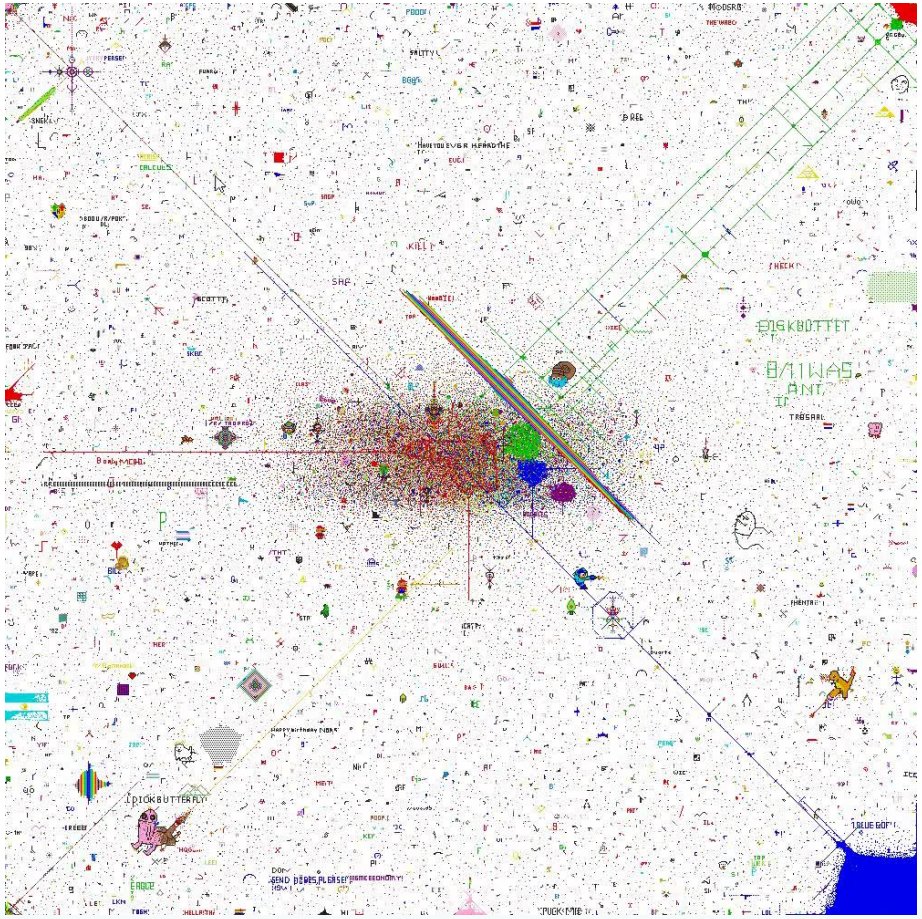
# Materials Lifecycle






Materials And Man's Needs, NAS (1974)

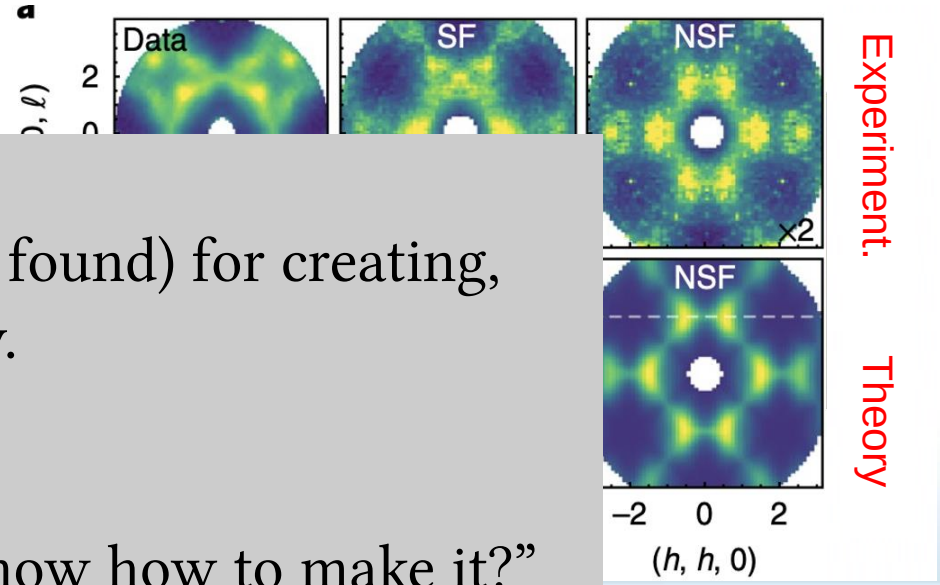
# Emergence… The Unifying Force



# Quantum materials… the landscape

- Strongly correlated electron materials: quantum spin liquids and other entangled order, superconductors, multiferroics, …
- Topological materials: quantum Hall & spin Hall insulators, quantum anomalous Hall insulators, topological insulators, Weyl and Dirac semimetals, topological crystalline insulators…
- 2D materials: transition metal dichalcogenides, graphene, phosphorene, stannene, …
- Single spin centers: defects (diamond, SiC, ZnO, etc.), molecular complexes, MOFs…






**The Challenge:**

"Homogeneous" is often not what is needed (or found) for creating, harnessing and controlling this phenomenology.
"Highly tuned / structured" is.

"once you know what to make… how do you know how to make it?"

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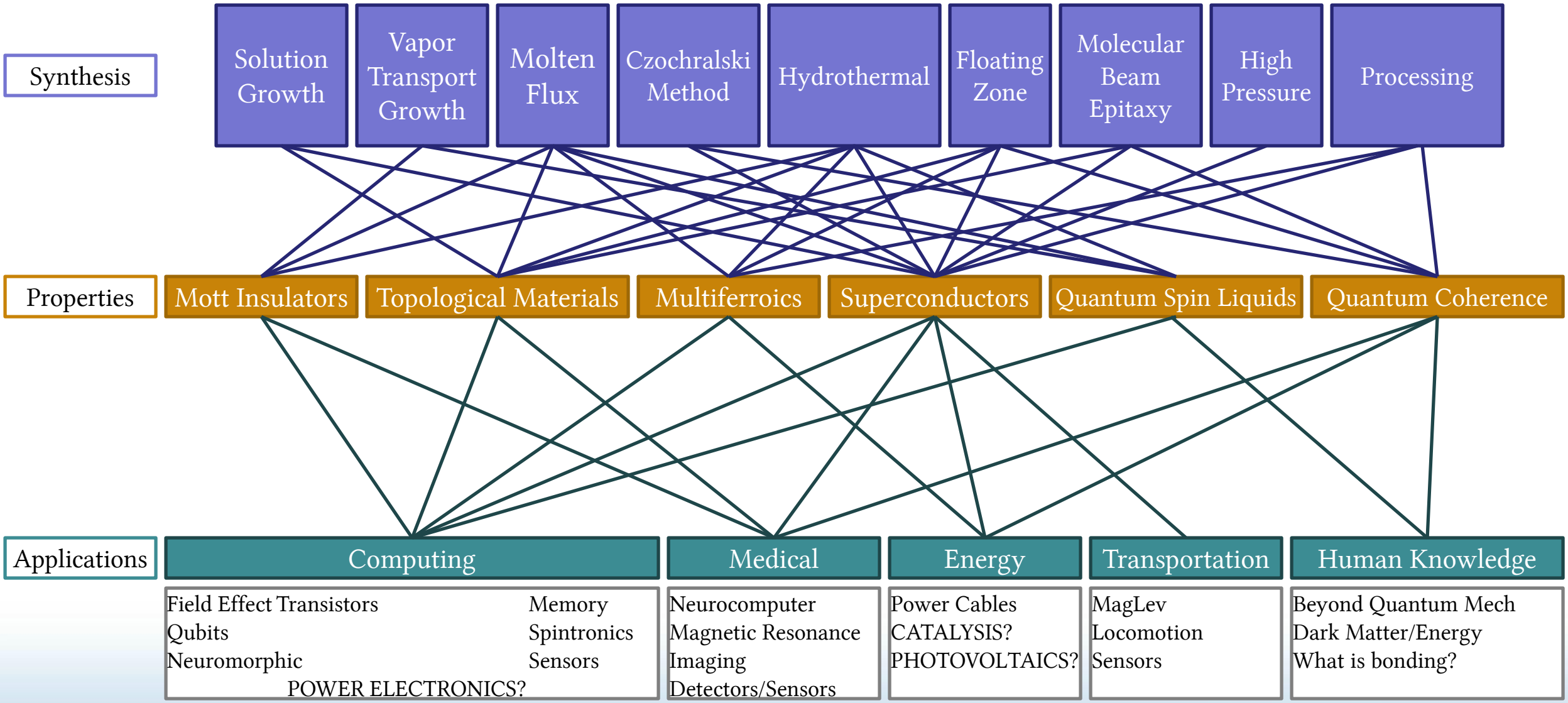
Thanks to Nitin Samarth (PSU) and Collin Broholm (JHU) for some slide content.

# How do Materials Fit In?



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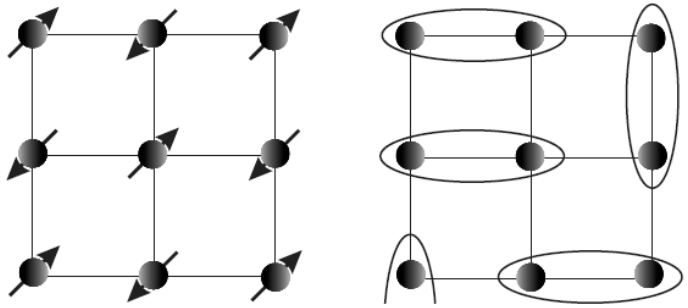
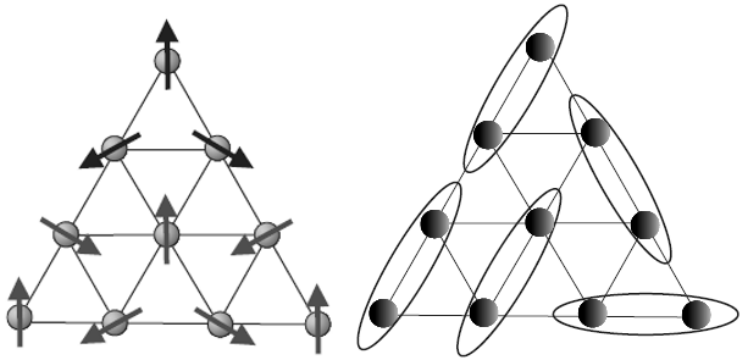
# Knowing what to make

## Go from this…



Neél order
(static, classical)

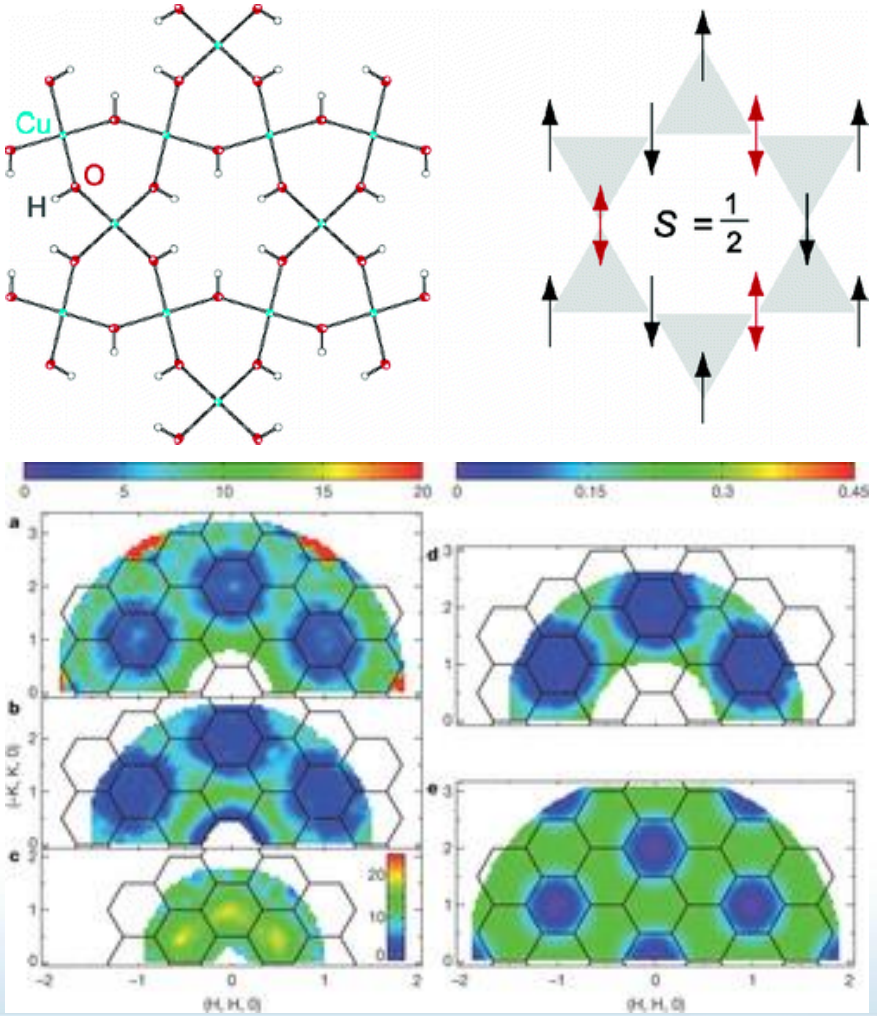
Quantum spin-liquid state



$$H = J \sum_{<ij>} \vec{S_i} \cdot \vec{S_j}$$

$ZnCu_3(OH)_6Cl_2$

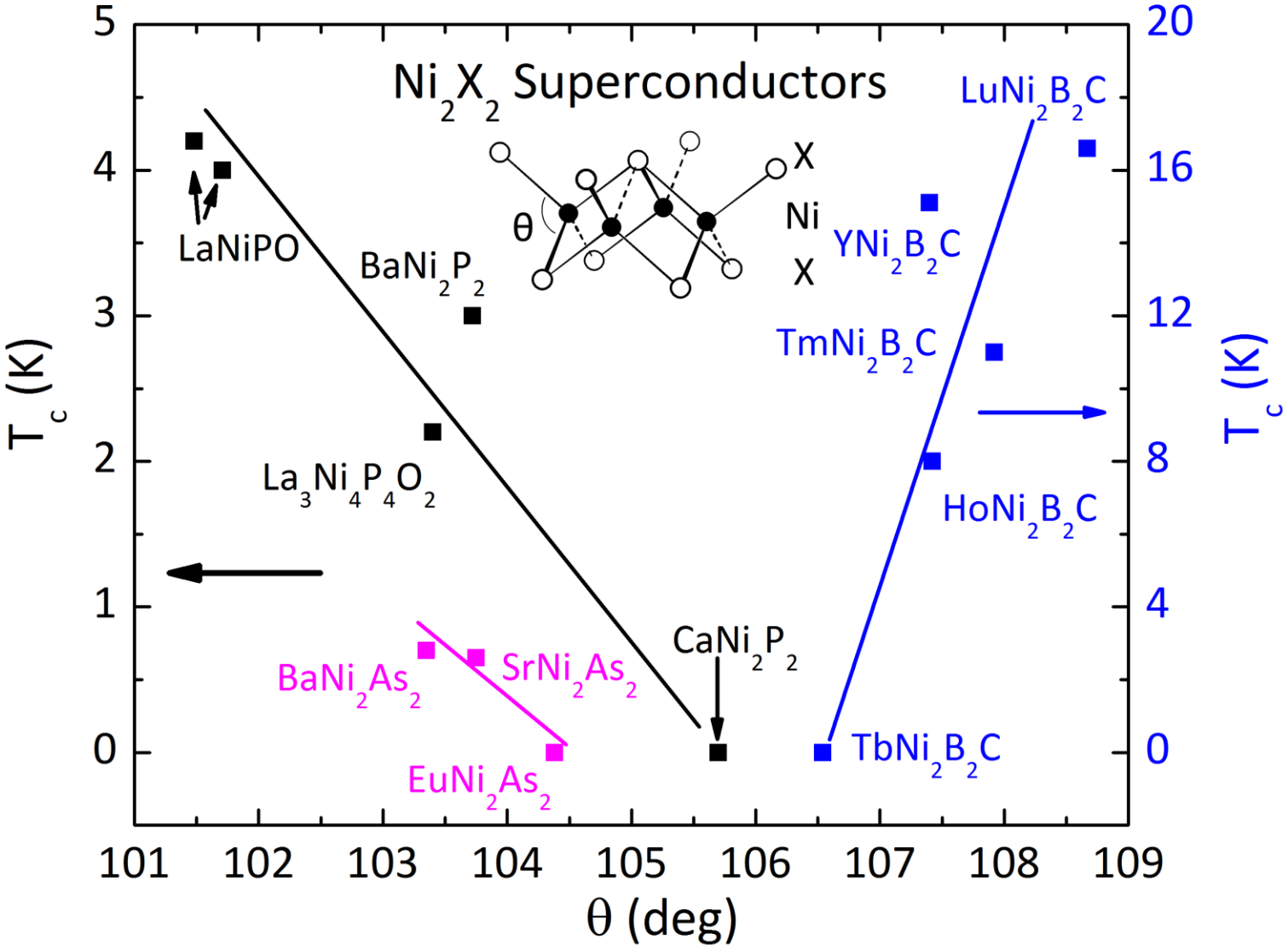
## …to this






P.W. Anderson, Mat. Res. Bull. 8, 153-160 (1973)
R. Moessner and S.L. Sondhi, Prog. Theor. Phys. (2002)
Y.S. Lee, et al. Nature 492, 406-10 (2012)

# Structure-property relationships




T.M. McQueen, et al. *Phys. Rev. B* **79**, 172502 (2009)

# Concrete Theories

PHYSICAL REVIEW B **76**, 045302 (2007)

**Topological insulators with inversion symmetry**

# A topological Dirac insulator in a quantum spin Hall phase

D. Hsieh[1], D. Qian[1], L. Wray[1], Y. Xia[1], Y. S. Hor[2], R. J. Cava[2] & M. Z. Hasan[1,3]

**When electrons are subject to a large external magnetic field, the conventional charge quantum Hall effect[1,2] dictates that an electronic excitation gap is generated in the sample bulk, but metallic conduction is permitted at the boundary. Recent theoretical models suggest that certain bulk insulators with large spin–orbit interactions may also naturally support conducting topological boundary states in the quantum limit[3–5], which opens up the possibility for studying unusual quantum Hall-like phenomena in zero external magnetic fields[6]. Bulk $Bi_{1-x}Sb_x$ single crystals are predicted to be prime candidates[7,8] for one such unusual Hall**

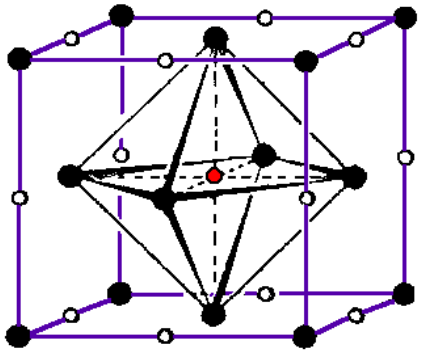
$\Delta$ between $L_a$ and $L_s$ closes and a massless, three-dimensional (3D) Dirac point is realized. As $x$ is further increased this gap re-opens with inverted symmetry ordering, which leads to a change in sign of $\Delta$ at each of the three equivalent L-points in the Brillouin zone. For concentrations greater than $x \approx 7\%$ there is no overlap between the valence band at T and the conduction band at L, and the material becomes an inverted-band insulator. Once the band at T drops below the valence band at L, at $x \approx 8\%$, the system evolves into a direct-gap insulator whose low-energy physics is dominated by the spin–orbit-coupled Dirac particles at L[7,17].

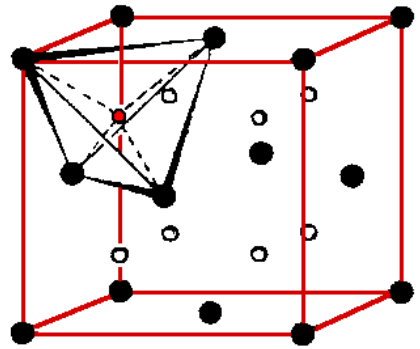
DOI: 10.1103/PhysRevB.76.045302 PACS number(s): 73.43.−f, 72.25.Hg, 73.20.−r, 85.75.−d

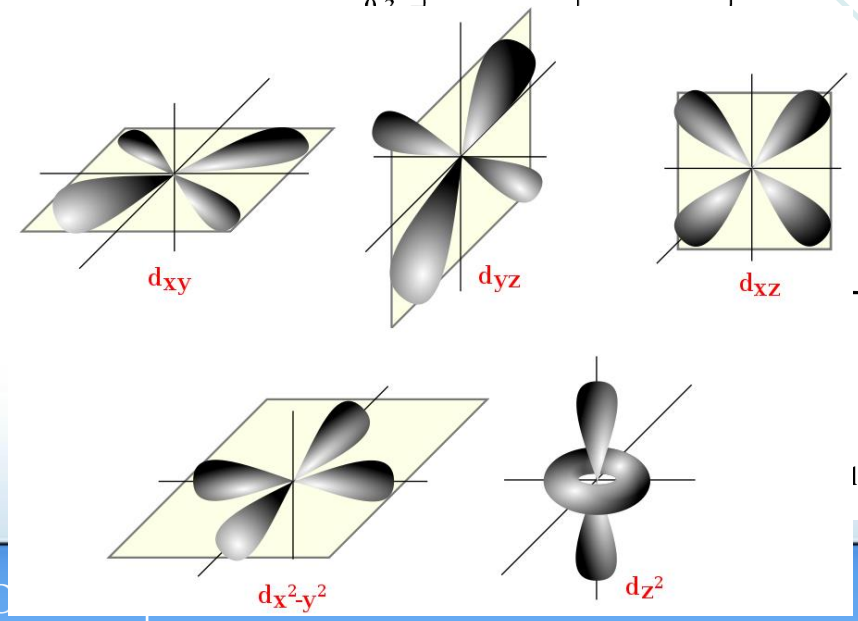


L. Fu and Kane, *Phys. Rev. B* **76**, 045202 (2007)
D. Hsieh, et al. *Nature* **452**, 970-5 (2008)

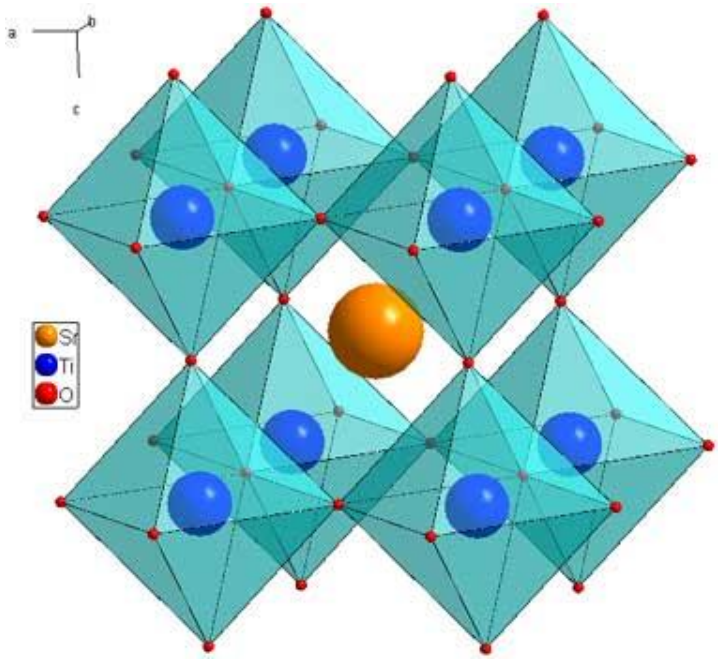
# Structure and electron count dictate properties



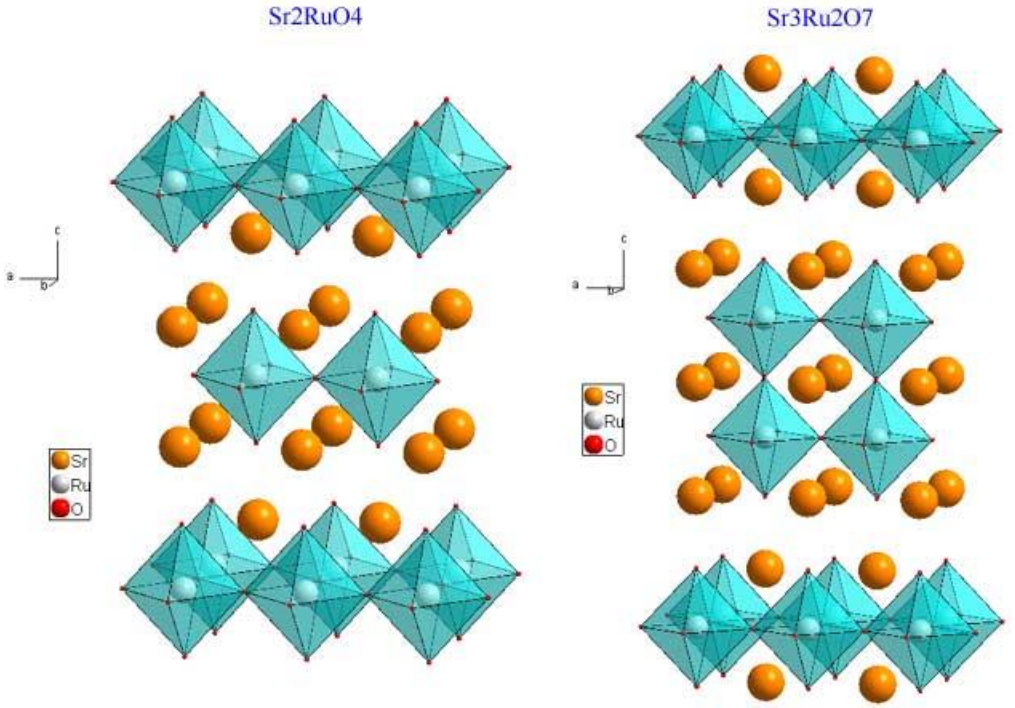




# Structure and electron count dictate properties



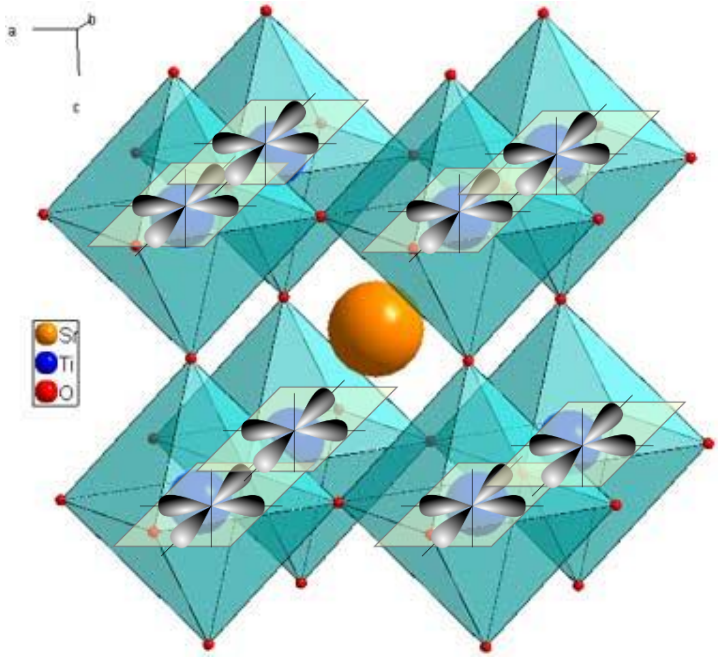

3-D Corner-sharing Octahedra
(Perovskite!)

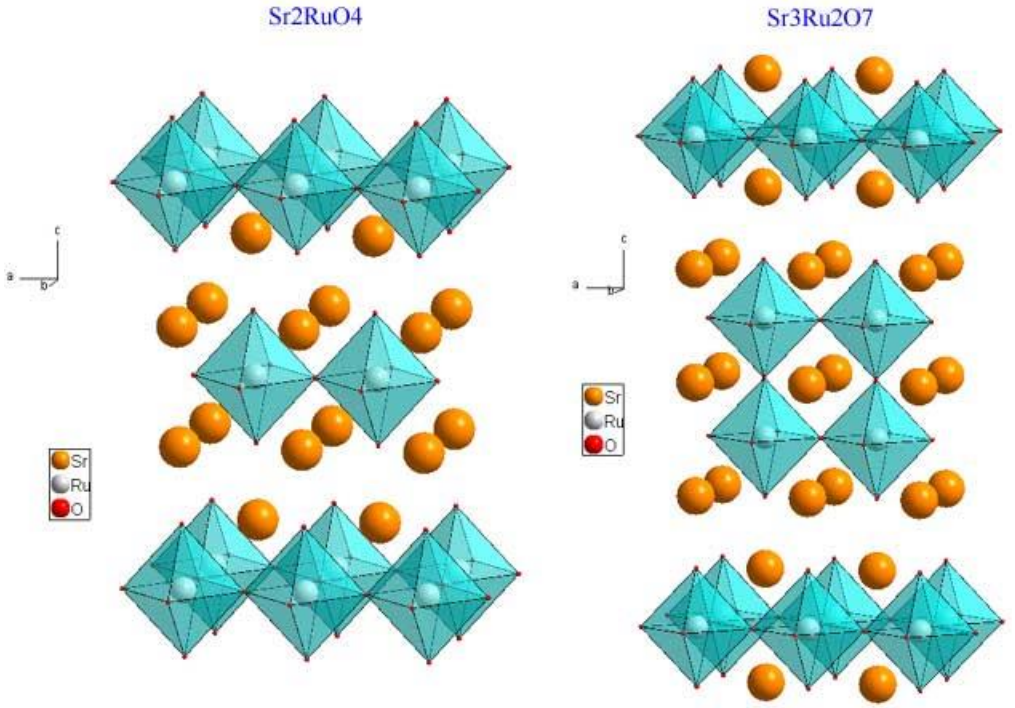



2+$\delta$-D Corner-sharing Octahedra
Ruddlesden-Popper

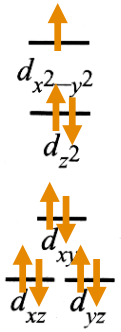
Polyhedral Connectivity Determines Orbital Overlap

# Structure and electron count dictate properties



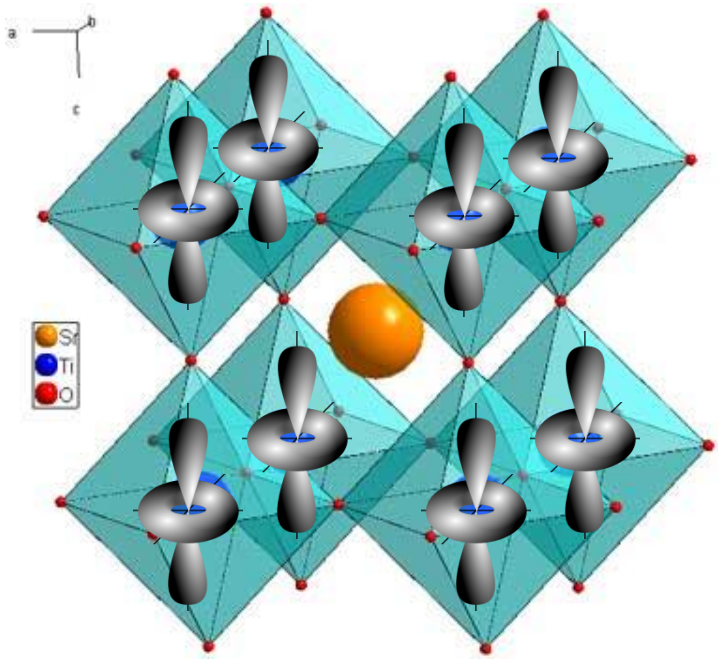

Effectively 2-D

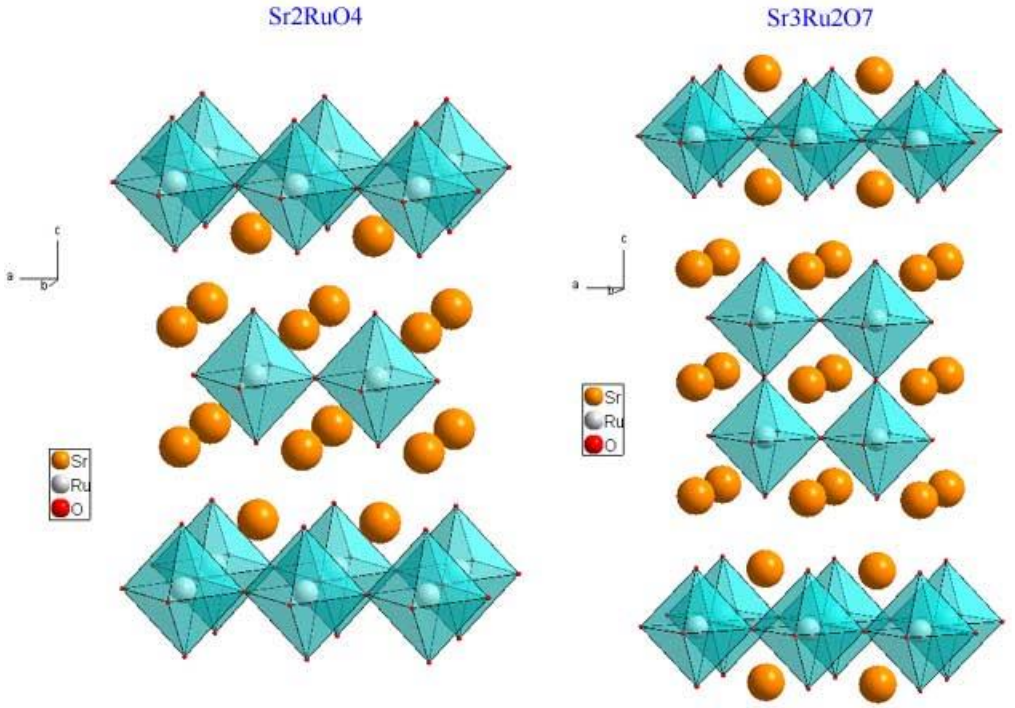



2+$\delta$-D Corner-sharing Octahedra
Ruddlesden-Popper

Polyhedral Connectivity Determines Orbital Overlap

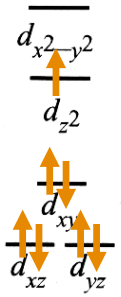
# Structure and electron count dictate properties



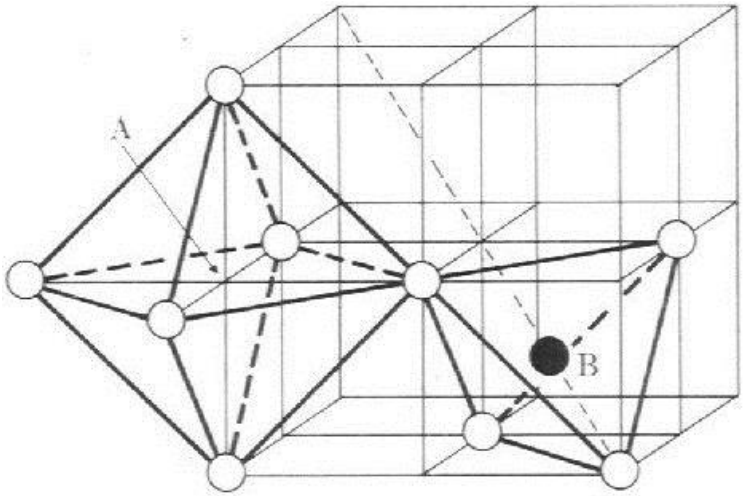

Effectively 1-D

2+$\delta$-D Corner-sharing Octahedra
Ruddlesden-Popper




Polyhedral Connectivity Determines Orbital Overlap
Electron Count Determines Orbital Filling and Effective Dimensionality (and Properties!)

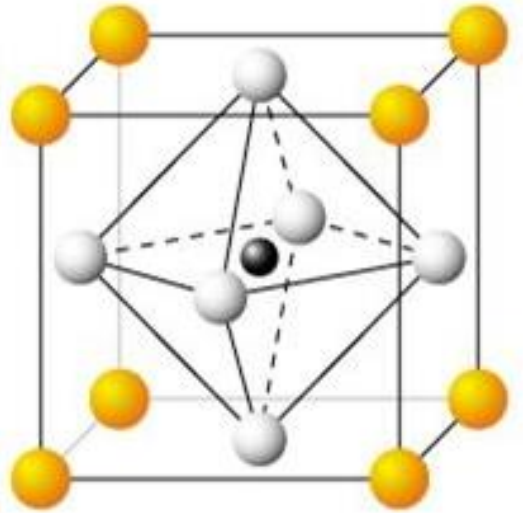
# Ionic size matters (a lot)




**Effective Ionic Radii in Oxides and Fluorides***

By R. D. Shannon and C. T. Prewitt

*Central Research Department * Experimental Station*
*nt de Nemours and Company, Wilmington, Delaware 19898, U.*



| 'IR' | ION | EC | CN | SP | A- |
|---|---|---|---|---|---|
| .50 | S +6 | 2P 6 | VI | | . |
| .60 * | SB+3 | 5S 2 | IVPY | | |
| .71 | | | V | | |
| | | | VI | ( | . |
| -.12 | SB+5 | 4D10 | VI | | . |
| | SC+3 | 3P 6 | VI | | . |
| .99 ? | | | VIII | | |
| 1.00 ? | SE-2 | 4P 6 | VI | | 1. |
| 1.02 | SE+4 | 4S 2 | VI | ( | . |
| 1.13 ? | SE+6 | 3D10 | IV | | |
| 1.16 ? | | | VI | | . |
| 1.32 ? | SI+4 | 2P 6 | IV | | |
| .71 ? | | | VI | .42 | .540 |
| .70 E | SM+3 | 4F 5 | VI | 1.00 | 1.104 |
| .69 R | | | VIII | | 1.23 |
| .32 ? | SN+2 | 5S 2 | VI | .93 | |
| .64 | | | VIII | | 1.36 |
| .66 | SN+4 | 4D10 | VI | .71 | .830 |
| .995 R | SR+2 | 4P 6 | VI | 1.12 | 1.30 |
| 1.12 R | | | VII | | 1.35 |
| 1.09 ? | | | VIII | | 1.39 |
| .700 R* | | | X | | 1.46 |
| .56 R | | | XII | | 1.58 |
| .60 E | TA+3 | 5D 2 | VI | | .81 |
| 1.10 | TA+4 | 5D 1 | VI | | .80 |
| 1.04 R | TA+5 | 5P 6 | VI | .68 | .78 |
| .98 R | | | VIII | | .83 |
| .71 | TB+3 | 4F 8 | VI | .93 | 1.063 |
| 1.35 | | | VIII | | 1.18 |
| 1.36 | TB+4 | 4F 7 | VI | .81 | .90 |
| 1.38 | | | VIII | | 1.02 |
| 1.40 | TC+4 | 4D 3 | VI | | .78 |
| 1.42 | TC+7 | 4P 6 | VI | .56 | |
| | TE-2 | 5P 6 | VI | 2.21P | |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | V | | 1.14 | 1.00 | ? | | |
| | | VI | .97 | 1.16 | 1.02 | | | |
| | | VII | | 1.27 | 1.13 | ? | | |
| | | VIII | | 1.30 | 1.16 | ? | | |
| | | IX | | 1.46 | 1.32 | ? | | |
| NB+2 | 4D 3 | VI | | .85 | .71 | ? | | |
| NB+3 | 4D 2 | VI | | .84 | .70 | E | | |
| NB+4 | 4D 1 | VI | ( .74) | .83 | .69 | R | | |
| NB+5 | 4P 6 | IV | | .46 | .32 | ? | | |
| | | VI | .69 | .78 | .64 | | | |
| | | VII | | .80 | .66 | | | |
| ND+3 | 4F 3 | VI | 1.04 | 1.135 | .995 | R | | |
| | | VIII | | 1.26 | 1.12 | R | | |
| | | IX | | 1.23 | 1.09 | ? | | |
| NI+2 | 3D 8 | VI | .69 | .840 | .700 | R* | | |
| NI+3 | 3D 7 | VI | LS | .70 | .56 | R | | |
| | | | HS | .74 | .60 | E | | |
| NP+2 | 5F 5 | VI | | 1.24 | 1.10 | | | |
| NP+3 | 5F 4 | VI | 1.10 | 1.18 | 1.04 | R | | |
| NP+4 | 5F 3 | VI | .95 | | | | | |
| | | VIII | | 1.12 | .98 | R | | |
| NP+7 | 6P 6 | VI | .71 | | | | | |
| O -2 | 2P 6 | II | | 1.21 | 1.35 | | | |
| | | III | | 1.22 | 1.36 | | | |
| | | IV | | 1.24 | 1.38 | | | |
| | | VI | 1.40 | 1.26 | 1.40 | | | |
| | | VIII | | 1.28 | 1.42 | | | |
| | | | | | | | .540 | .400 R* |
| | | | | | | | 1.104 | .964 R |
| | | | | | | | 1.23 | 1.09 R |
| | | | | | | | 1.36 | 1.22 R |
| | | | | | | | .830 | .690 R* |
| | | | | | | | 1.30 | 1.16 |
| | | | | | | | 1.35 | 1.21 |
| | | | | | | | 1.39 | 1.25 |
| | | | | | | | 1.46 | 1.32 |
| | | | | | | | 1.58 | 1.44 |
| | | | | | | | .81 | .67 |
| | | | | | | | .80 | .66 R |
| | | | | | | | .78 | .64 |
| | | | | | | | .83 | .69 |
| | | | | | | | 1.063 | .923 R |
| | | | | | | | 1.18 | 1.04 R |
| | | | | | | | .90 | .76 R |
| | | | | | | | 1.02 | .88 |
| | | | | | | | .78 | .64 R |

# Nonsense Example

PRL **108,** 140405 (2012) PHYSICAL REVIEW LETTERS week ending 6 APRIL 2012

## Dirac Semimetal in Three Dimensions

S. M. Young,[1] S. Zaheer,[2] J. C. Y. Teo,[2,*] C. L. Kane,[2] E. J. Mele,[2] and A. M. Rappe[1]

[1]*The Makineni Theoretical Laboratories, Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323, USA*

[2]*Department of Physics and Astronomy, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6396, USA*

(Received 13 December 2011; published 6 April 2012)

We show that the pseudorelativistic physics of graphene near the Fermi level can be extended to three dimensional (3D) materials. Unlike in phase transitions from inversion symmetric topological to normal insulators, we show that particular space groups also allow 3D Dirac points as symmetry protected degeneracies. We provide criteria necessary to identify these groups and, as an example, present *ab initio* calculations of $\beta$-cristobalite $BiO_2$ which exhibits three Dirac points at the Fermi level. We find that $\beta$-cristobalite $BiO_2$ is metastable, so it can be physically realized as a 3D analog to graphene.

DOI: 10.1103/PhysRevLett.108.140405 PACS numbers: 05.30.Fk, 31.15.−p, 71.20.−b

Si: 0.26 Å
O: 1.40 Å

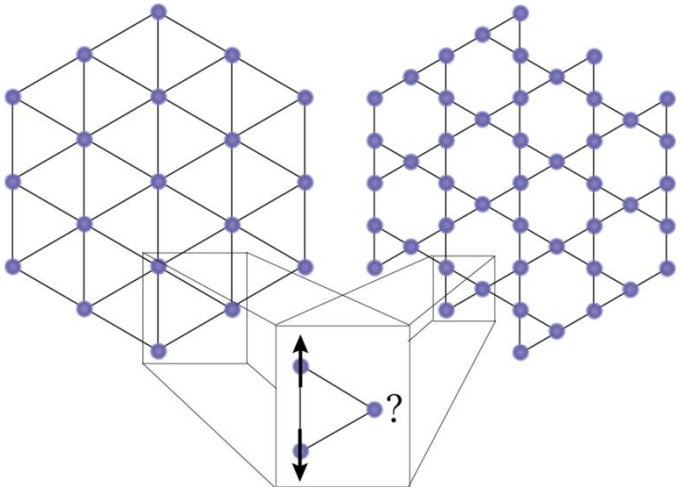
Bi: 0.99 Å
O: 1.40 Å

$2\ Bi^{4+} \rightarrow Bi^{3+} + Bi^{5+}$ U = -8 eV



S.M. Young, et al. *Phys. Rev. Lett.* **108**, 140405 (2012)

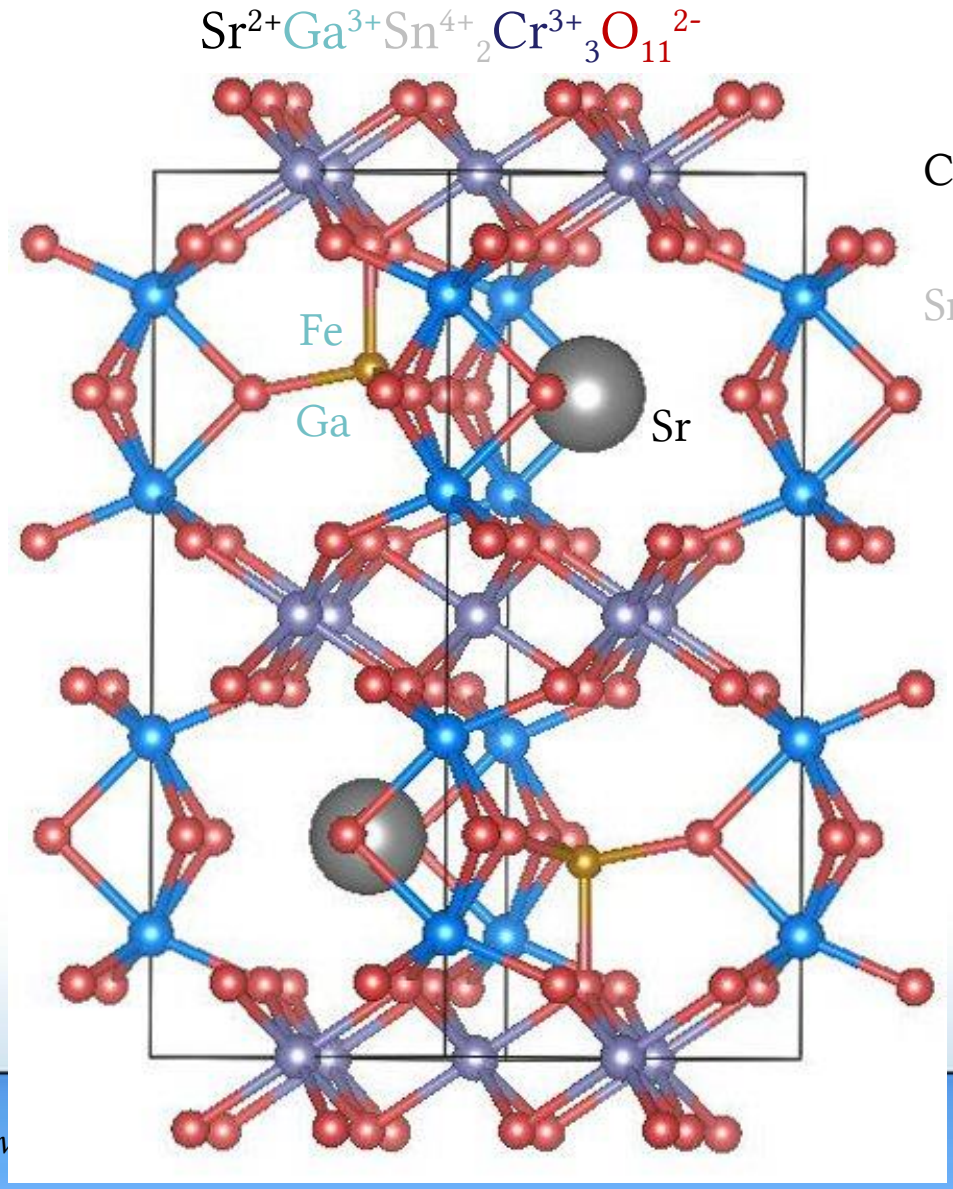
# Better Example: $SrSn_2GaCr_3O_{11}$




Take as givens:

1) Want 2-D kagomé layer
2) Want $Cr^{3+}$ as magnetic ion

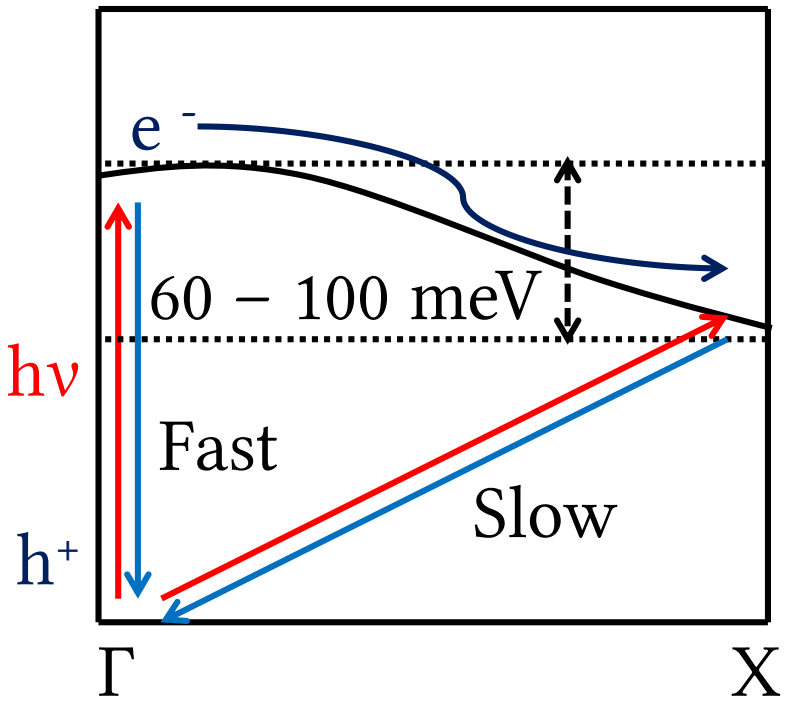
Match sizes for different coordination environments and disfavor site mixing, while keeping charge balance

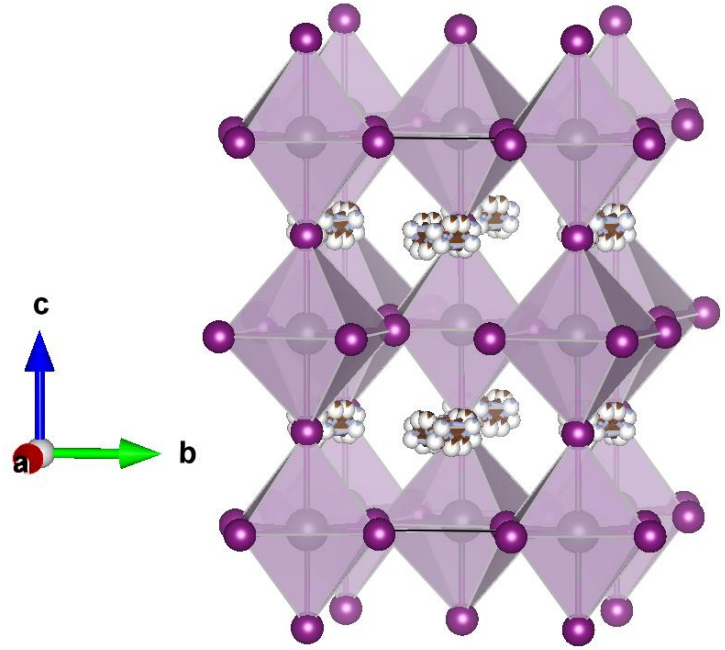





I.D. Posen, *Phys. Rev*

# Another Example



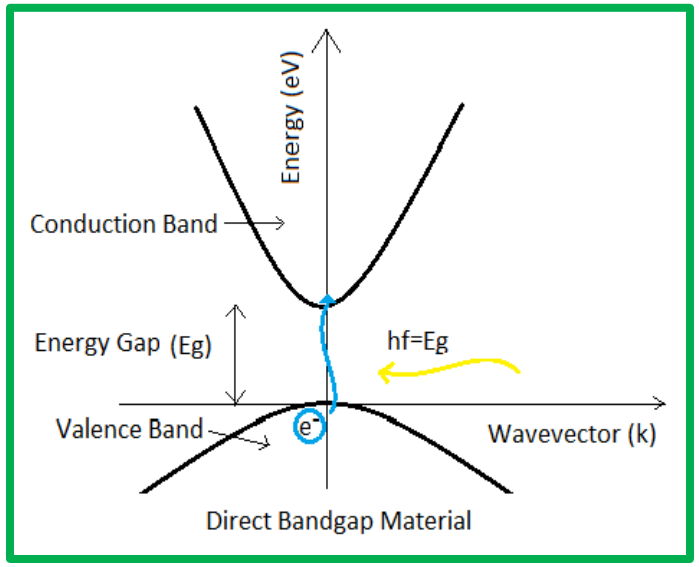

$(CH_3NH_3)PbI_3$

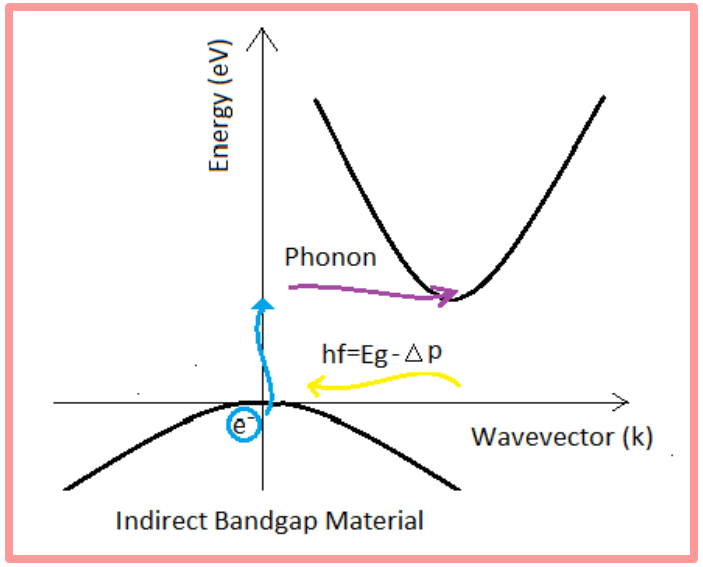
How to systematically engineer this band structure?



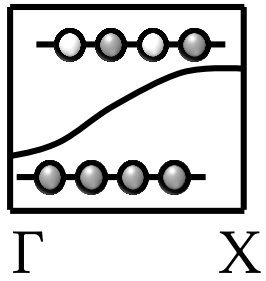
E.M. Hutter, et. al. *Nat. Mater.* ***16****, 115-120* (2017)

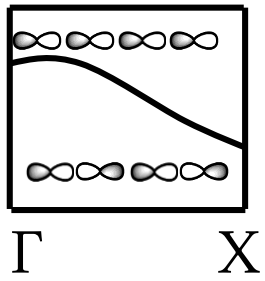
# Design Strategy




1. Conduction band minimum: tuned from s- to p-orbital derived bands




s-orbital derived bands → p-orbital derived bands

2. Valence band maximum: unchanged

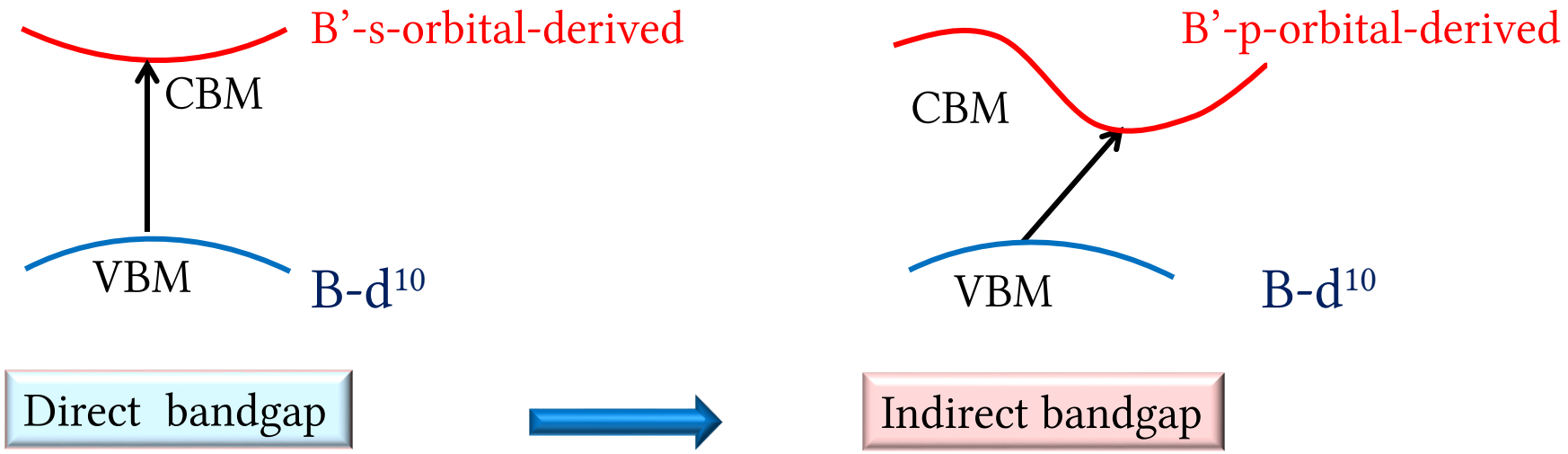


T.T. Tran, et. al. *Materials Horizons* (2017)

# Design Strategy

$A_2B^{+}\ B'^{3+}X_6$

Valence electron: $d^{10}$ $s^0/s^2$



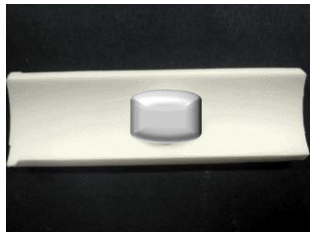



T.T. Tran, et. al. *Materials Horizons* (2017)

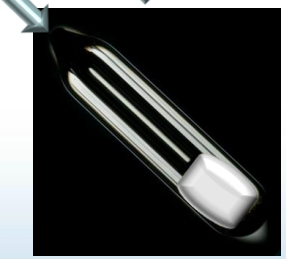
# Synthesis

Solid State Reactions
$Cs_2AgSbCl_6$, $Cs_2AgInCl_6$
$Cs_2AgSb_xIn_{1-x}Cl_6$ (x = 0.2, 0.4, 0.5)
CsCl : AgCl : $SbCl_3$ ($InCl_3$)

Ar-atmosphere



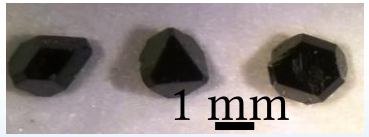
Quartz ampoule



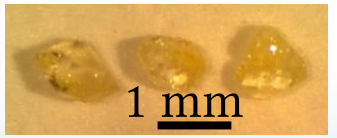
200 – 400 °C
3 days

Solvothermal Reactions
$Cs_2AgSbCl_6$ + HCl
$Cs_2AgInCl_6$ + HCl

120 – 160 °C
3 days




$Cs_2AgSbCl_6$

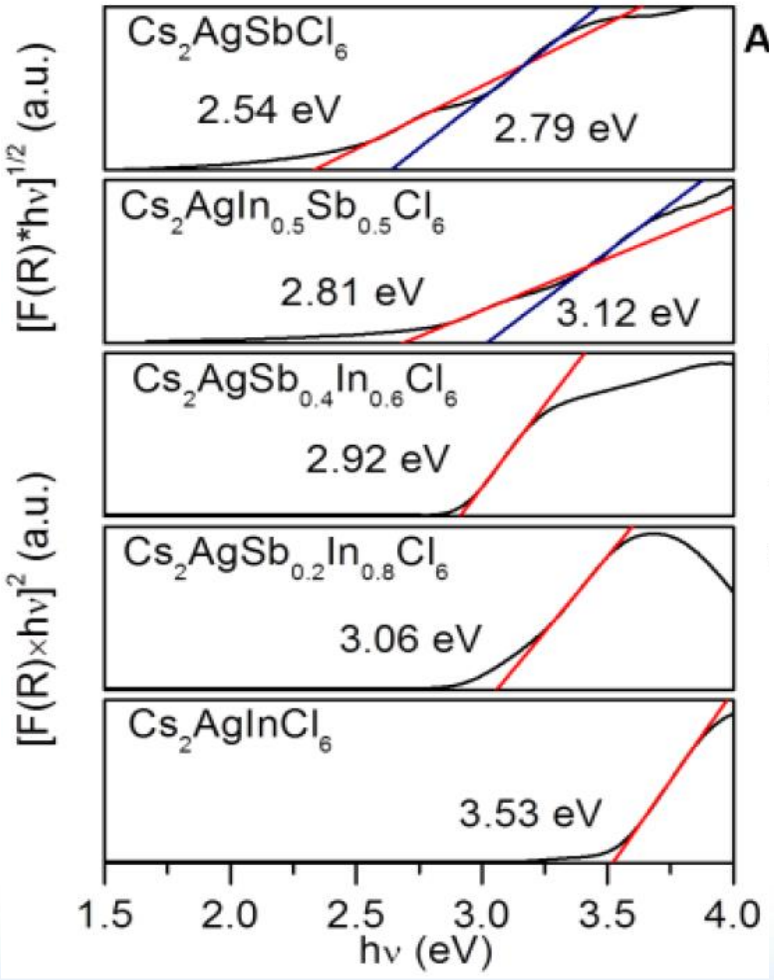


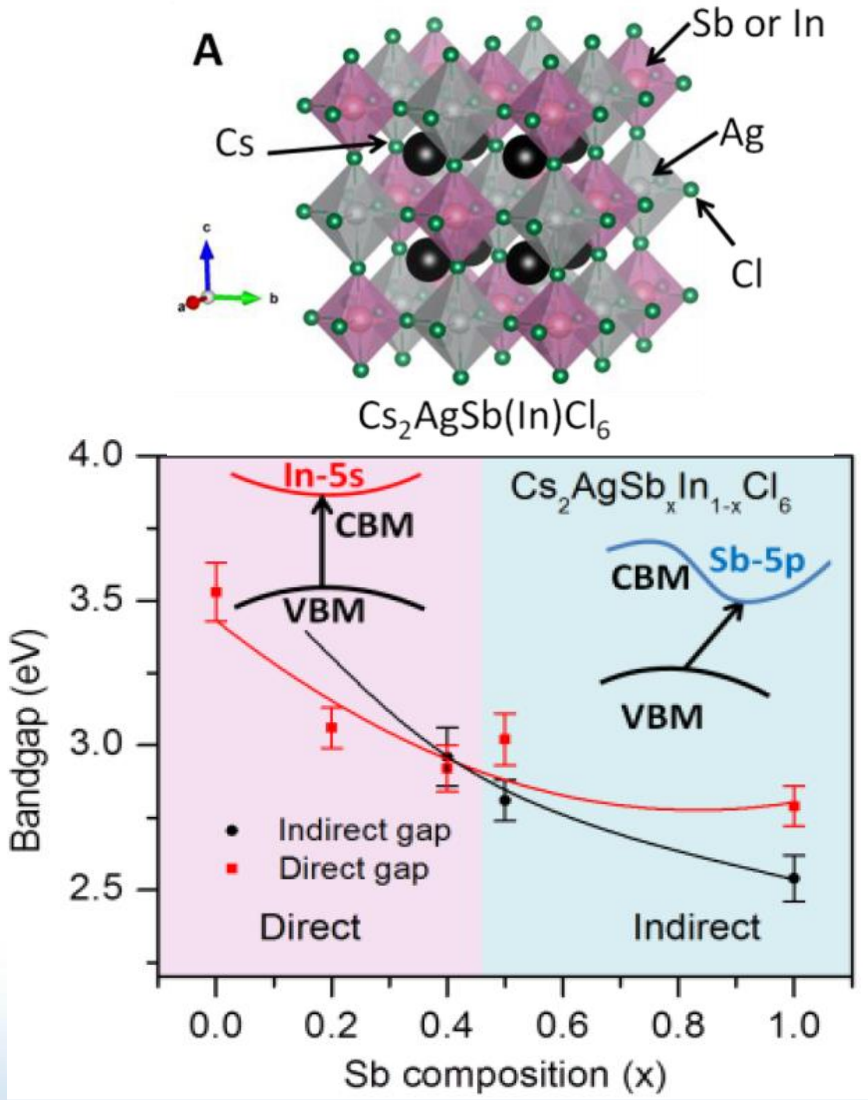

$Cs_2AgInCl_6$



T.T. Tran, et. al. *Materials Horizons* (2017)

# It works…

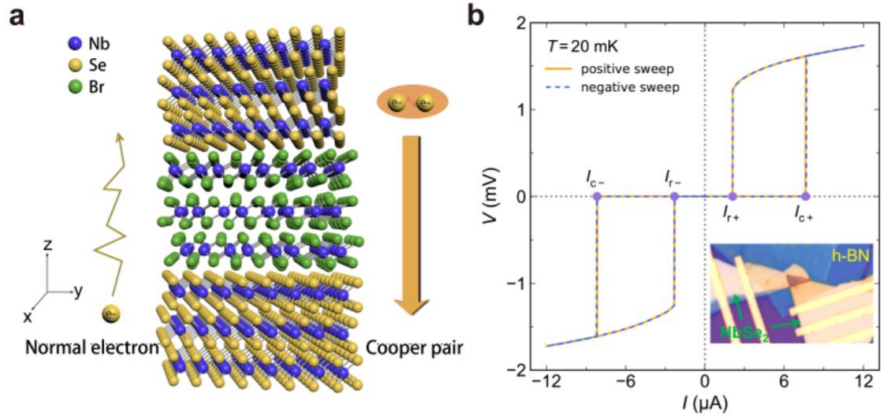




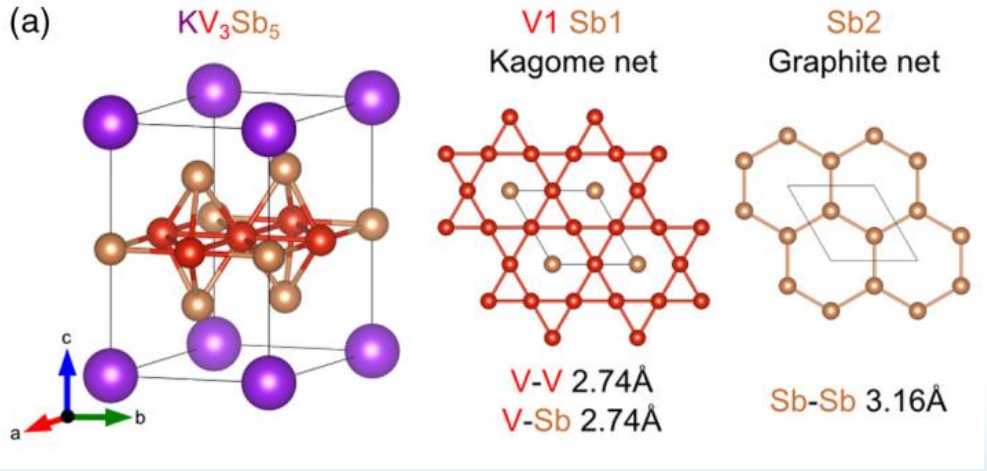

T.T. Tran, et. al. *Materials Horizons* (2017)

# And on it goes…

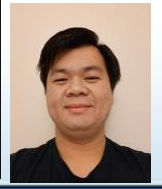


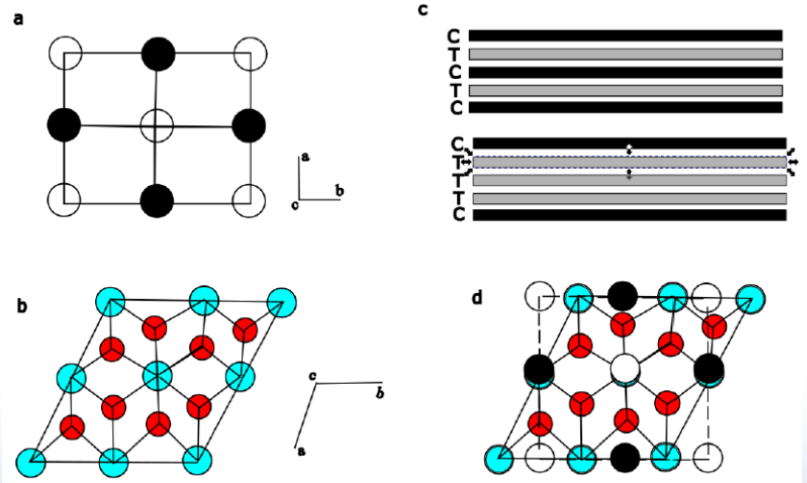

H. Wu, et al. Nature **604**, *653-656 (2022)*

W.A. Phelan, et al. *PRX* (2014) and *Sci. Rep.* (2016)




B.R. Ortiz, et al. *PRM* (2019) and S.-Y. Yang, et. al. *Sci. Adv.* **6** *(2020)*





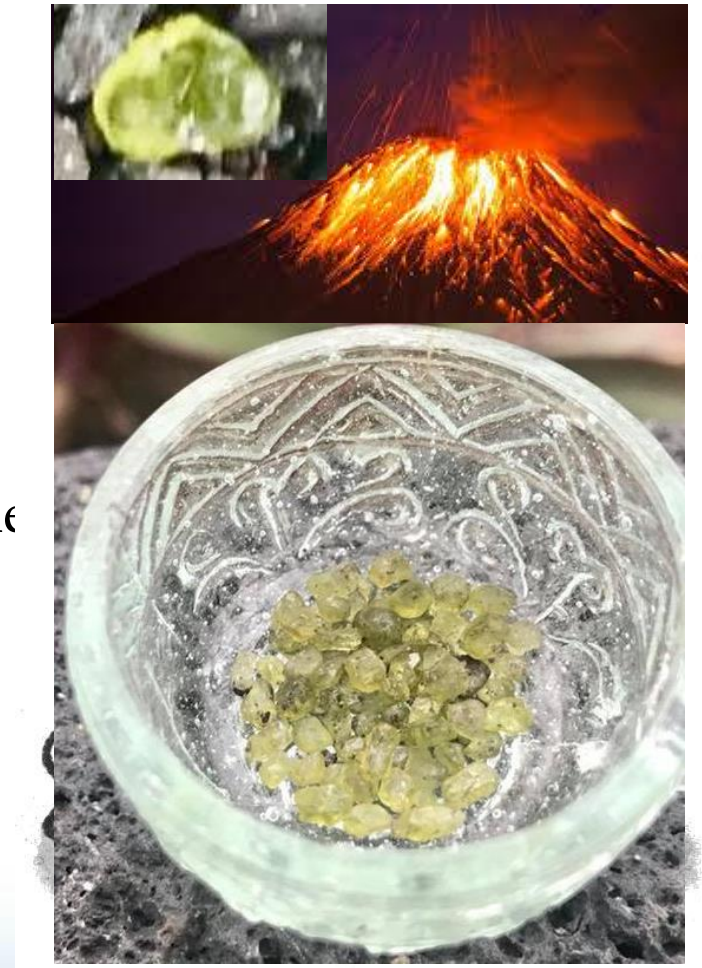

N. Ng and T.M. McQueen, *APL Mater.* **10**, 100901 (2022)

# Outline

- Materials Lifecycle and Defining Quantum Materials
- The Importance of Design
- Synthesis Preliminaries
- Characterization and “Defects, Defects, Defects!”
- Advancing Materials Synthesis
- Role of AI/ML Methods
- The Future

# The Elephant in the Room…

- **Once you know what to make… how do you make it?**
- **Solid-Gas**
  - chemical vapor deposition (CVD/PVD)
  - evaporation
  - vapor phase epitaxy (VPE)
  - molecular beam epitaxy (MBE)
- **Solid-Liquid**
  - direct melting (Arcmelting, Floating Zone
  - high temperature solvent (Flux)
  - hydrothermal or solvothermal
- **Solid-Solid**
  - precipitation-combustion
  - metathesis
  - grind and heat (“shake and bake”)

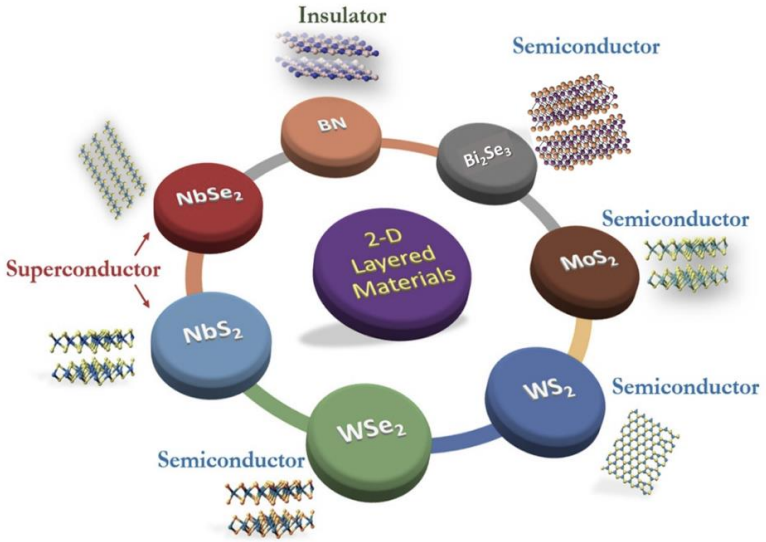


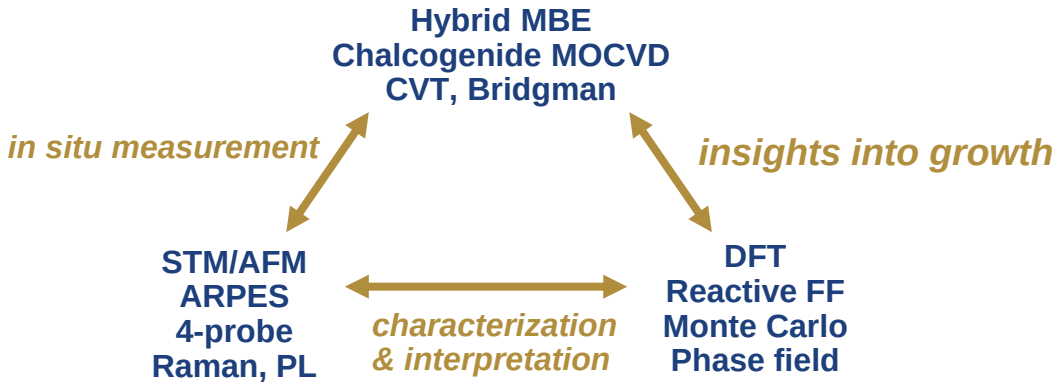
# 2D Crystal Consortium
## NSF Materials Innovation Platform

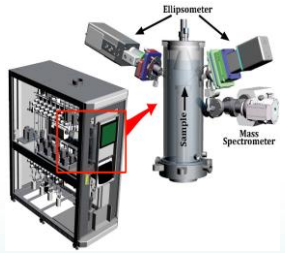
PennState

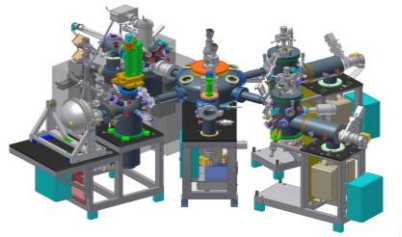
## Broad access to compelling synthetic tools with integrated theory support

2D chalcogenide monolayers, surfaces and interfaces are emerging as a compelling class of systems with transformative new science that can be harnessed for novel device technologies in next-generation electronics.



An NSF user facility with broad access:

- Open calls for user proposals,
- No user fees for academic use
- Access to a team of local experts
- Community knowledge-base of synthetic protocols

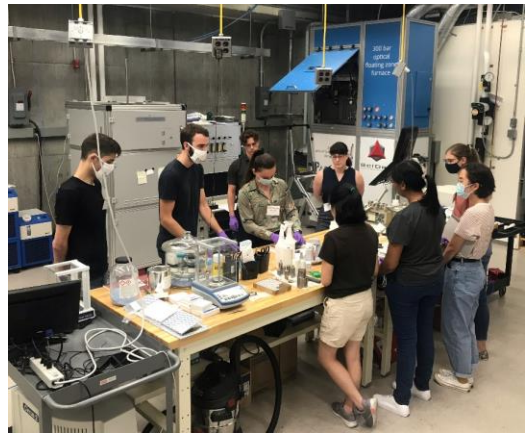
- Webinars, Workshops, Website resources
- Partnership opportunities with PUI, MSI

Johns Hopkins University

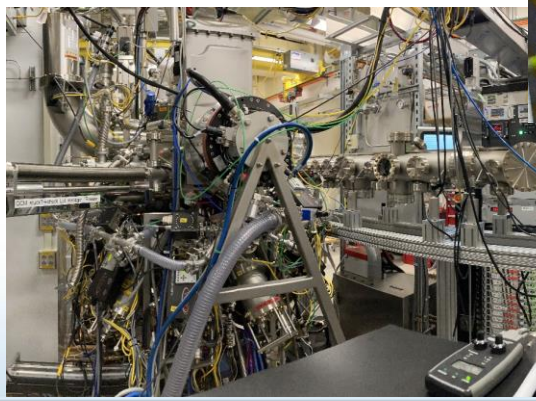
mip.psu.edu

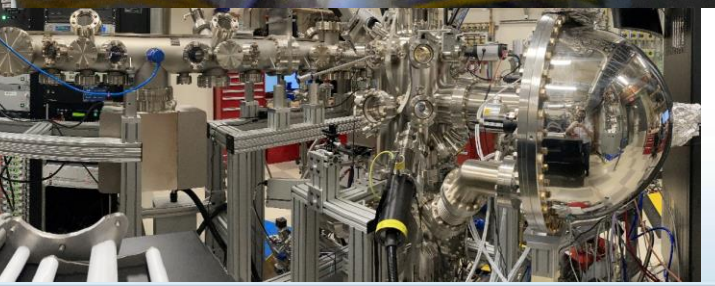
PARADIM
AN NSF MATERIALS INNOVATION PLATFORM

www.paradim.org



- **Focus: Inorganic single crystals and epitaxial thin films with superior electronic characteristics, particularly interface quantum materials**
- **Major User Facilities:**
  - Thin-film growth: MBE (62 elements) with ARPES & laser sample heating (new)
  - Transmission Electron Microscopy (Spectra) with 2nd-generation EMPAD (new)
  - Theory and Simulation: electronic properties and mismatched interface theory
  - Bulk crystal growth (at Johns Hopkins): world's first floating-zone furnace (FZF) with 300-atm $O_2$, tilted laser-diode FZF, and laser-heated 1000-atm pedestal furnace



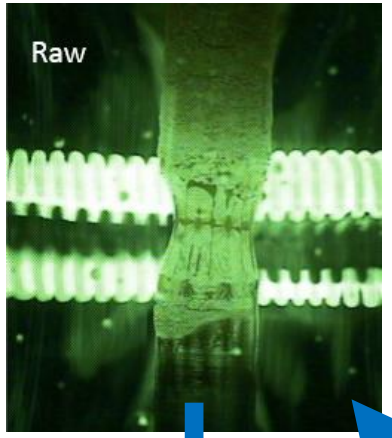


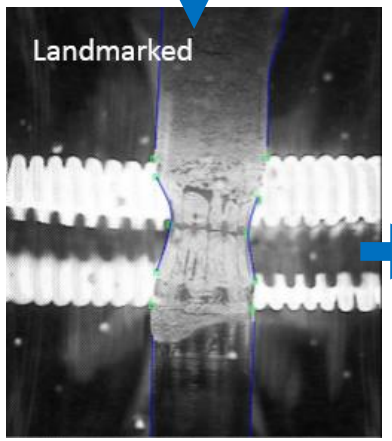
- Major Activities:
  - Accept user proposals year-round – no user fee
  - Summer schools (all recorded & available online)
  - Public data sets and analysis codes associated with published papers available at PARADIM website (new)

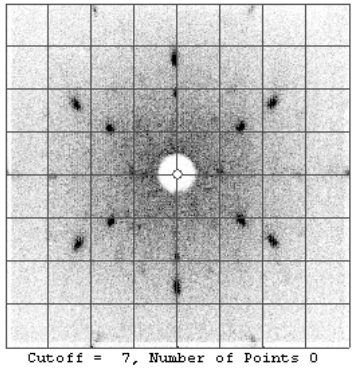
# PARADIM - Data Availability and Usability

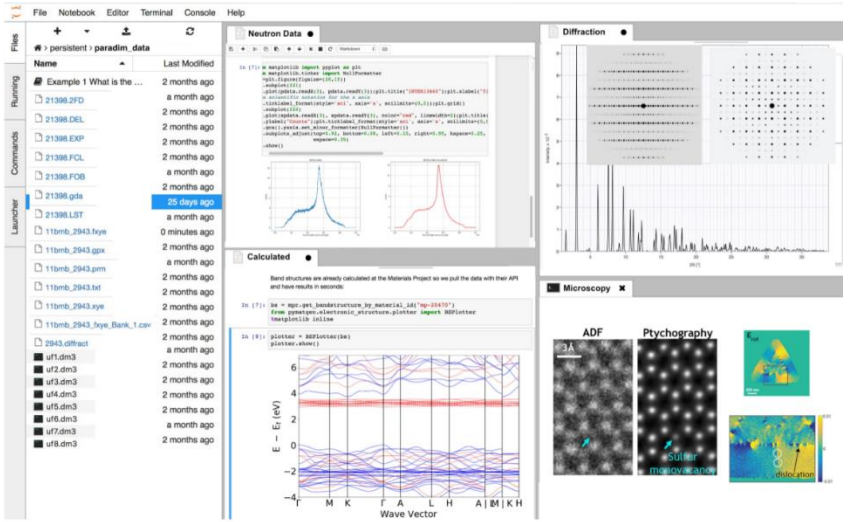
**"Collect Everything," "Use everything," "Make available everything"**

Machine Learning





SciServer

idies

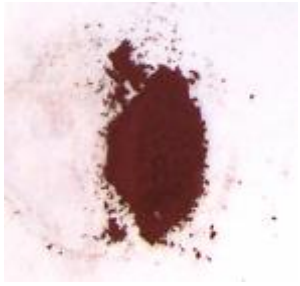
nanoHUB

# Typical solid state synthesis

$$Na_2O_2 + Fe_2O_3 \xrightarrow[\text{overnight}]{700\ ^\circ C\ /\ air} 2\ NaFeO_2 + \tfrac{1}{2}O_2$$



+



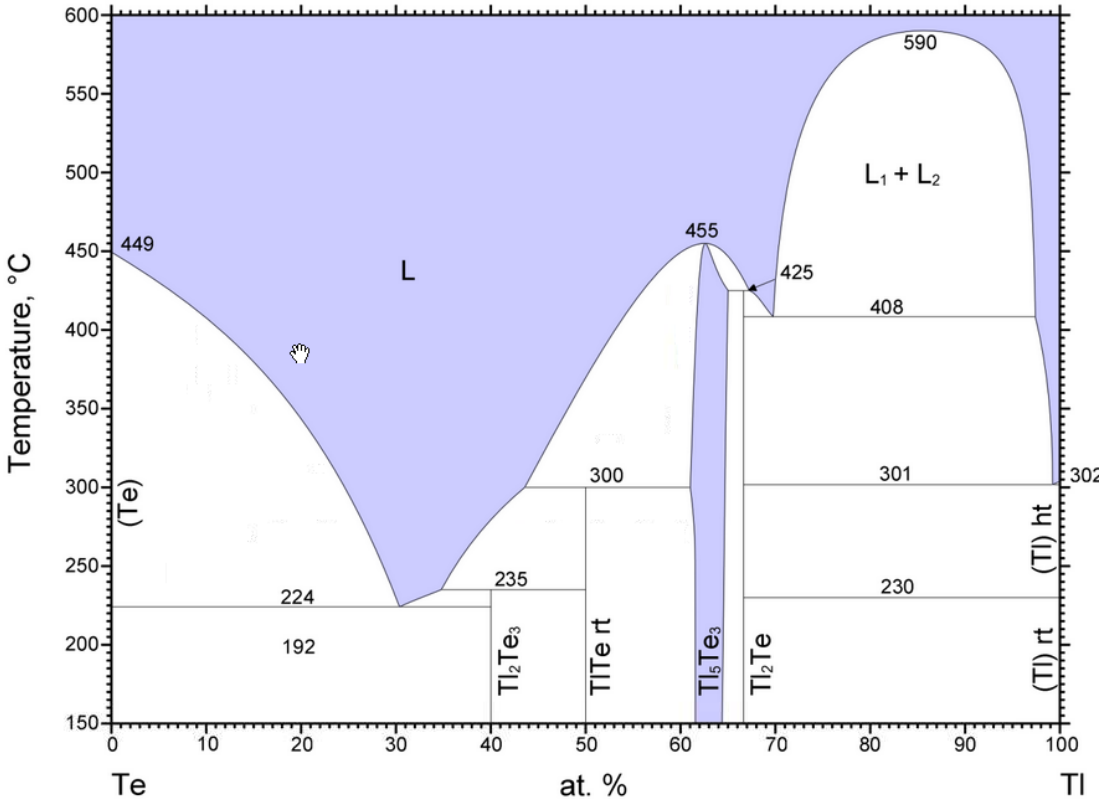
# Starting materials

- **Want starting materials to be reactive**
  - Small particle size
  - Similar melting points
- **But still have well-defined compositions**
  - Some are easy: $Cr_2O_3$ (green), $TiO_2$ (white)
  - 99.9% SrO usually has ~5% $SrCO_3$ + $Sr(OH)_2$
  - 99.999% $La_2O_3$ usually has ~5% $La(OH)_3$
  - 99.999% $Al_2O_3$ usually has ~5% $NaAl_{11}O_{17}$
  - NiO usually $Ni_{1-x}O$ with x ~ 0.05-0.2
- **In short: purify first!**

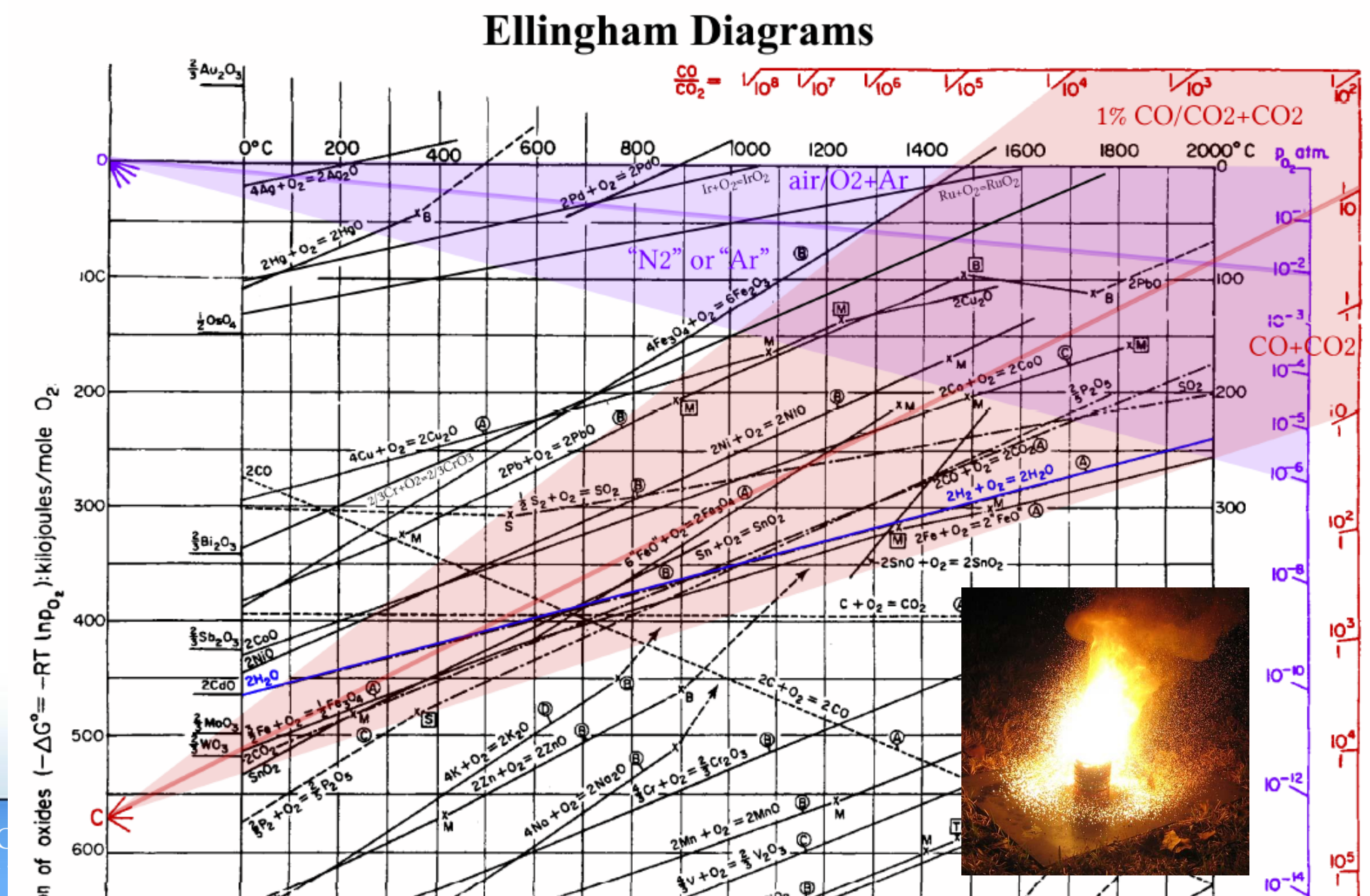
"Purification of Laboratory Chemicals" W.L.F. Armarego and C. Chai, ISBN 1856175677

# Reaction conditions

- Temperature: Usually need to get ‘close’ to reagents for appreciable reactivity to occur
- Pressure: Higher pressure stabilizes higher numbers, and ‘unusual’ oxidation states (e.g
- Sample form: Pellets better for solid-solid d better for gas interaction
  - Polycrystalline better for precise stoichiom single phase regions
  - Single crystals better for control of extende
- Reaction Atmosphere: Control of oxidation replacement (e.g. N or F for O)



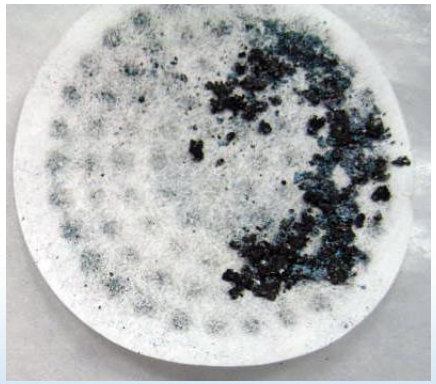
# Ellingham Diagrams



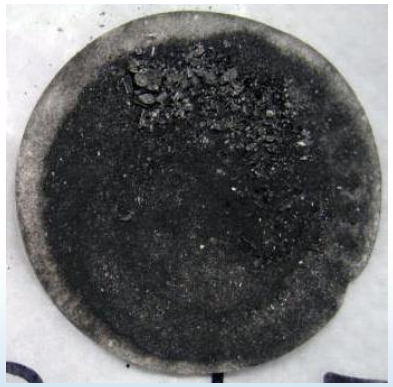
# $(A_xCu_{1-x})Cu_3(OH)_6Cl_2$ Syntheses

$$2.2\ ZnCl_2 + 3\ Cu_2(OH)_2CO_3 \xrightarrow[\text{hydrothermal}]{\sim 180\ ^\circ C,\ 2\ d.} Zn_{0.85}Cu_{3.15}(OH)_6Cl_2$$

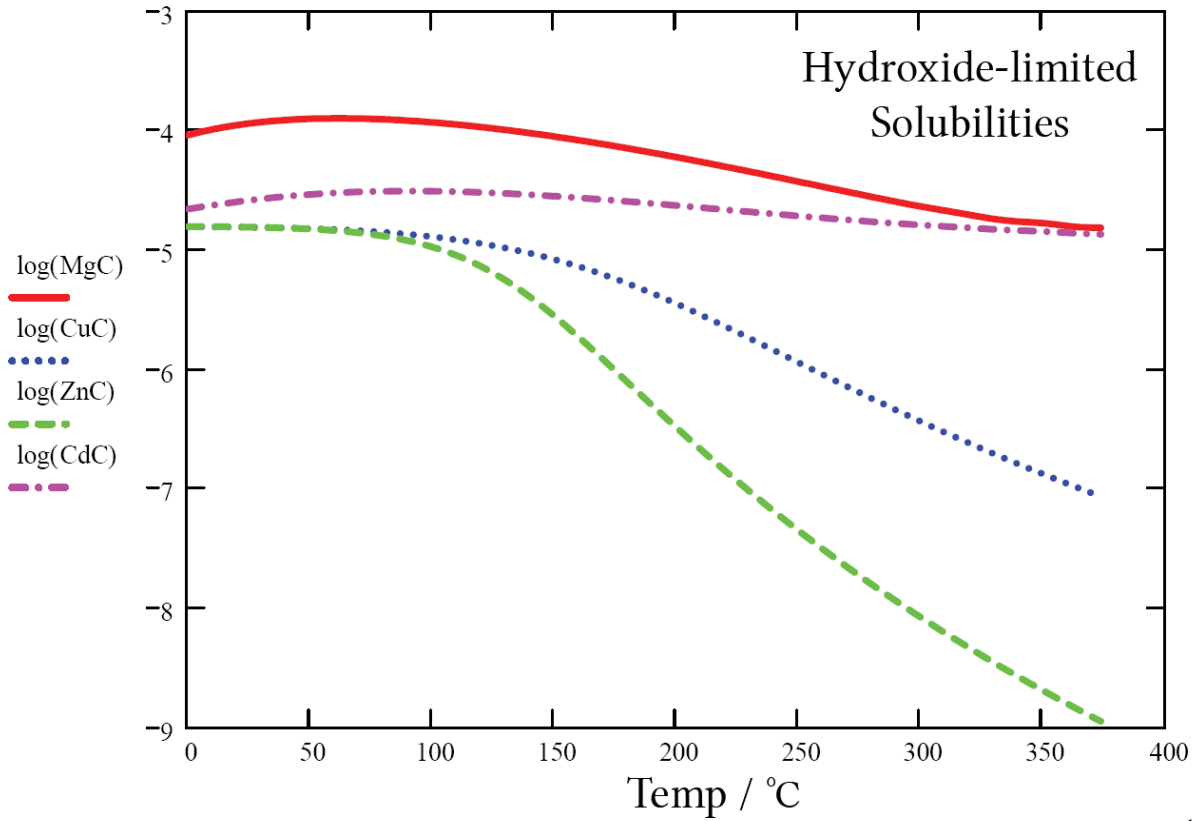
Single phase blue-green product

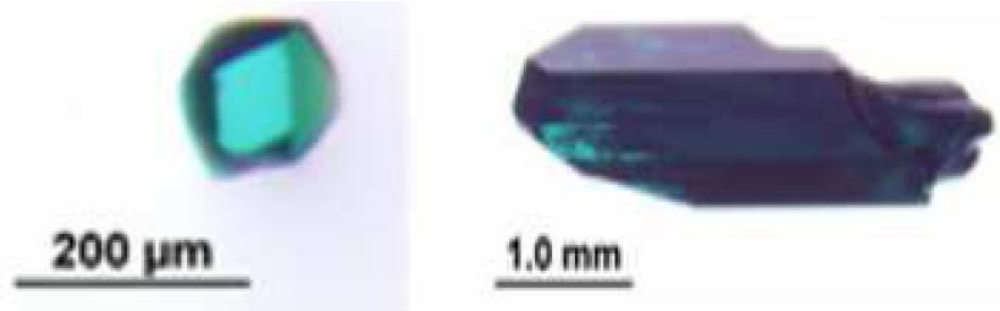


Early synthetic attempts for A = Mg (left) or A = Cd (right) using same protocol as for A = Zn just gave CuO (black) instead of desired phases



# $(A_xCu_{1-x})Cu_3(OH)_6Cl_2$ Syntheses




$$12\ MgCl_2 + 3\ Cu_2(OH)_2CO_3 \xrightarrow[\text{hydrothermal}]{\sim 180\ ^\circ C,\ 2\ d.} Mg_{0.75}Cu_{3.25}(OH)_6Cl_2$$

Single phase blue-green product

$$5\ CdCl_2 + 3\ Cu(OH)_2 \xrightarrow[\text{hydrothermal}]{\sim 130\ ^\circ C,\ 2\ d.} CdCu_3(OH)_6Cl_2$$

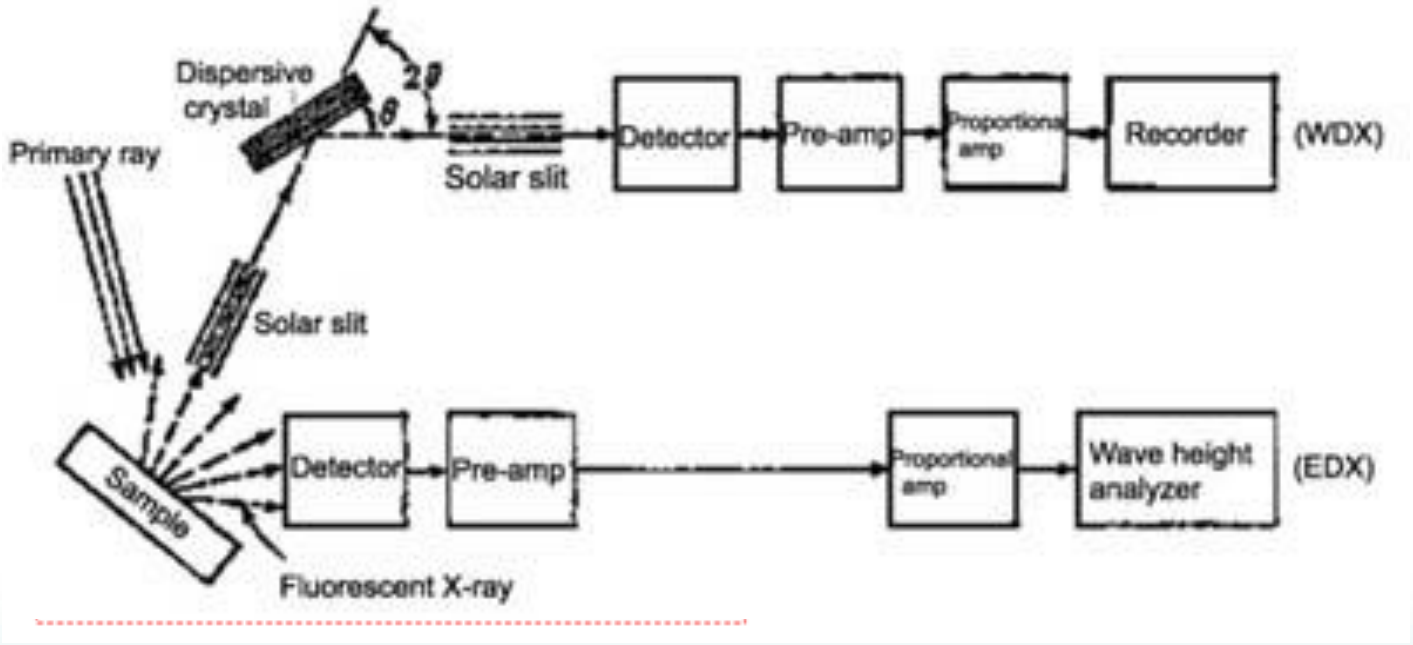
Single phase blue product

# Outline

- Materials Lifecycle and Defining Quantum Materials
- The Importance of Design
- Synthesis Preliminaries
- Characterization and “Defects, Defects, Defects!”
- Advancing Materials Synthesis
- Role of AI/ML Methods
- The Future

# Sample characterization: Quick Iteration w/ Growth

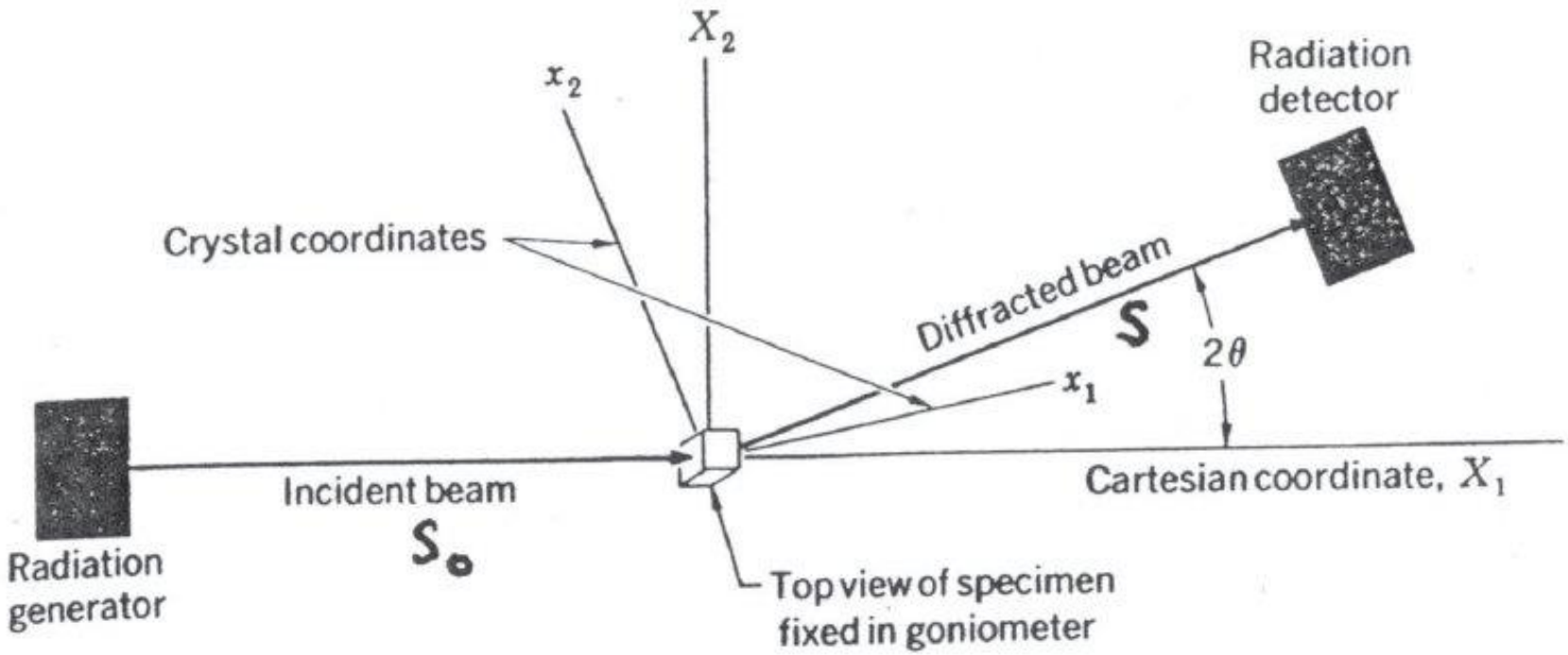
- **Elemental Analysis**
  - Whole sample: ICP-OES, Graphite AA, etc.
  - Area-resolved: EDX/WDX, XPS, etc.



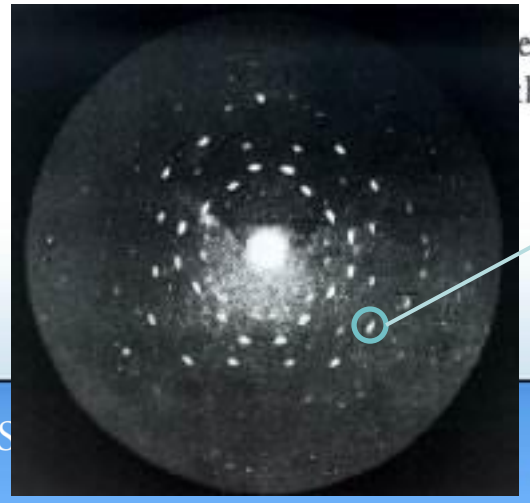
# Sample characterization

- **Elemental Analysis**
  - Whole sample: ICP-OES, Graphite AA, etc.
  - Area-resolved: EDX/WDX, XPS, etc.
- **Limits: incomplete dissolution, interfering anions, impurity phases (whole sample methods), sample-dependent absorption/emission (EDX/WDX), only surface sensitivity (EDX/WDX,XPS), etc.**
- **In practice: rarely accurate to better than 10-15% (precision can be <1%)**

# Diffraction




erimental arrangement that fixes the values of $S_0$, S, and $\lambda$ (and there-
he vector **s**).

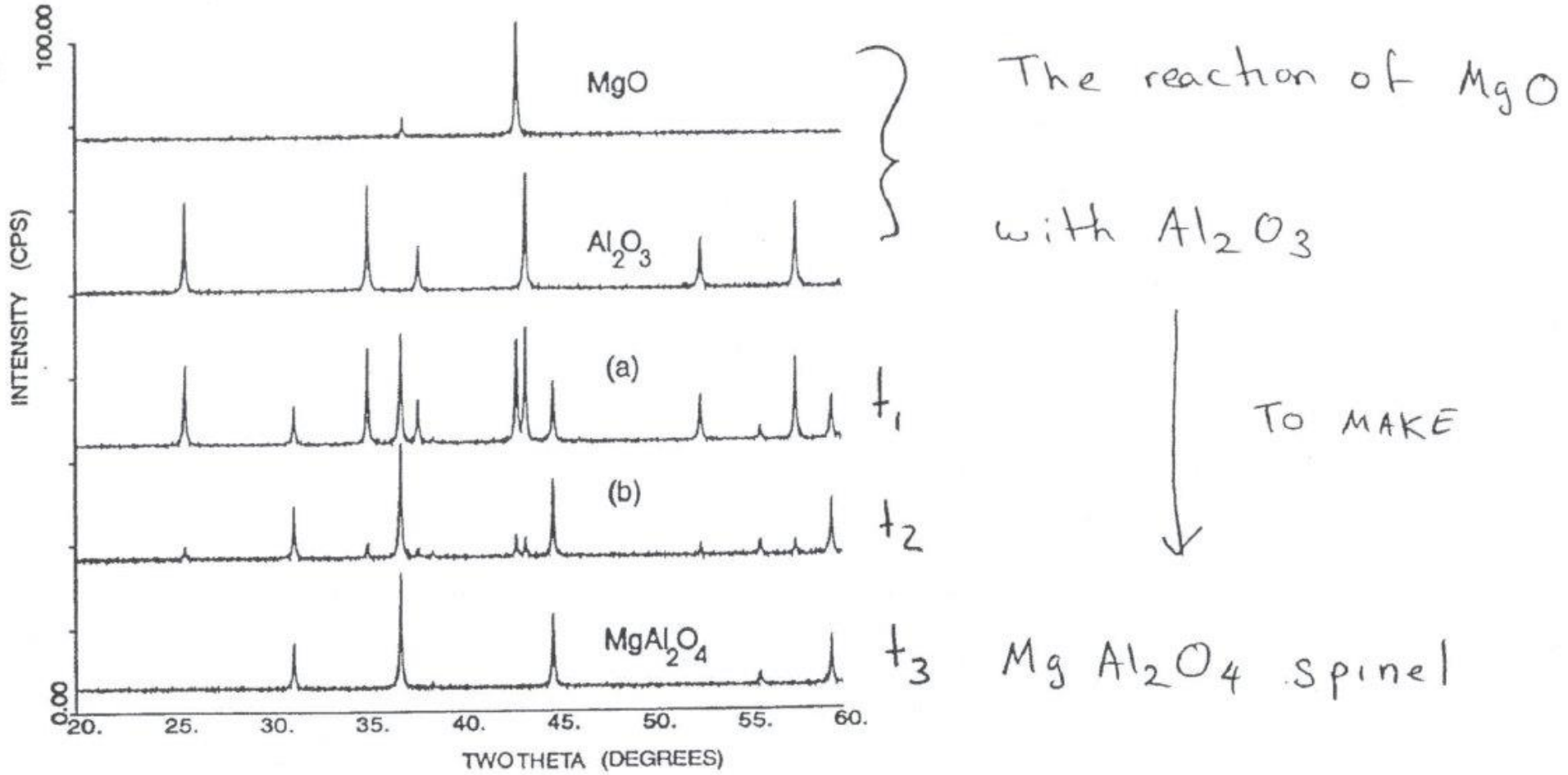


Constructive (periodic part): Bragg's law, etc.

Peak positions: unit cell size and shape

Peak intensities: atom type and positions within unit cell

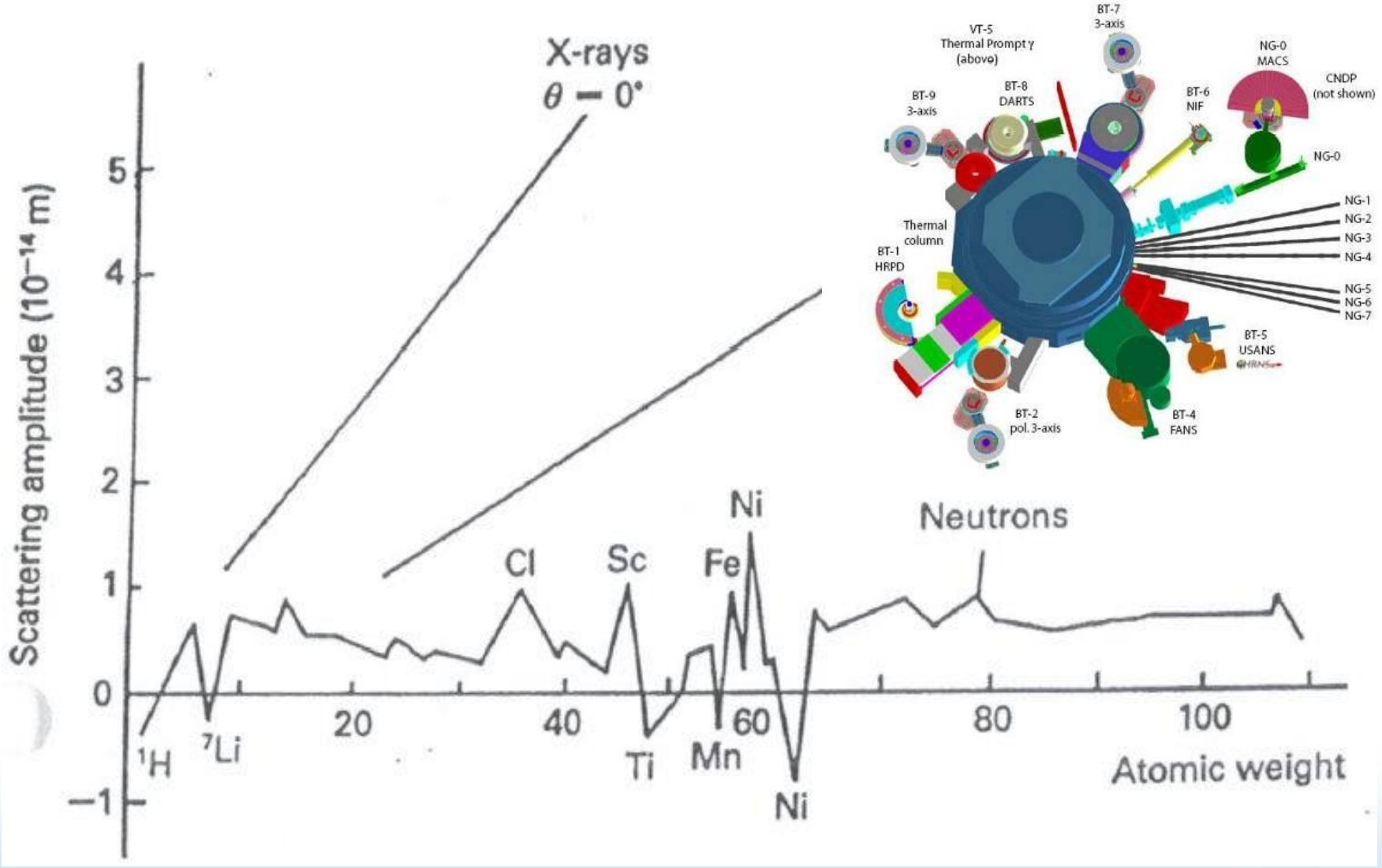
# Lab x-ray diffraction



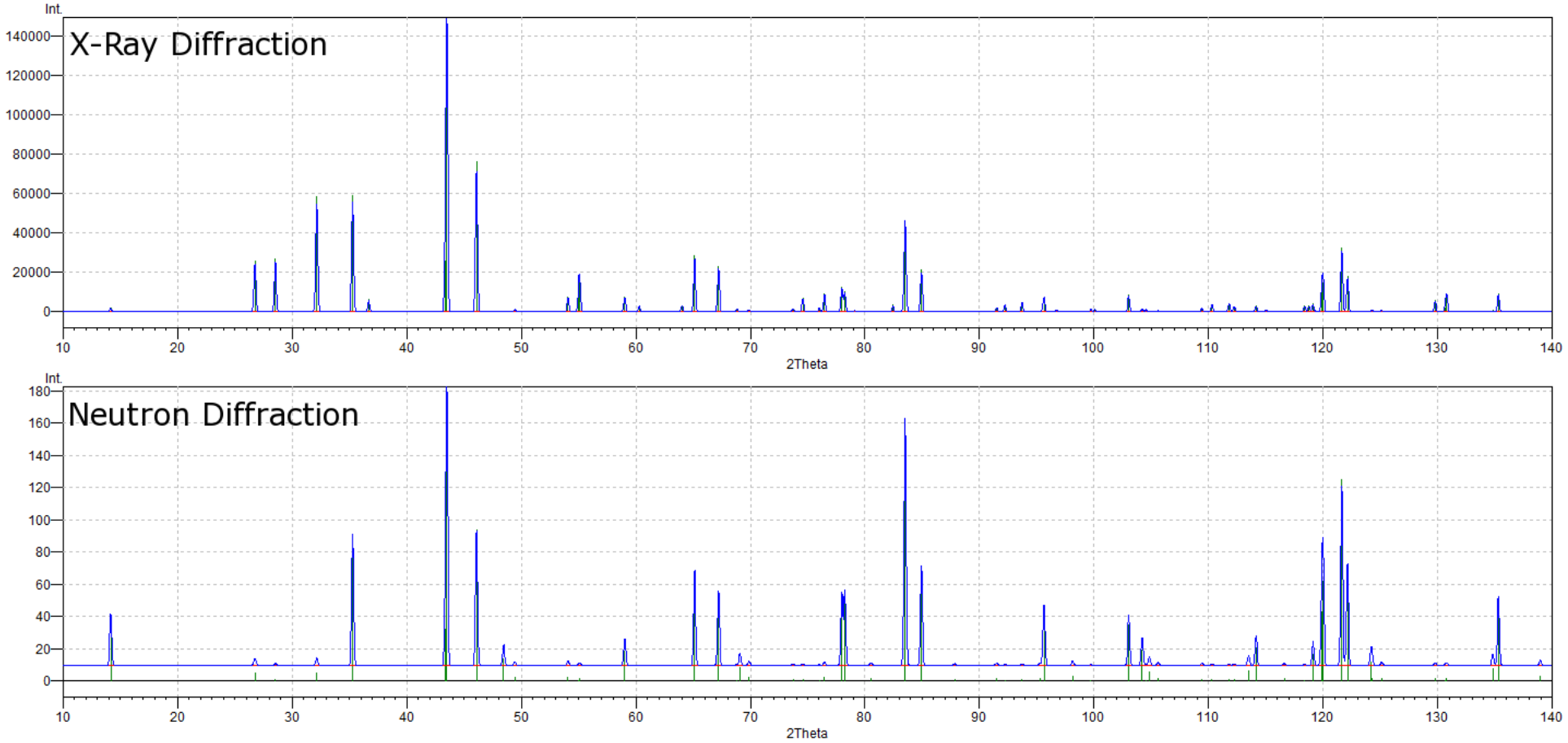

Peak positions: unit cell size and shape

Peak intensities: atom type and positions within unit cell

# X-ray vs Neutrons



# X-ray vs Neutrons

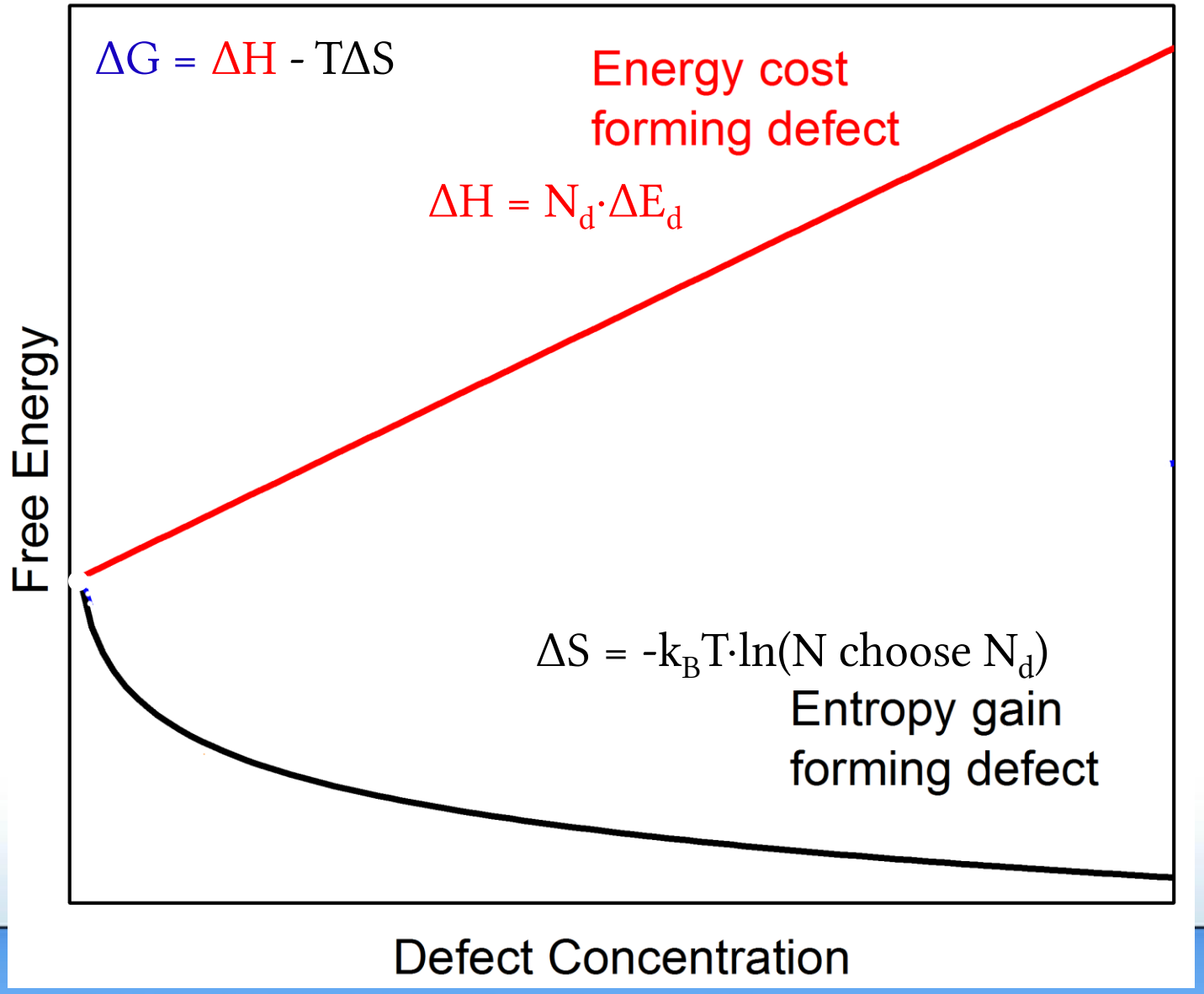



Same compound, same unit cell, so same peak positions, but intensities different due to difference in x-ray and neutron scattering factors

# Defects and local structure govern properties

- **$SrTiO_3$: white insulator**
  - But $SrTiO_{3-\delta}$, $\delta \sim 0.05$, a blue-black metal
- **$Y_2TiNbO_7$: non-magnetic, almost white**
  - $Y_2TiNbO_{7-\delta}$, $\delta \sim 0.05$, magnetic, black!
- **$YBa_2Cu_3O_{7.5}$: antiferromagnetic insulator**
  - $YBa_2Cu_3O_7$, 93 K superconductor
- **$Al_2O_3$: poor oxygen ion conductor**
  - $(Na_{0.17}Al_{1.83})O_{0.95}$, good oxygen ion conductor
- **NaI: clear/white insulator**
  - $(Na_{1-\delta}Tl_{\delta})I$, $\delta \sim 0.01$, gamma ray scintillator

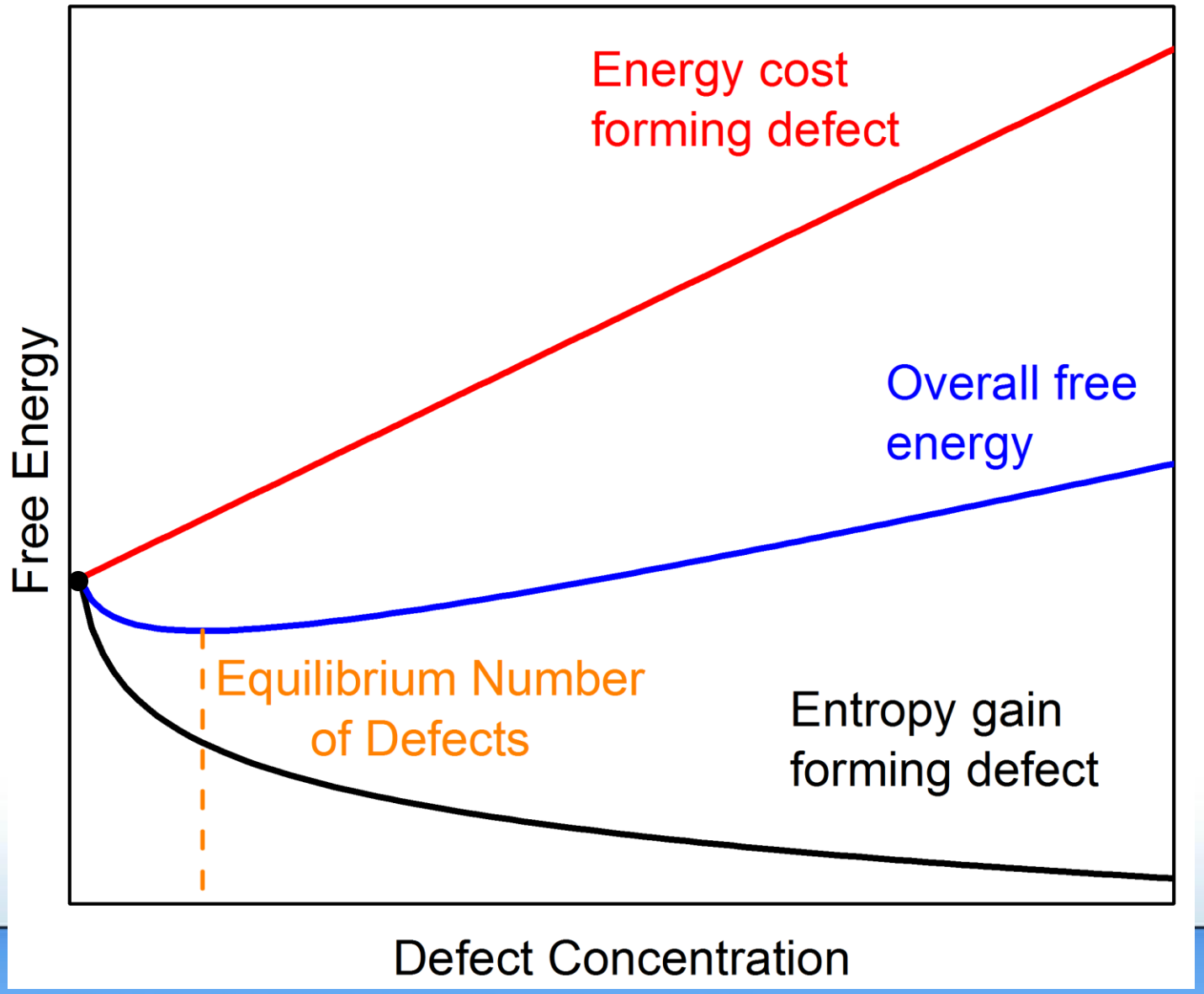
# Thermodynamics favors defects






McQueen, *The Chemistry of Quantum Materials*, in Comprehensive Inorganic Chemistry III

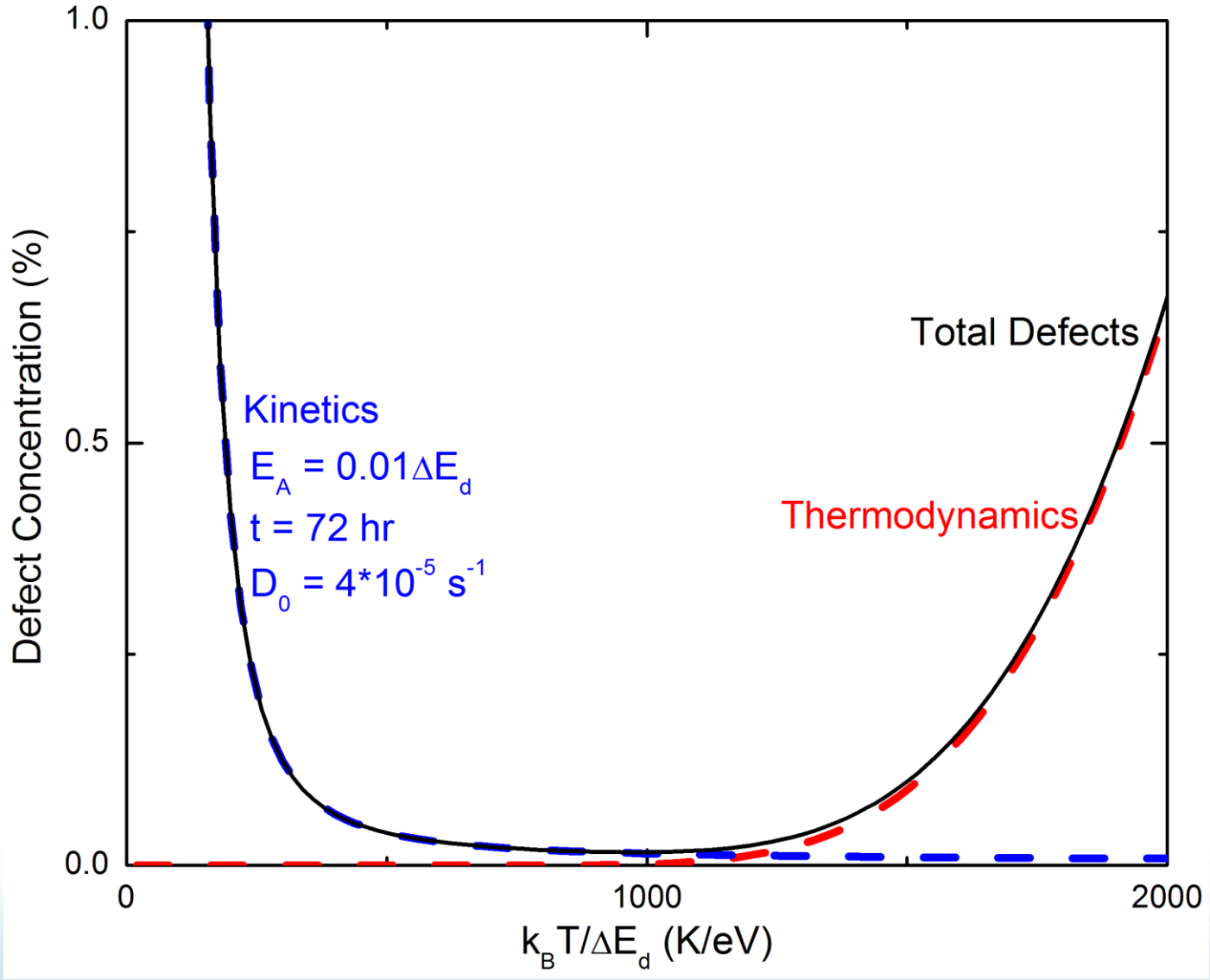
# Thermodynamics favors defects






McQueen, *The Chemistry of Quantum Materials*, in Comprehensive Inorganic Chemistry III

# So does kinetics



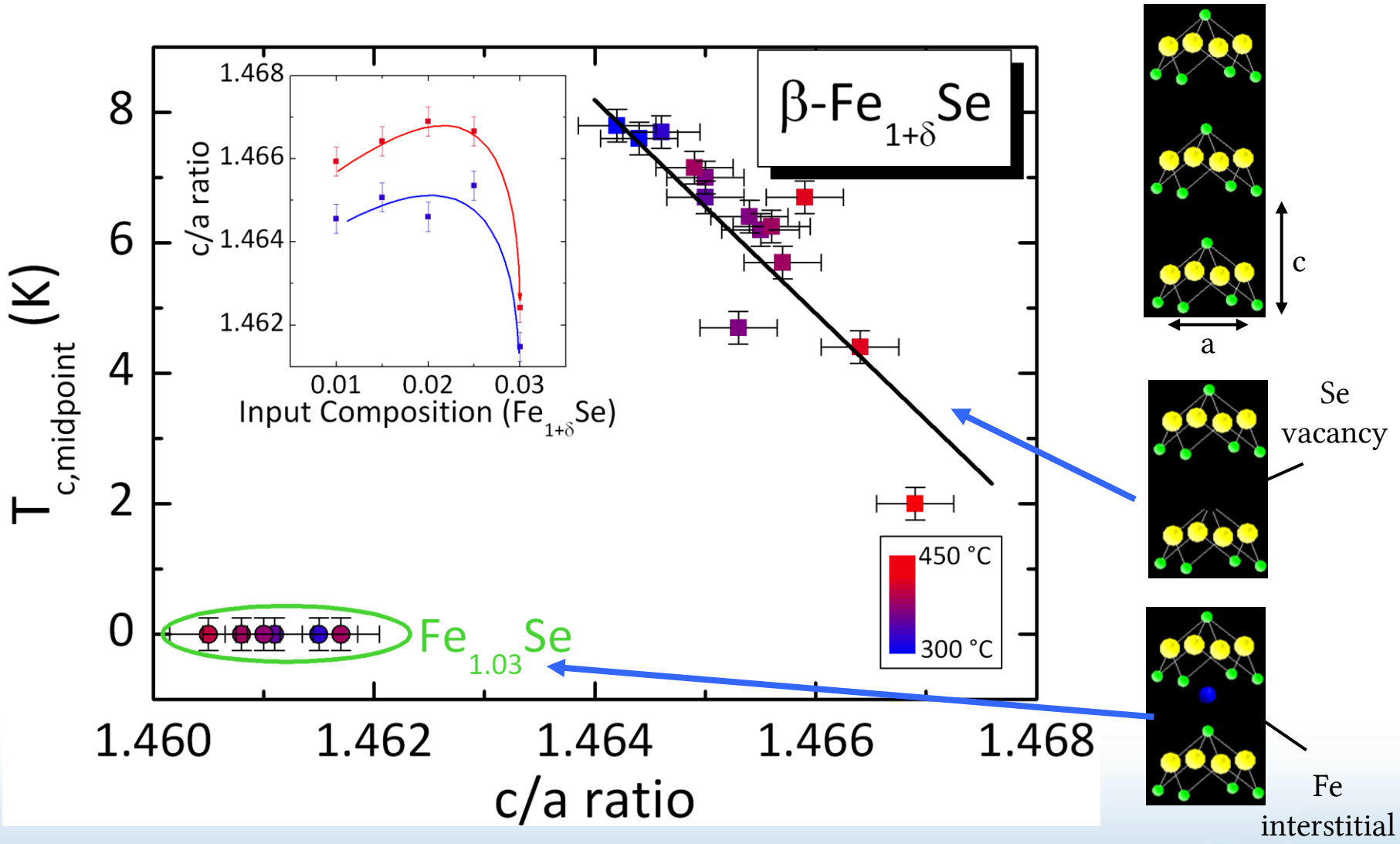



McQueen, *The Chemistry of Quantum Materials*, in Comprehensive Inorganic Chemistry III

# Difficult to directly observe

- **Usually at or below true sensitivity of most methods**
- **Most sensitive quantities are indirect:**
  - Sample weight changes (esp. oxygen)
  - Unit cell volume changes
    (e.g. $Ni_{1-x}O$ versus $NiO_{1+x}$)
  - Physical properties changes (carrier density, impurity magnetic moment density, etc.)

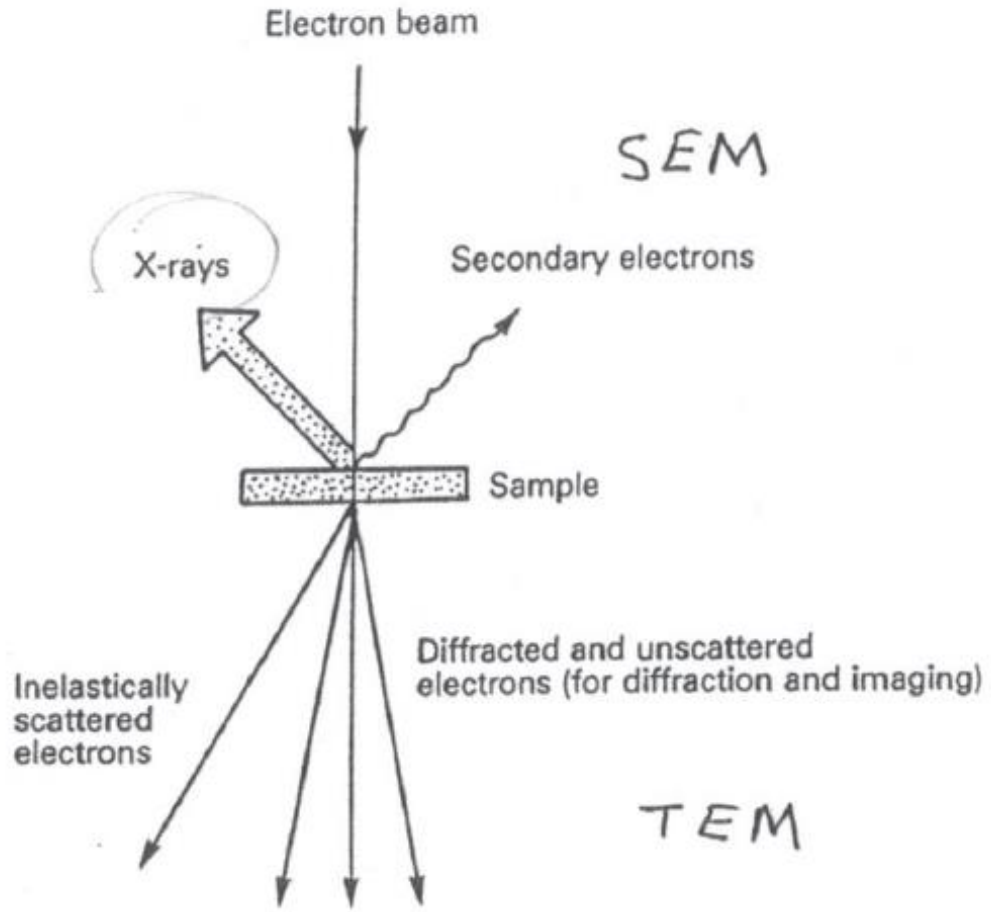
# Example indirect observation of defects

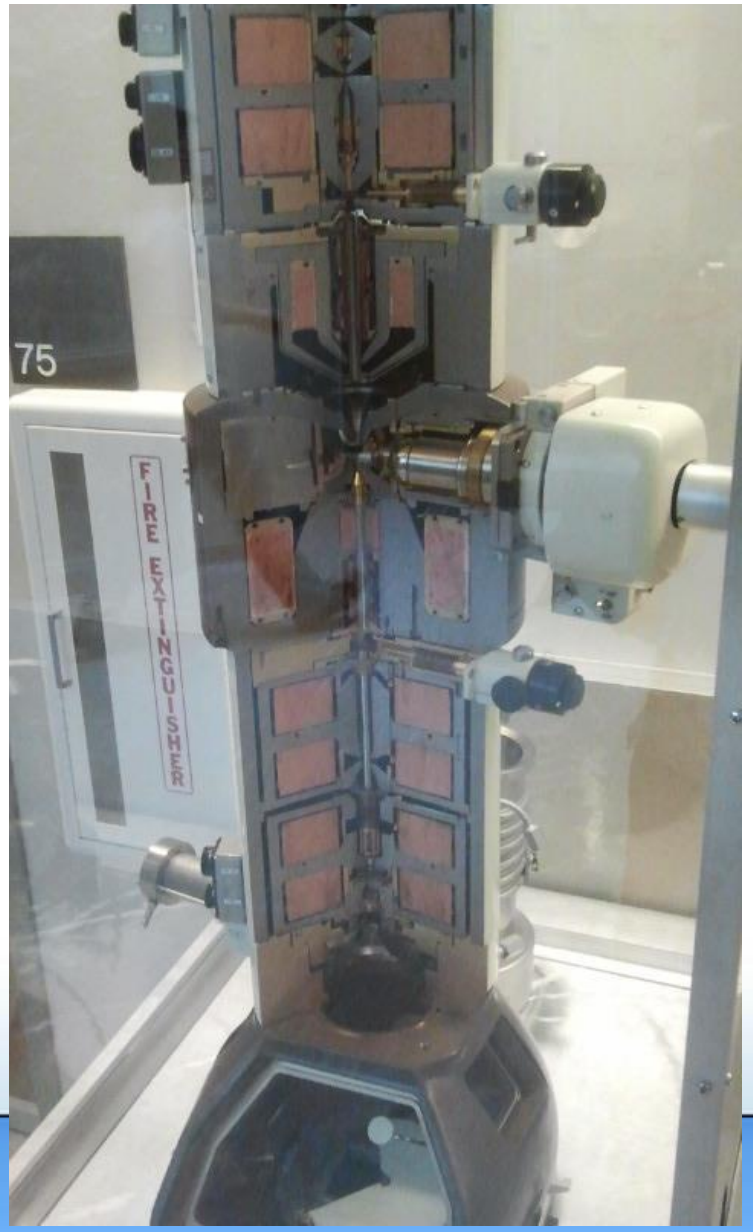





T.M. McQueen, et al. *Phys. Rev. B* **79**, 014522 (2009)

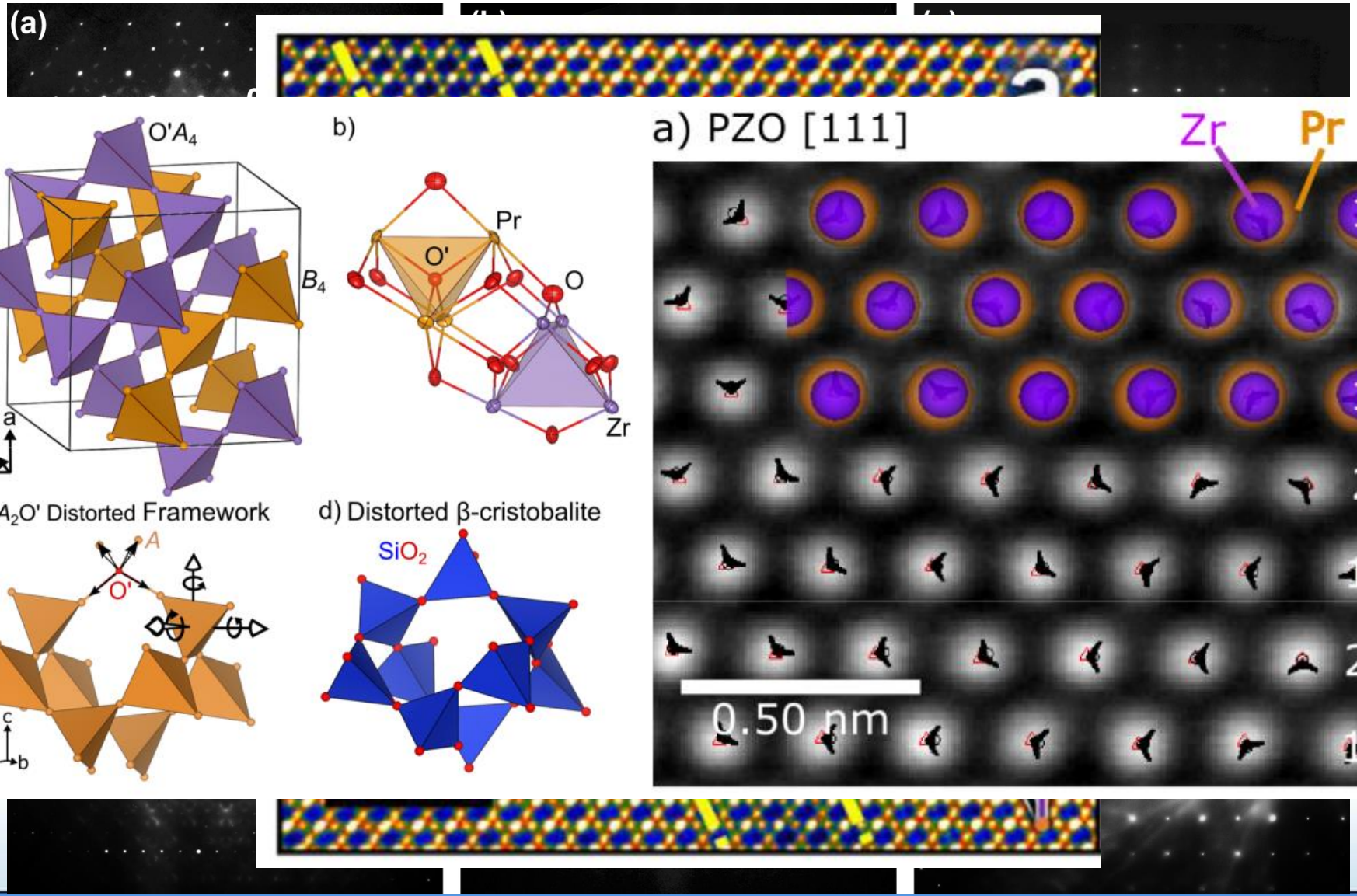
# Electron microscopy




λ ~ 0.02 Å (very short)
Charged, strongly interacting
Can be focused to 2-6 nm

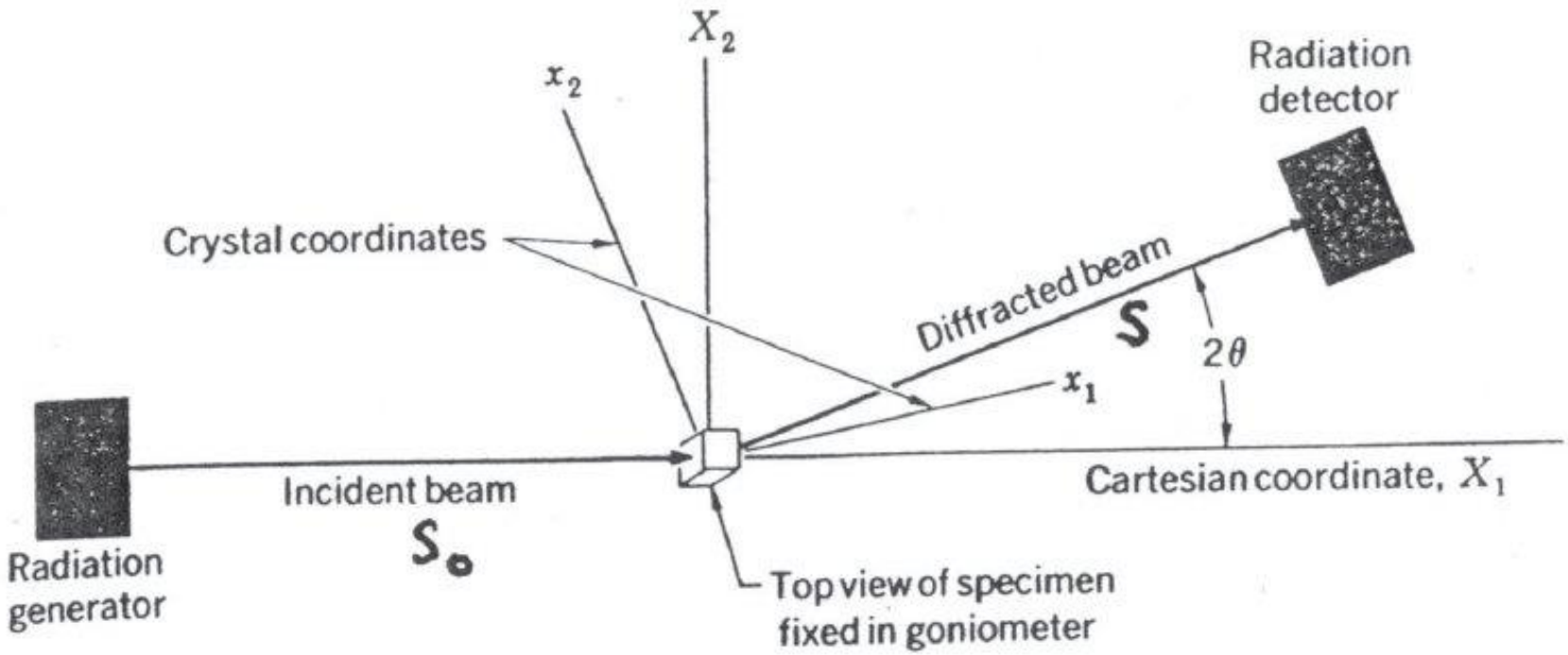
# Electron diffraction



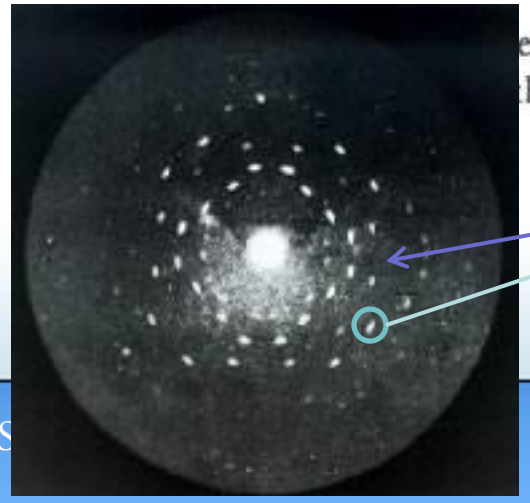


T.M. McQueen, et al. J. Phys. Cond. Mat. 20, 235210 (2008)
A. Mostaed, et al. Acta Materialia 143, 291-7 (2018)
B.A. Trump, et al. Nat. Commun. (2018)

# Diffraction




erimental arrangement that fixes the values of $S_0$, S, and λ (and there-
he vector s).



Diffuse (aperiodic part)

Constructive (periodic part): Bragg's law, etc.

Peak positions: unit cell size and shape

Peak intensities: atom type and positions within unit cell

# Pair Distribution Function Analysis

12-24 hr measurement time (lab)

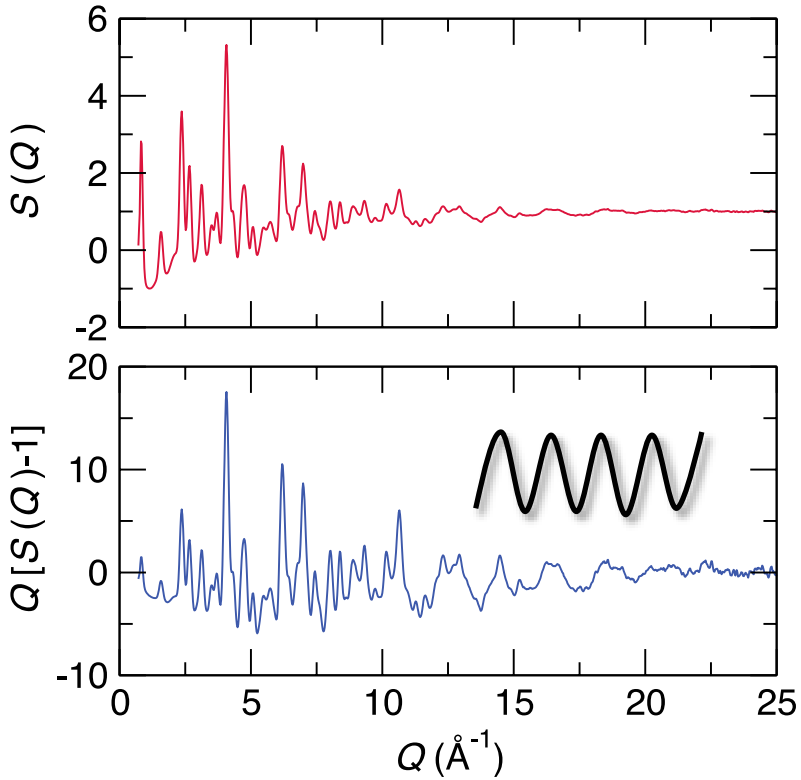
Measure **total** scattering, $I(Q)$

$Q$ ~ diffracted angle: $Q = \frac{4\pi \sin(\theta)}{\lambda}$

3 months + few minutes (synchrotron)

Normalize by composition and apply corrections, $S(Q)$

$$S(Q) = 1 + \frac{I^{coh}(Q) - \sum c_i |f_i(Q)|^2}{|\sum c_i f_i(Q)^2|}$$




In development (TEM)

Fourier transformation yields a weighted-average of atom-atom distances in direct space (**pair distribution function,** or **PDF**)

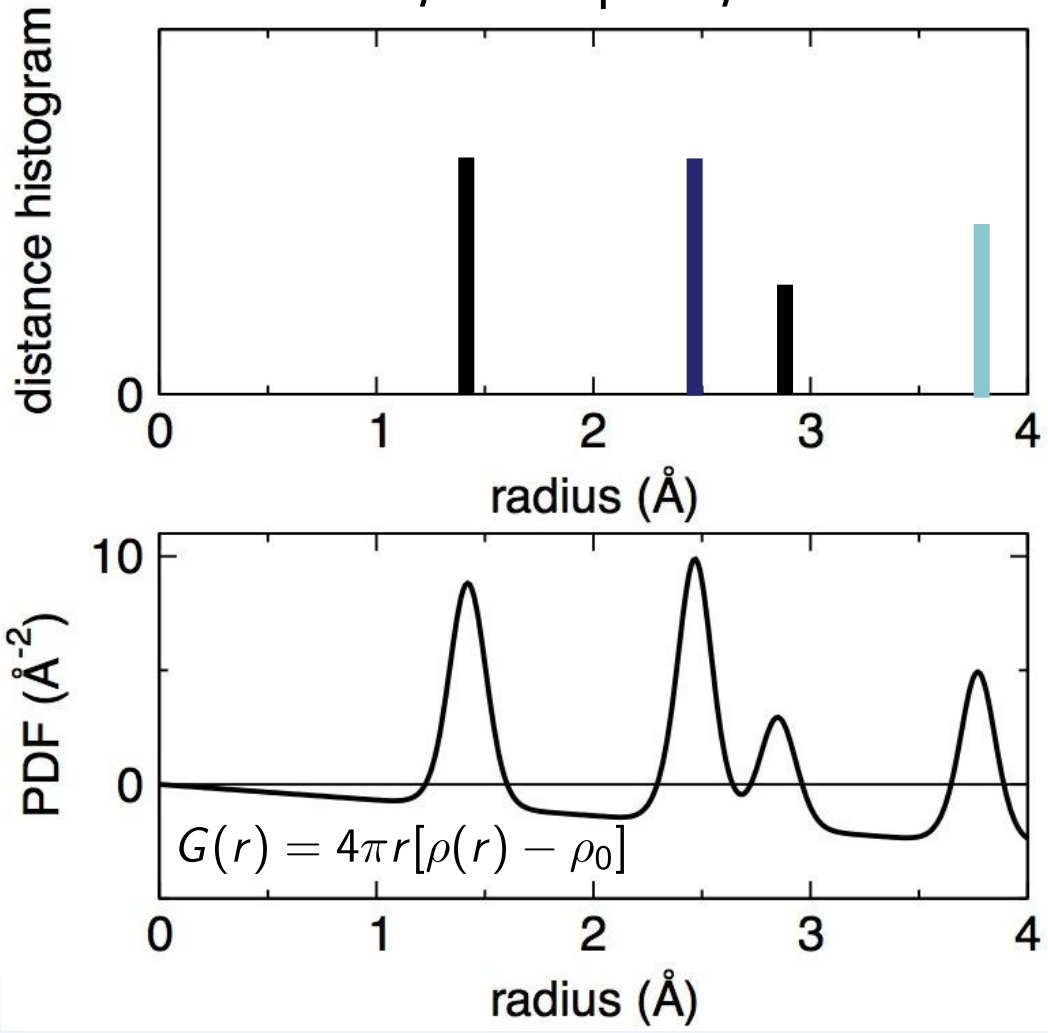
$$G(r) = 4\pi r[\rho(r) - \rho_0] = \frac{2}{\pi} \int_0^{Q_{max}} Q[S(Q) - 1] \sin(Qr) dQ$$

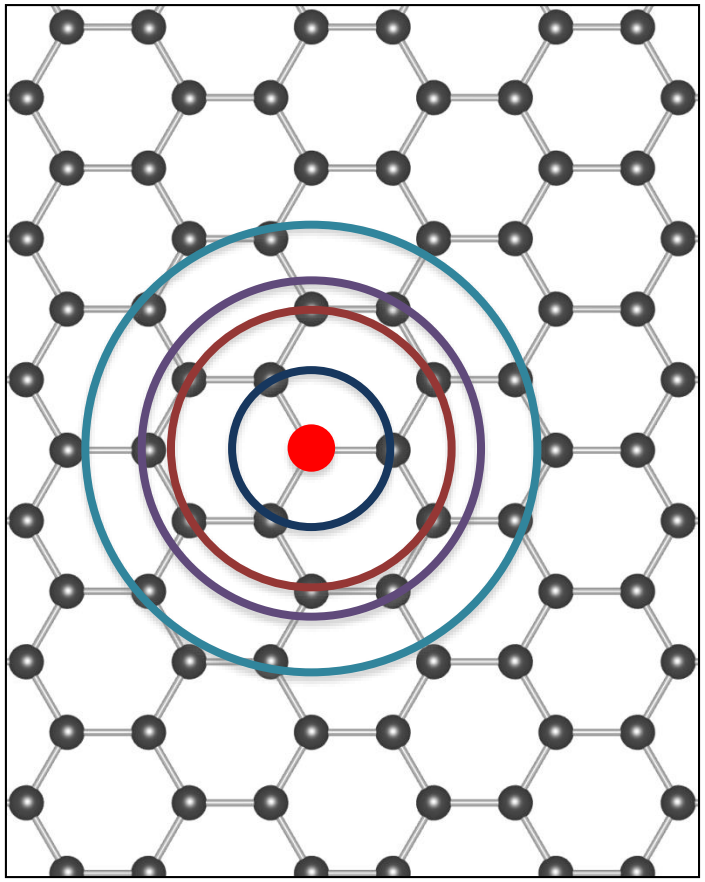


Egami and Billinge, Underneath the Bragg Peak, Pergamon Press (2003)

# Pair Distribution Function Analysis

PDF: ensemble, real-space, atom-atom histogram



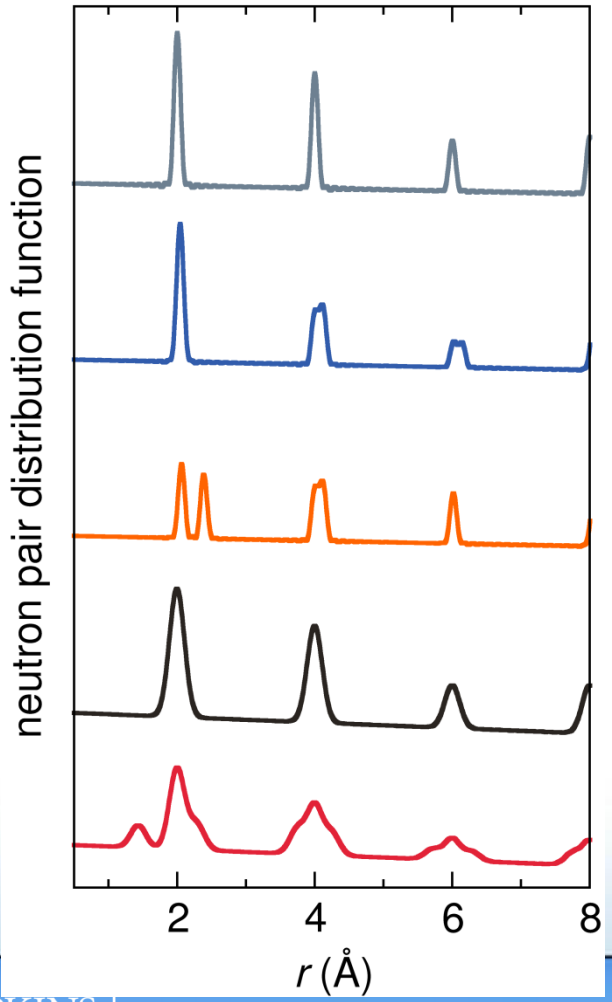
Need distance *relaxed* atomic boxes for comparisons… simple SQSs not sufficient. This is the same constraint as EXAFS



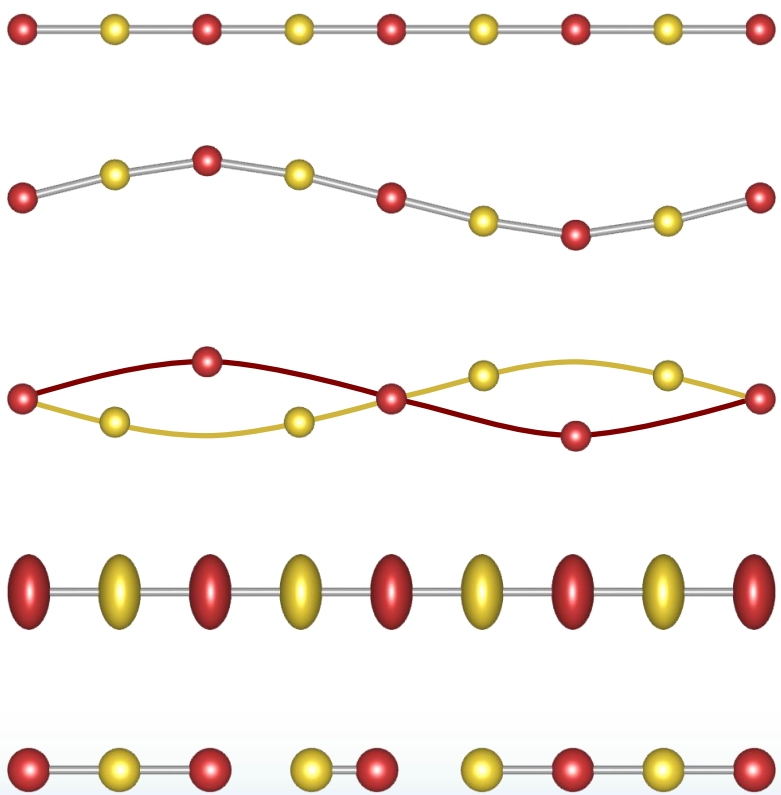
Egami and Billinge, Underneath the Bragg Peak, Pergamon Press (2003)

# Total scattering PDF analysis

PDF: ensemble, real-space, atom-atom histogram that resolves **incoherent** displacements, from Fourier transform of S(Q)




NaCl chains



no modes

acoustic

optic

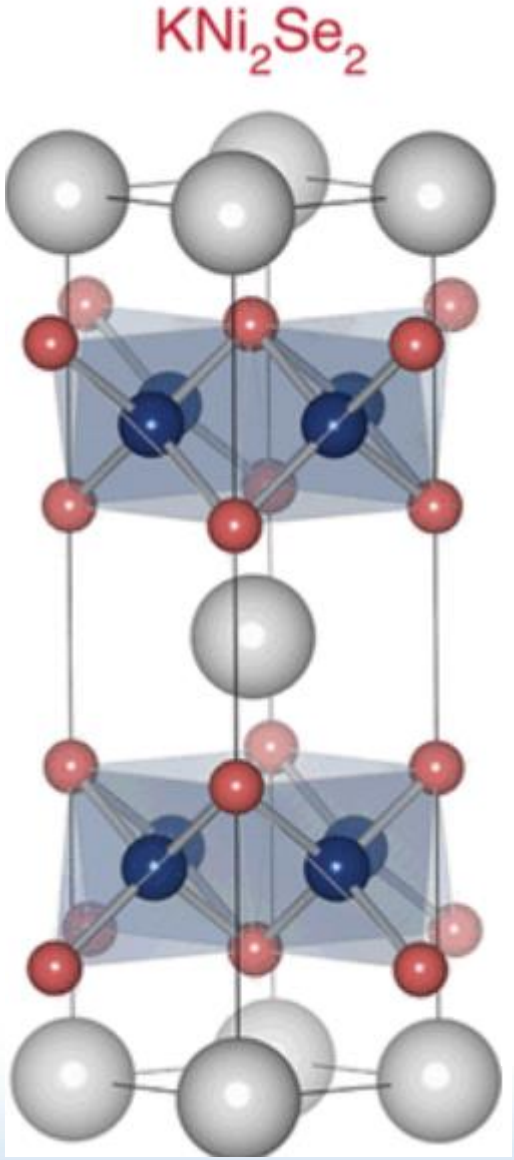
Debye-Waller

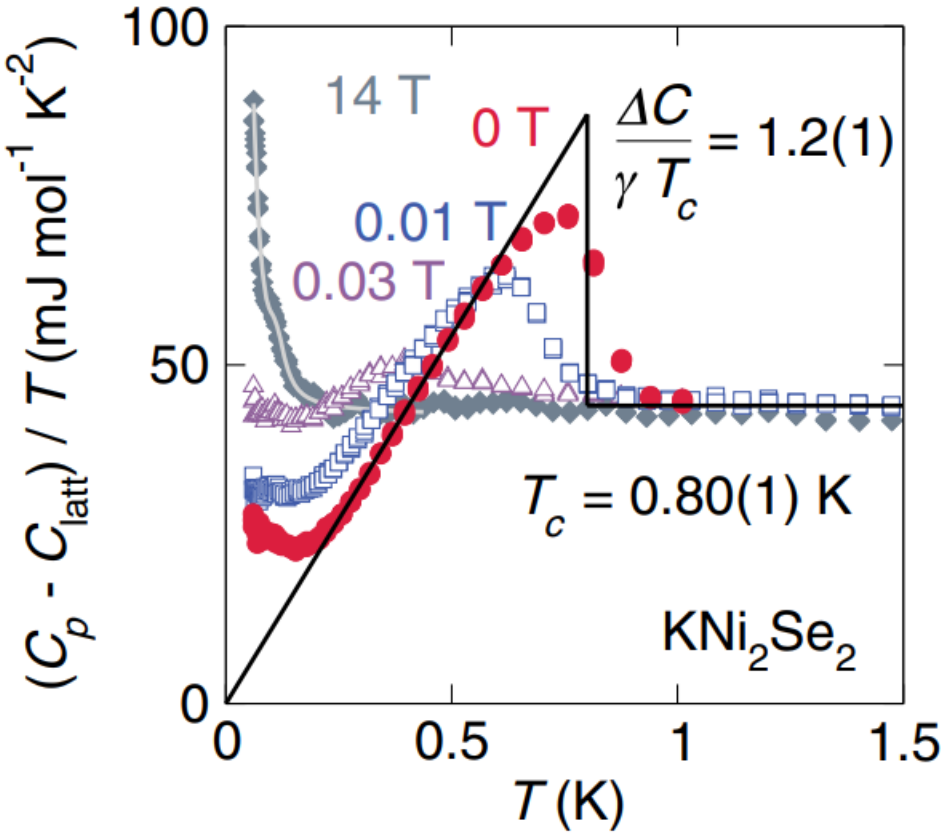
incoherent displacement

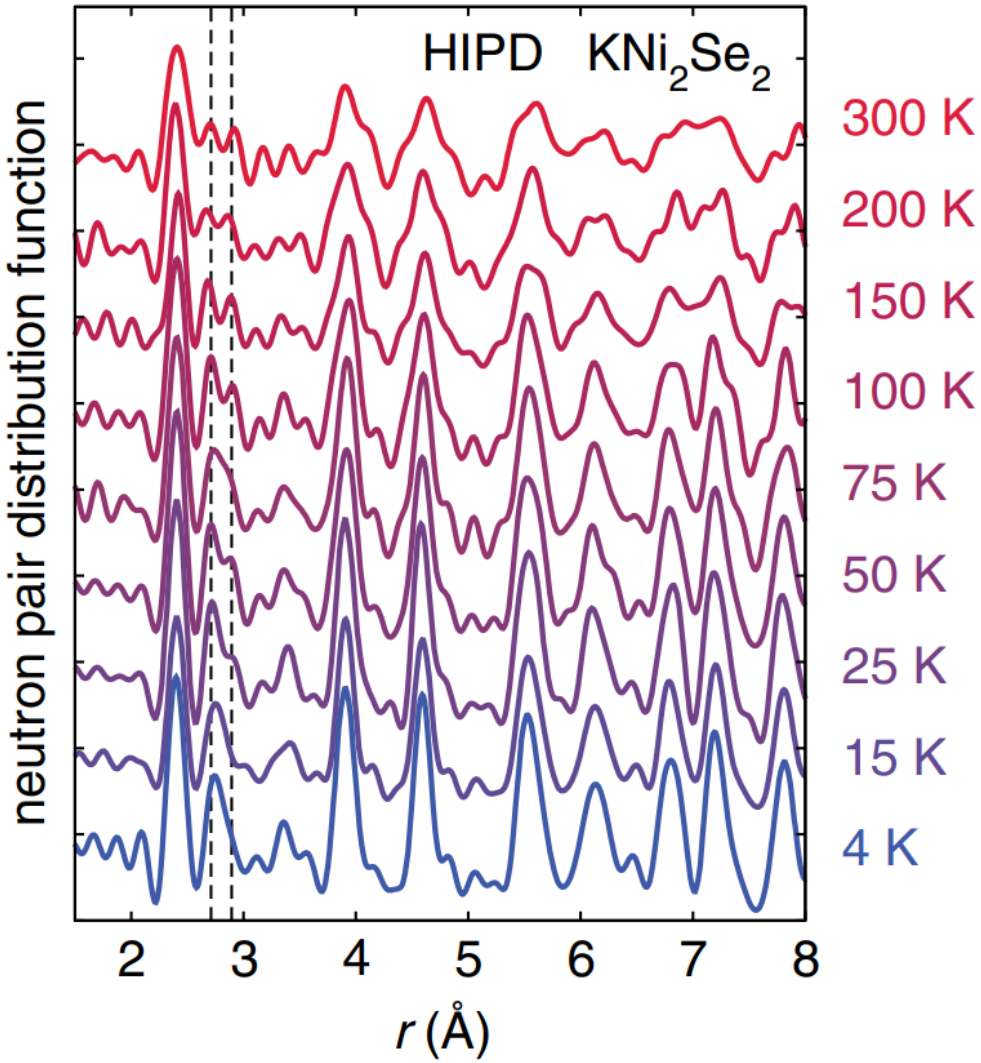
Slide Courtesy Jamie Neilson.

Egami and Billinge, *Underneath the Bragg Peak*, Pergamon Press (2003)

# Example: $KNi_2Se_2$



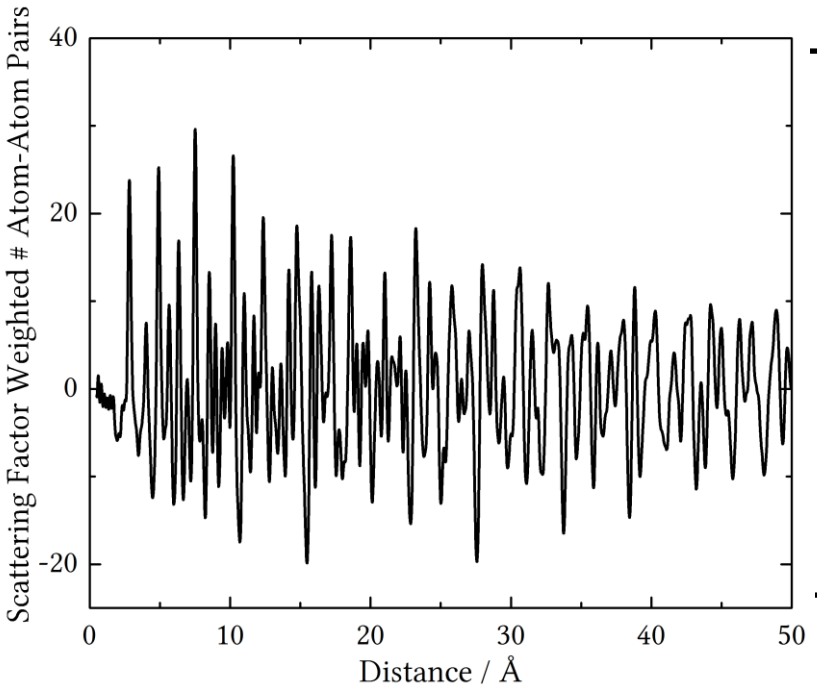





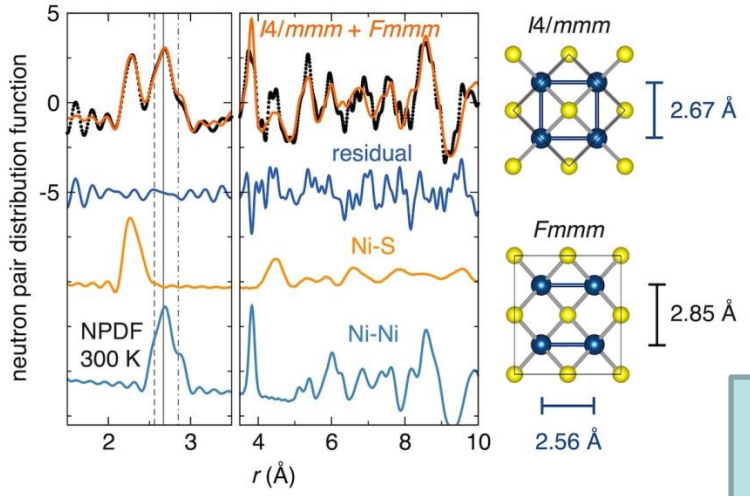

Neilson, et al. PRB 86, 054512 (2012) and ZAAC 202200042 (2022)

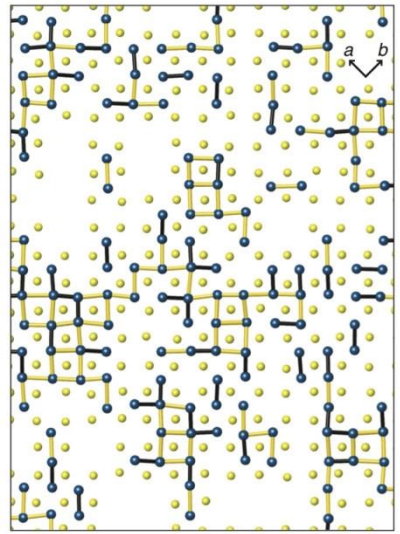
# Example: $KNi_2X_2$

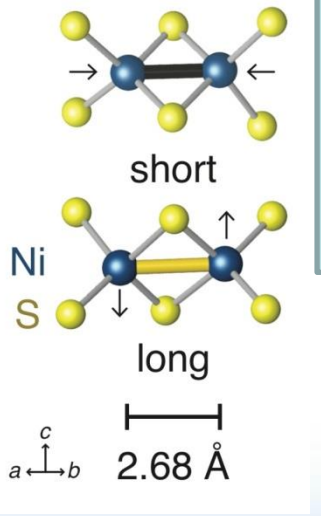


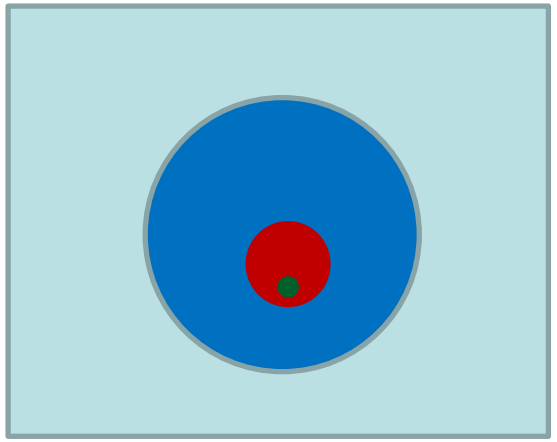

Analytical Modeling

Numerical Simulation



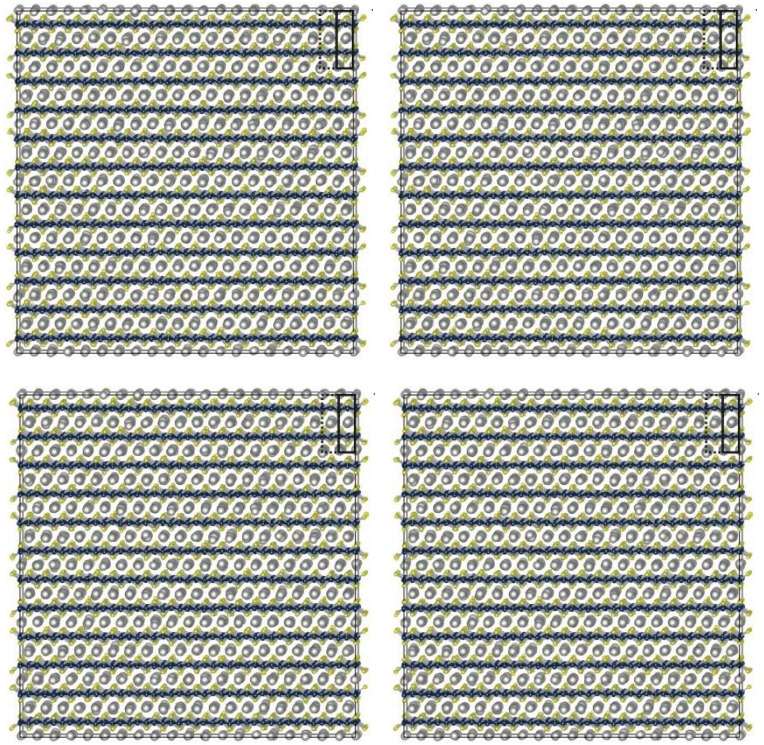



# Alternative Analysis Approaches

Independent RMC Simulations of the Same Data are Like Different Photographs of the Reality



100's to 10,000's of these

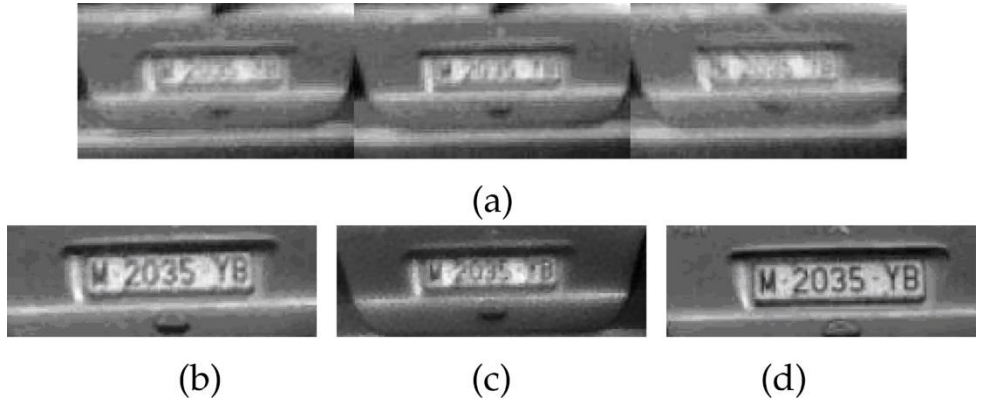
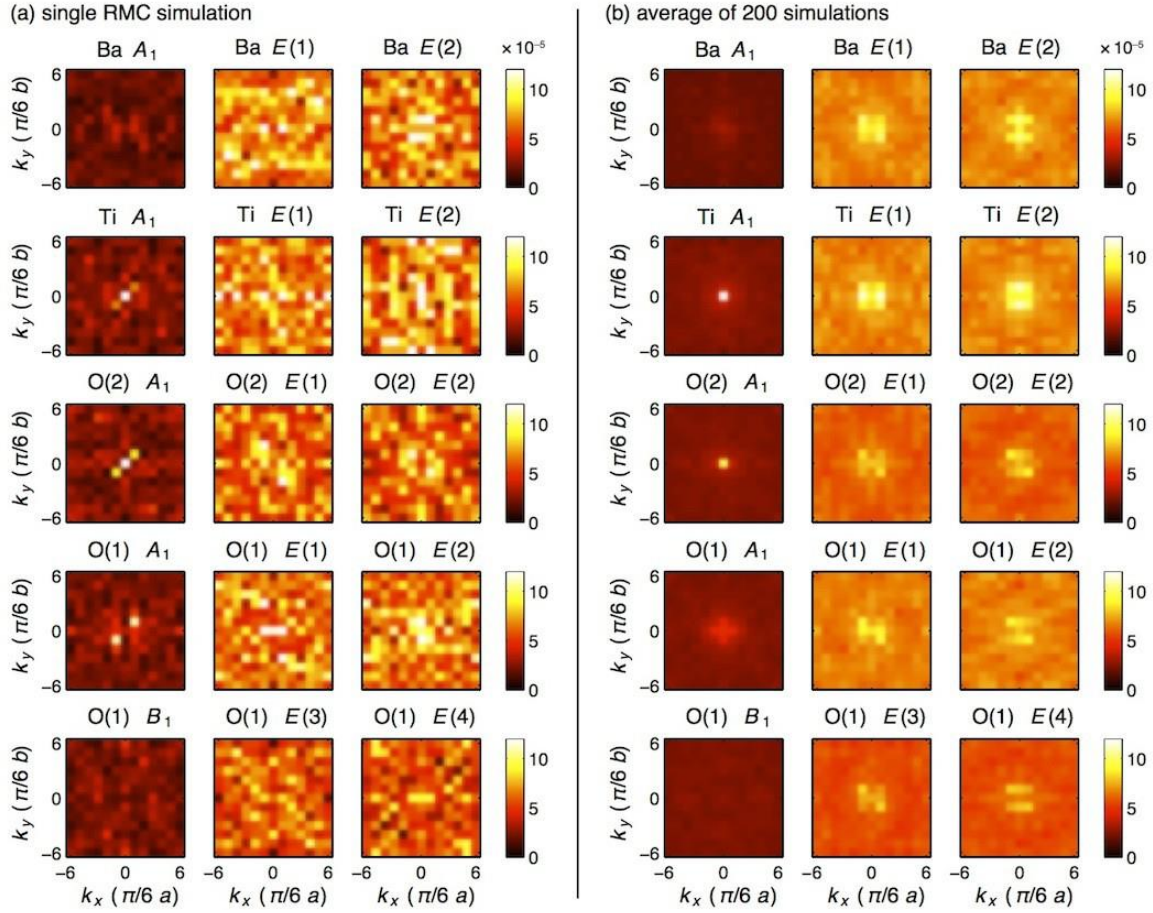
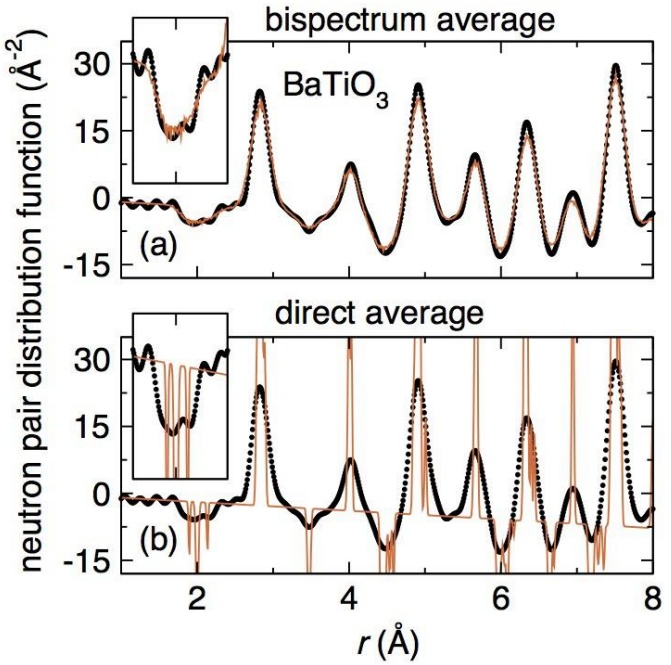





Image on Right from F. Sroubek, et al. DOI: 10.1117/2.1200712.0943
SR Imaging: A. W. Lohmann, et al. Applied Optics, 22, 4028–4037 (1983)

# It Works!




Likely has much broader applications

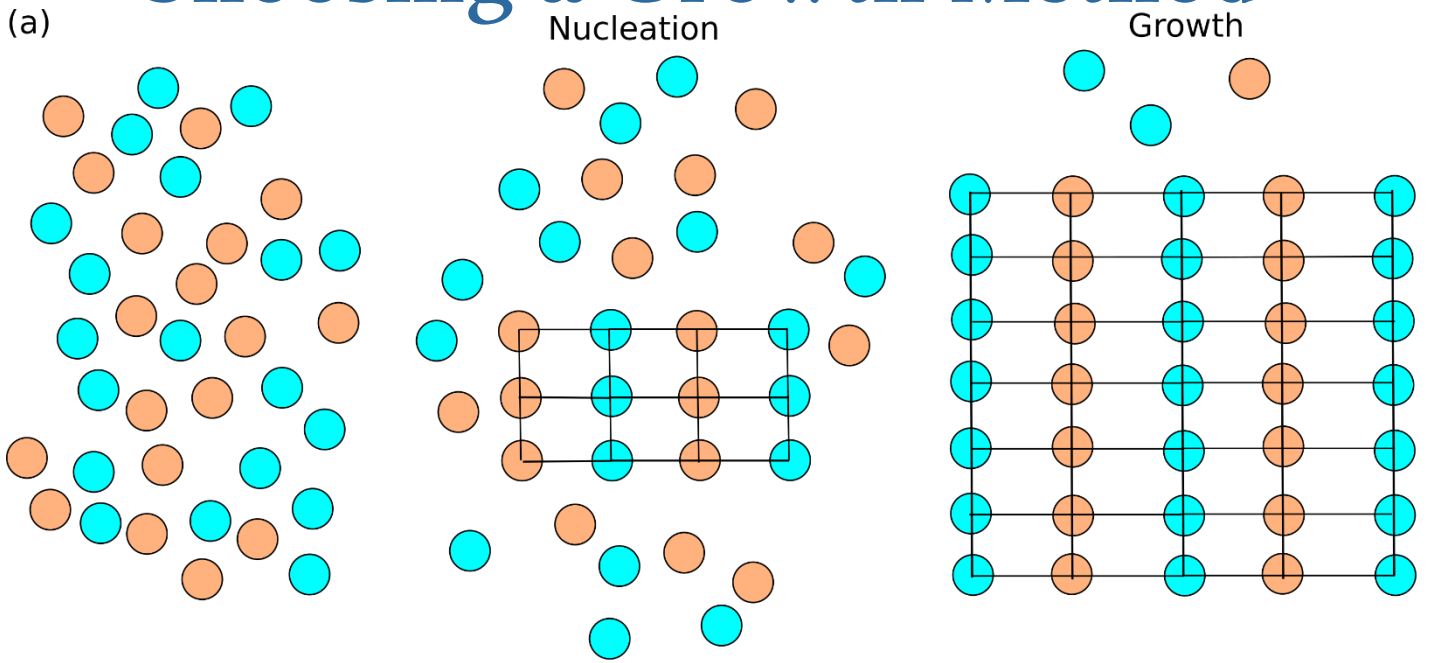


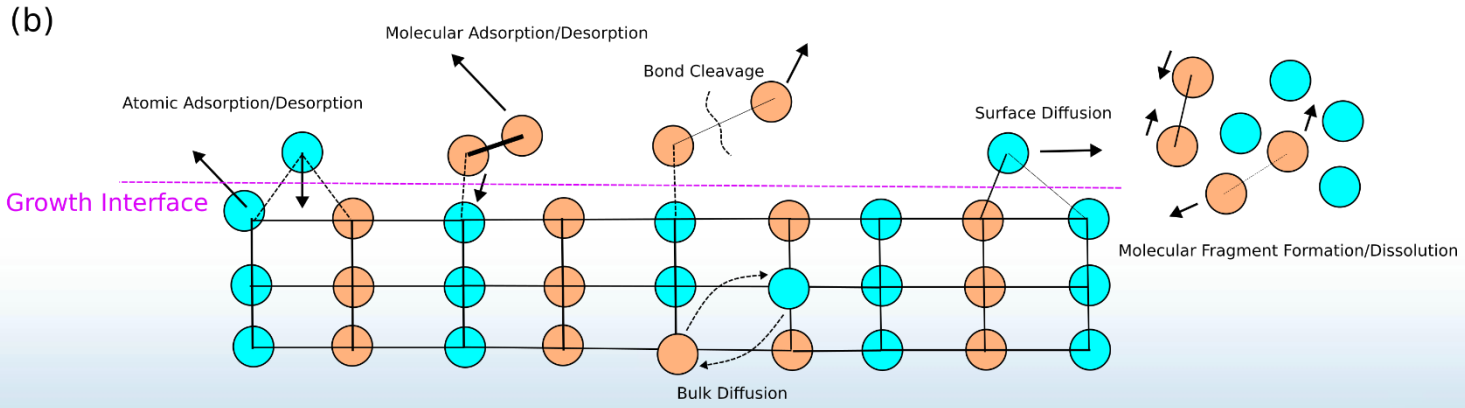
Data Courtesy Kate Page (Lujan/LANSCE/LANL)

# Outline

- Materials Lifecycle and Defining Quantum Materials
- The Importance of Design
- Synthesis Preliminaries
- Characterization and “Defects, Defects, Defects!”
- Advancing Materials Synthesis
- Role of AI/ML Methods
- The Future

# Choosing a Growth Method

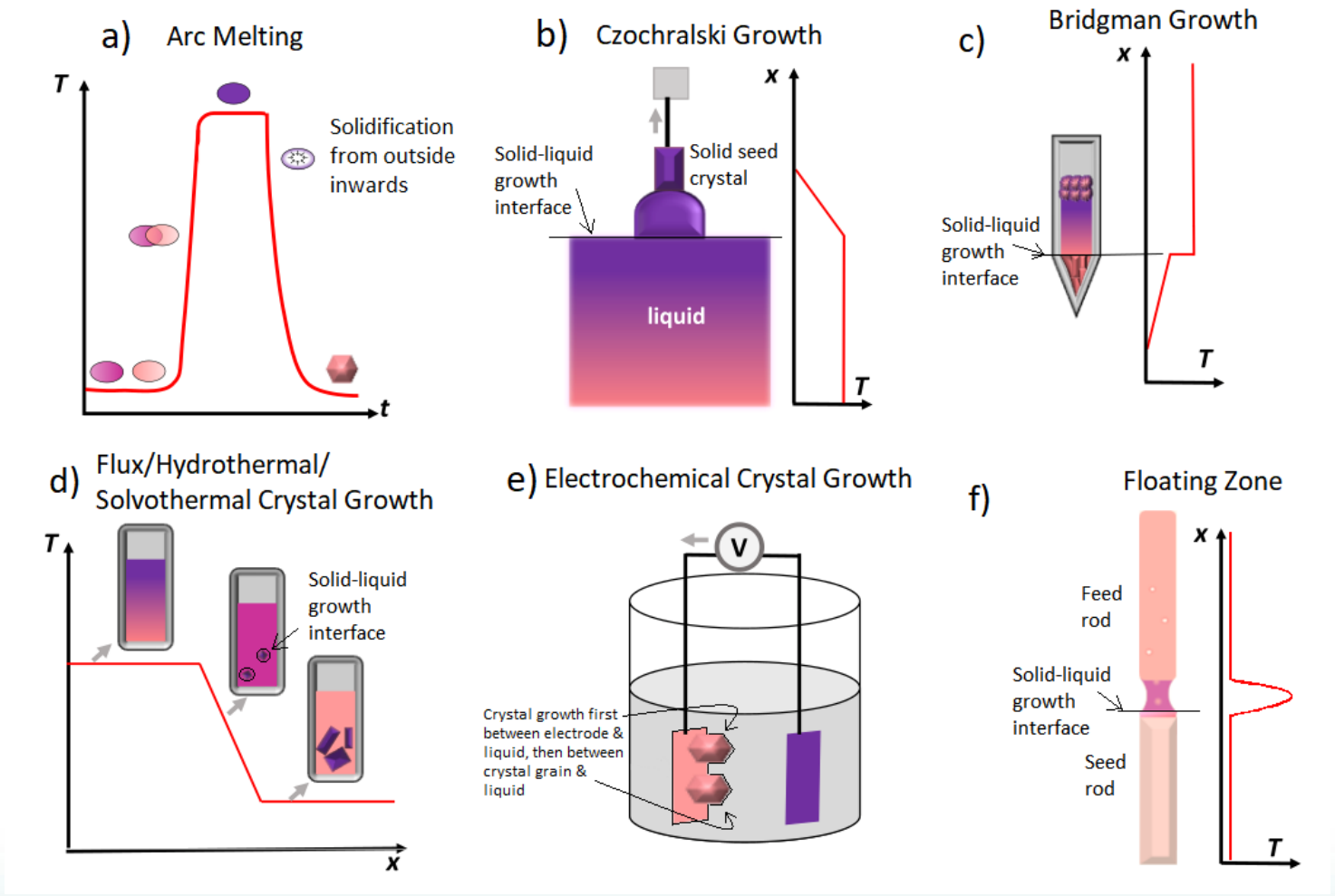





T. Berry, N. Ng, T.M. McQueen, Chem. Mater. (2024)

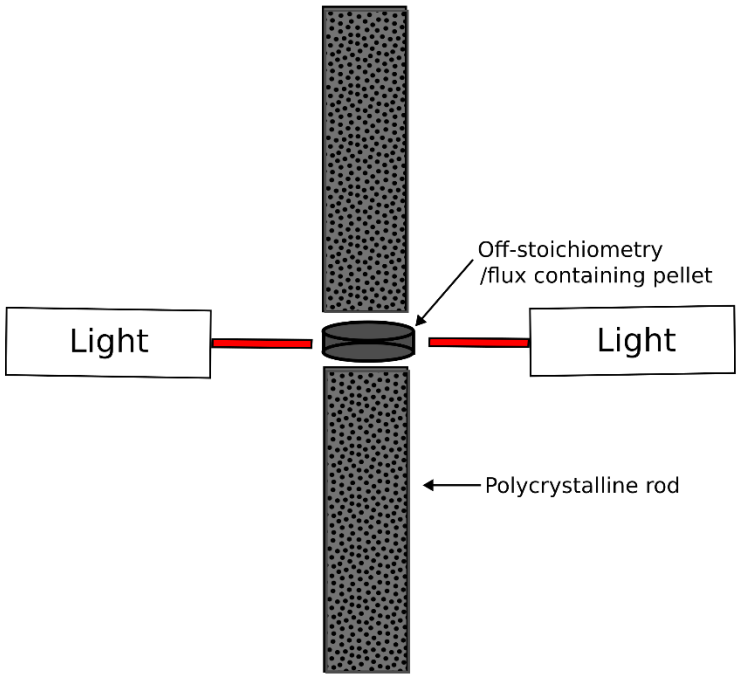
# Choosing a Growth Method

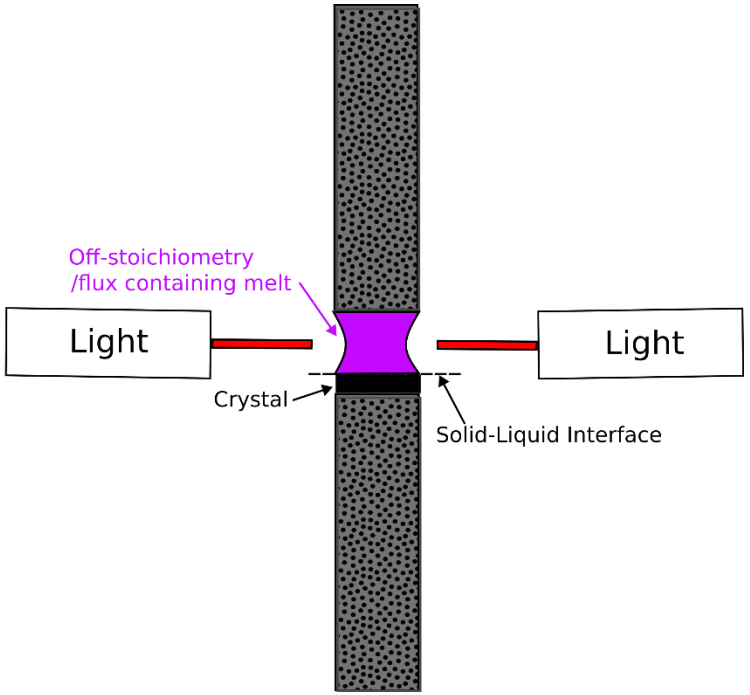


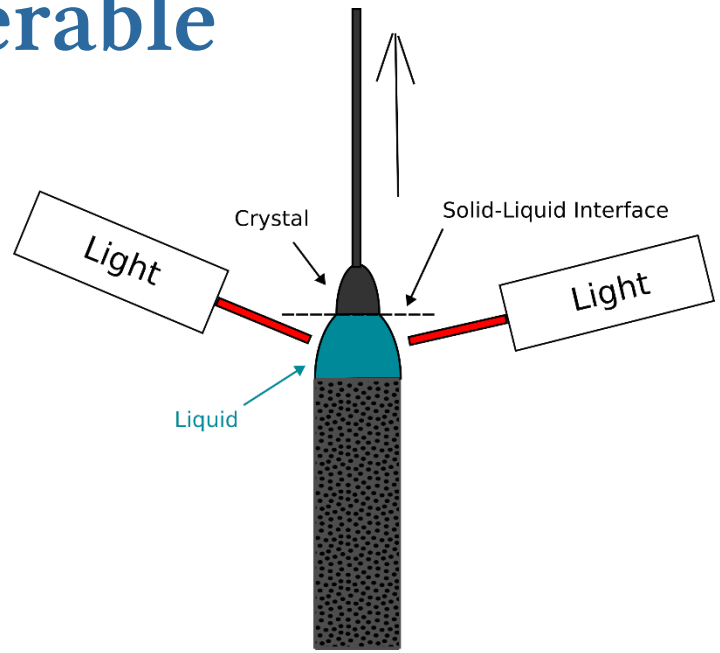


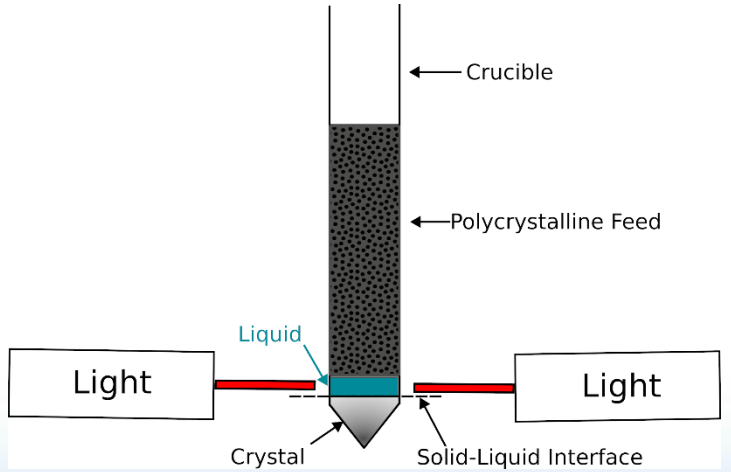

T. Berry, N. Ng, T.M. McQueen, Chem. Mater. (2024)

# Growth Variations Innumerable



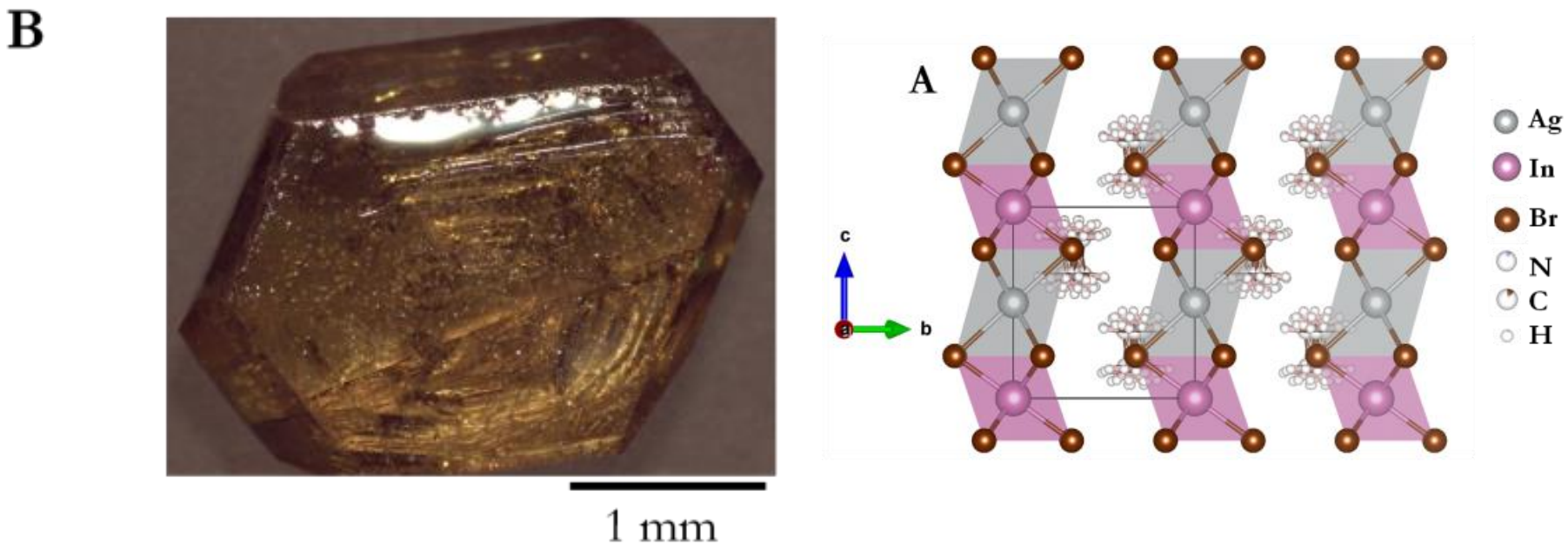



T. Berry, N. Ng, T.M. McQueen, Chem. Mater. (2024)

# Designed Synthesis

Initial attempts to make $(CH_3NH_3)_2AgInBr_6$ failed… only $(CH_3NH_3)_4InBr_7$ formed

Then a surprise… accidental addition of a small amount of $(CH_3NH_3)PbI_3$ and…



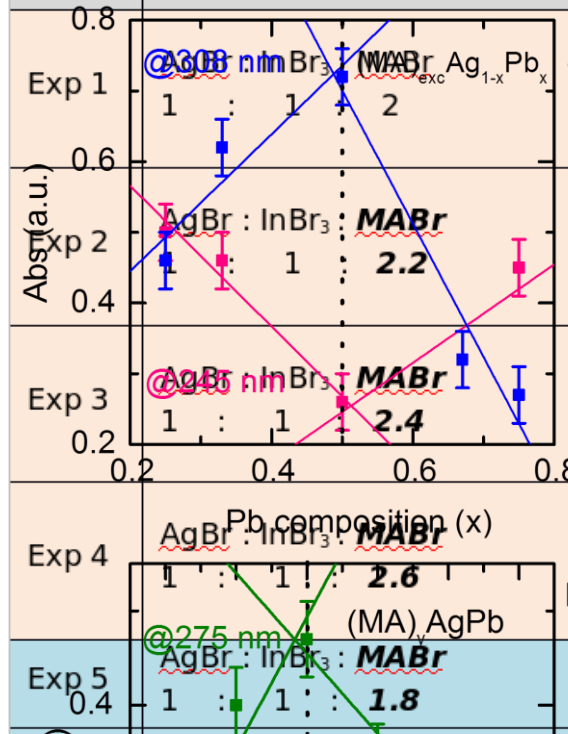

How does that work…?!?!?

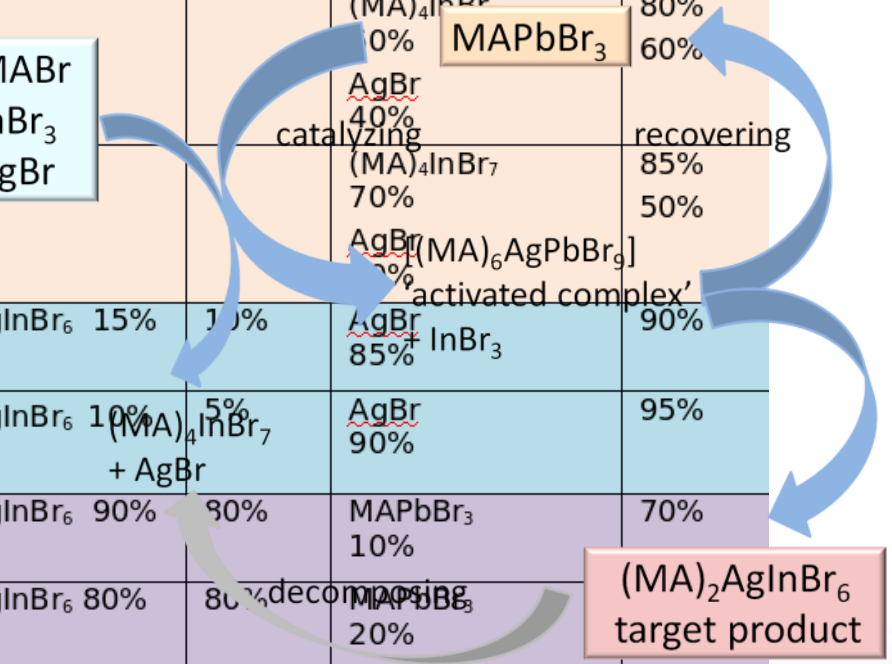


T.T. Tran, et. al. *Cryst. Eng. Comm.* **20**, 5929-34 (2018)

**Table 1. A survey of experiments (at 150°C) with different ratios of starting materials and in the presence (*in situ* or *ex situ*) or absence of $MAPbBr_3$**

| Exp | Starting materials (molar ratios) | Target product | | Side products | |
|---|---|---|---|---|---|
| | | % weight portion | % yield | % weight portion | % yield |
| Exp 1 | AgBr : $InBr_3$ : MABr : $MABr_{exc}$ : $Ag_{1-x}Pb_x$<br>1 : 1 : 2 | - | | $(MA)_4InBr_7$ 60%<br>AgBr 40% | 70%<br>90% |
| Exp 2 | AgBr : $InBr_3$ : ***MABr***<br>1 : 1 : ***2.2*** | $(MA)_2AgInBr_6$ 10% + $MA_4InBr_{7(s)}$ | 5% | $(MA)_4InBr_7$ 30%<br>AgBr 60% | 60%<br>80% |
| Exp 3 | AgBr : $InBr_3$ : ***MABr***<br>1 : 1 : ***2.4*** | - | | $(MA)_4InBr_7$ 30%<br>AgBr 40% | 80%<br>60% |
| Exp 4 | AgBr : $InBr_3$ : ***MABr***<br>1 : 1 : ***2.6*** | - | | $(MA)_4InBr_7$ 70%<br>AgBr 30% | 85%<br>50% |
| Exp 5 | AgBr : $InBr_3$ : ***MABr***<br>1 : 1 : ***1.8*** | $(MA)_2AgInBr_6$ 15% | 10% | AgBr 85% + $InBr_3$ | 90% |
| Exp 6 | AgBr : $InBr_3$ : ***MABr***<br>1 : 1 : ***1.6*** | $(MA)_2AgInBr_6$ 10% | 5% | AgBr 90% | 95% |
| Exp 7 | AgBr : $InBr_3$ : ***MABr : PbBr2***<br>1 : 1 : ***2.2 : 0.2*** | $(MA)_2AgInBr_6$ 90% | 80% | $MAPbBr_3$ 10% | 70% |
| Exp 8 | AgBr : $InBr_3$ : ***MABr : PbBr2***<br>1 : 1 : ***2.4 : 0.4*** | $(MA)_2AgInBr_6$ 80% | 80% | $MAPbBr_3$ 20% | 70% |
| Exp 9 | AgBr : $InBr_3$ : ***MABr : $MAPbBr_3$***<br>1 : 1 : ***2 : 0.2*** | $(MA)_2AgInBr_6$ 90% | 80% | $MAPbBr_3$ 10% | 70% |
| Exp 10 | AgBr : $InBr_3$ : MABr : ***$(MA)_2AgInBr_6$***<br>1 : 1 : 2 : ***0.2*** | $(MA)_2AgInBr_6$ 20% | 20% | $(MA)_4InBr_7$ 40%<br>AgBr 40% | 80%<br>70% |



# Chimie Douce: Controlled bond making/bre … e?

$$LiCoO_2 \leftrightarrow Li_xCoO_2 \ (x \sim 0.3)$$

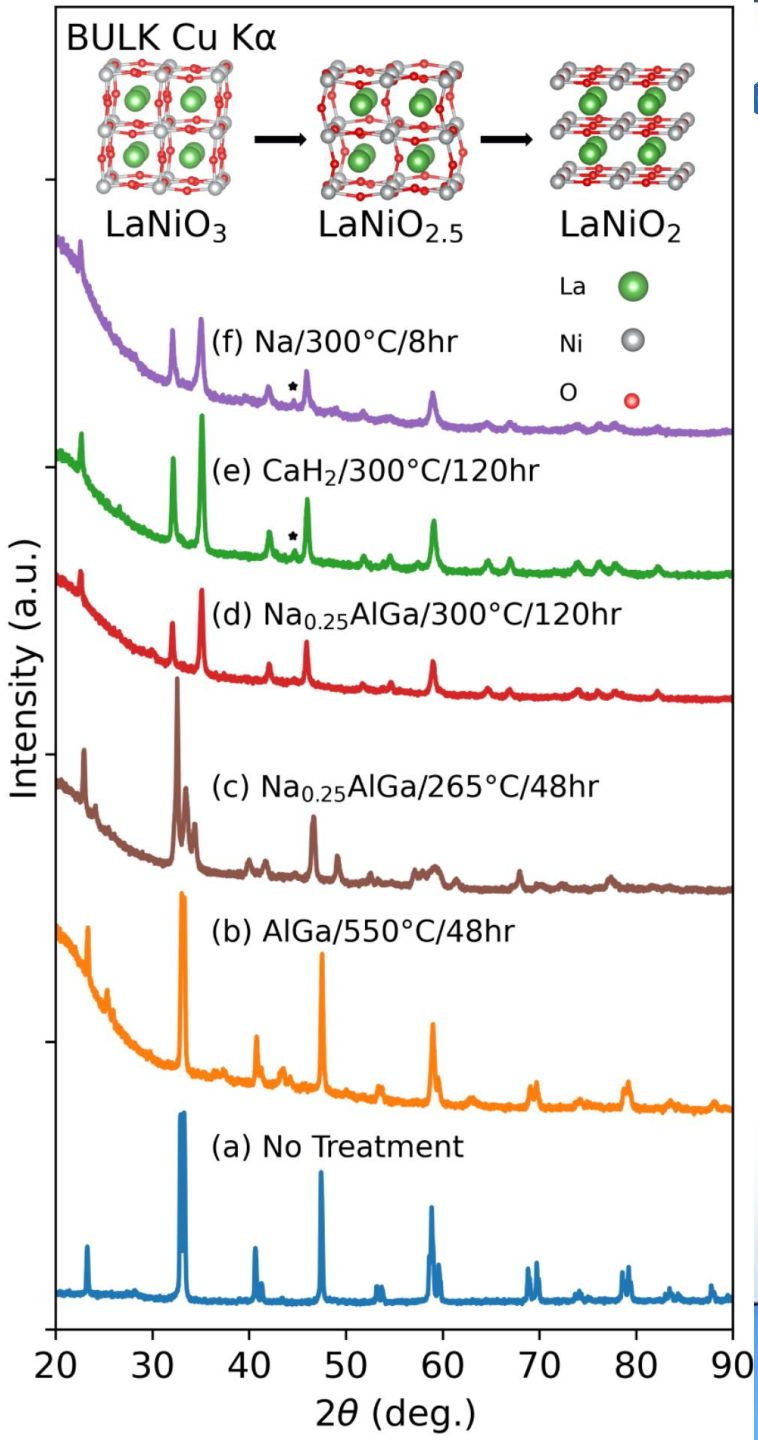
1) Build an electrochemical cell, apply a voltage
2) Use $I_2$/AcN or $Br_2$/AcN plus stirring and time
3) Butyl-Li to go in reverse direction

… use a … = Na,K)

$$LaNiO_3 \longrightarrow LaNiO_2$$

$CaH_2$ or NaH / controlled temperature

… but can this be done without H?

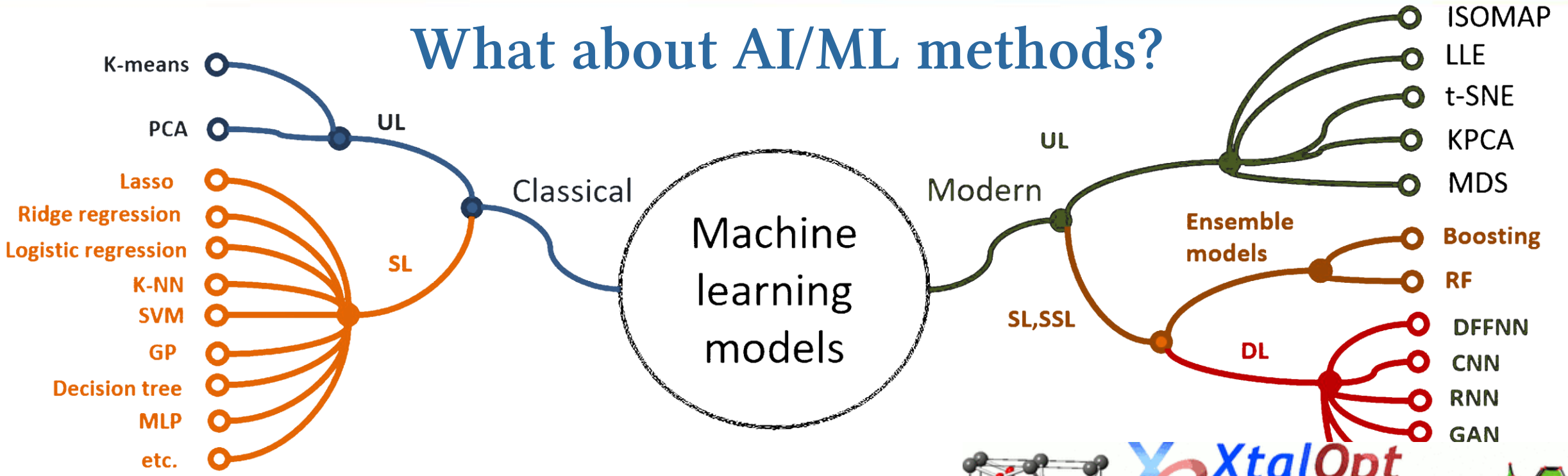





P. Odier, et al, JSSC 178, 1326-34 (2005), M.A. Hayward, et al, JACS 121, 8843-54 (1999)
T. Whoriskey, et al, Chem. Mater. (2024)

# And on and on it goes…

# What about AI/ML methods?




The Materials Project

**An open experimental database for exploring inorganic materials**

Andriy Zakutayev, Nick Wunder, Marcus Schwarting, John D. Perkins, Robert White, Kristin Munch, William Tumas & Caleb Phillips

*Scientific Data* **5**, Article number: 180053 (2018) | Cite this article

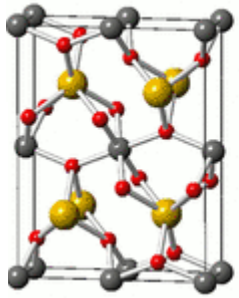
**15k** Accesses | **105** Citations | **52** Altmetric | Metrics

**Abstract**

The use of advanced machine learning algorithms in experimental materials science is limited by the lack of sufficiently large and diverse datasets amenable to data mining. If publicly open, such data resources would also enable materials research by scientists without access to expensive experimental equipment. Here, we report on our progress towards a publicly open High Throughput Experimental Materials (HTEM) Database (htem.nrel.gov). This database currently contains 140,000 sample entries, characterized by

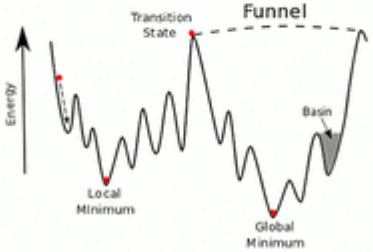
AFLOW

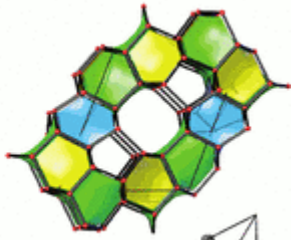
Automatic-FLOW for Materials Discovery

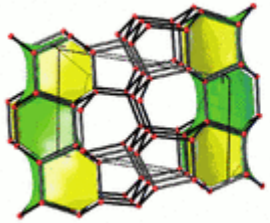


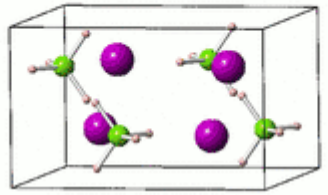
XtalOpt

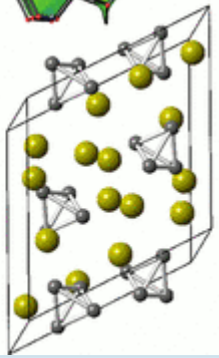
Evolutionary Crystal Structure Prediction





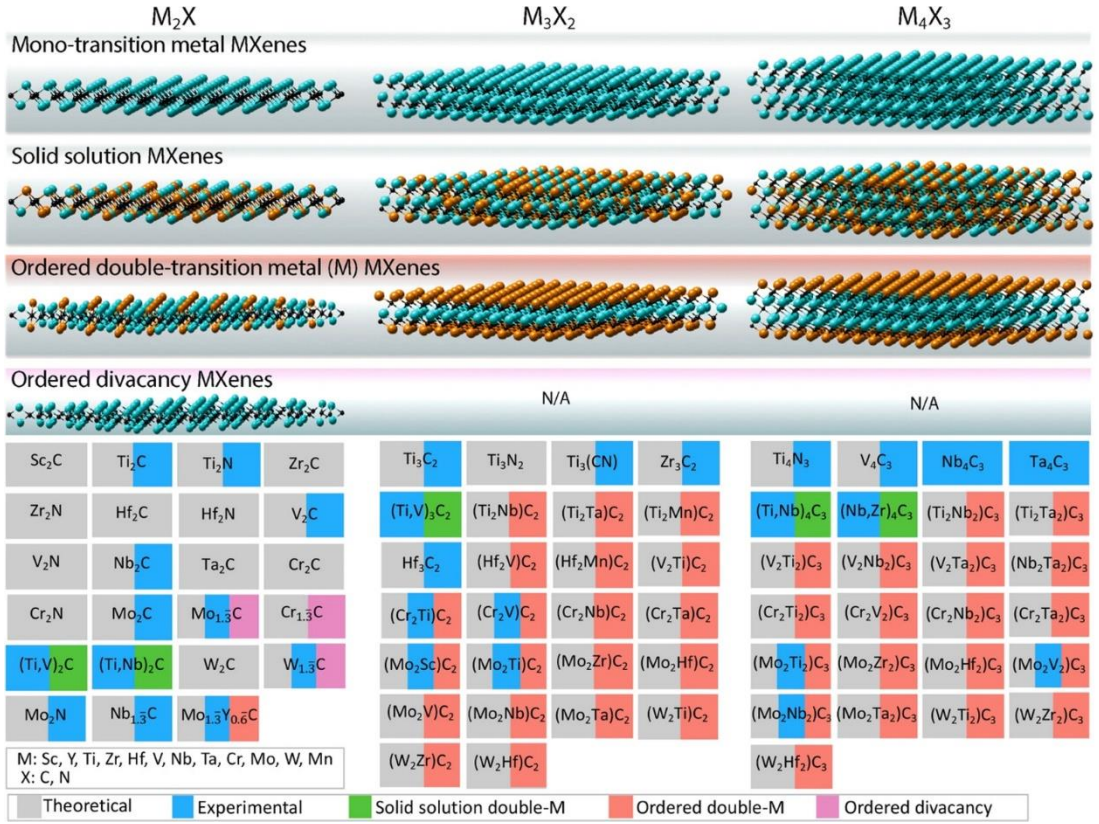


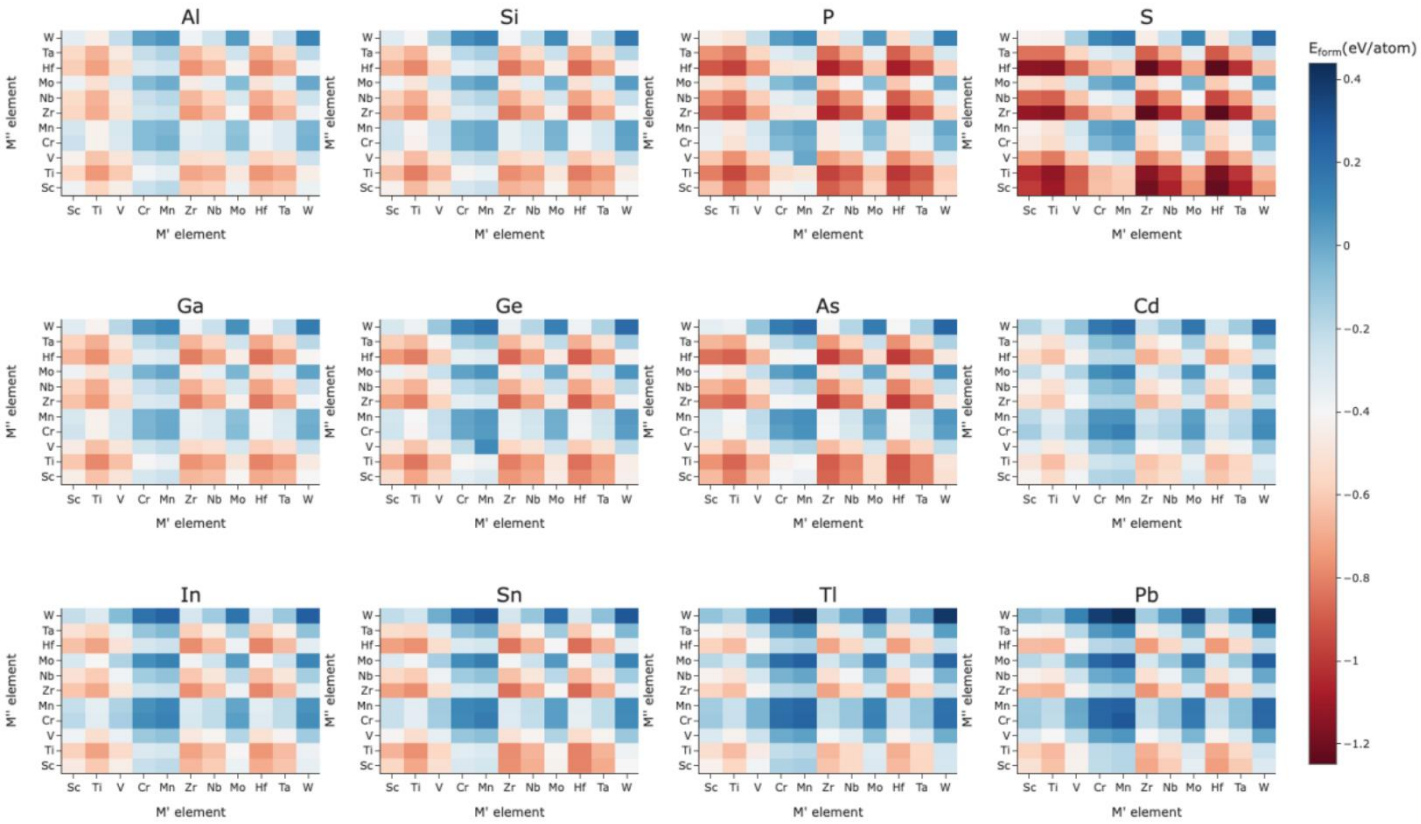




Mukhamediev, et al. *Mathematics* **10**, 2552 (2022) Zurek, et al. J. *Phys. Chem. C* **125**, 1601 (2020)

# Screening for new compounds in known structures






Y. Gogotsi and B. Anasori, ACS Nano 13, 8491-8494 (2019)

K. Nykiel and A. Strachan, *arXiv:2307.14250* (2023)

# And predicting new structure types

XTALOPT: An open-source evolutionary algorithm for crystal structure prediction ☆

David C. Lonie, Eva Zurek *

*Department of Chemistry, State University of New York at Buffalo, Buffalo, NY 14260-3000, United States*

ARTICLE INFO

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Evolutionary algorithm
Genetic algorithm
Crystal structures
Titanium dioxide

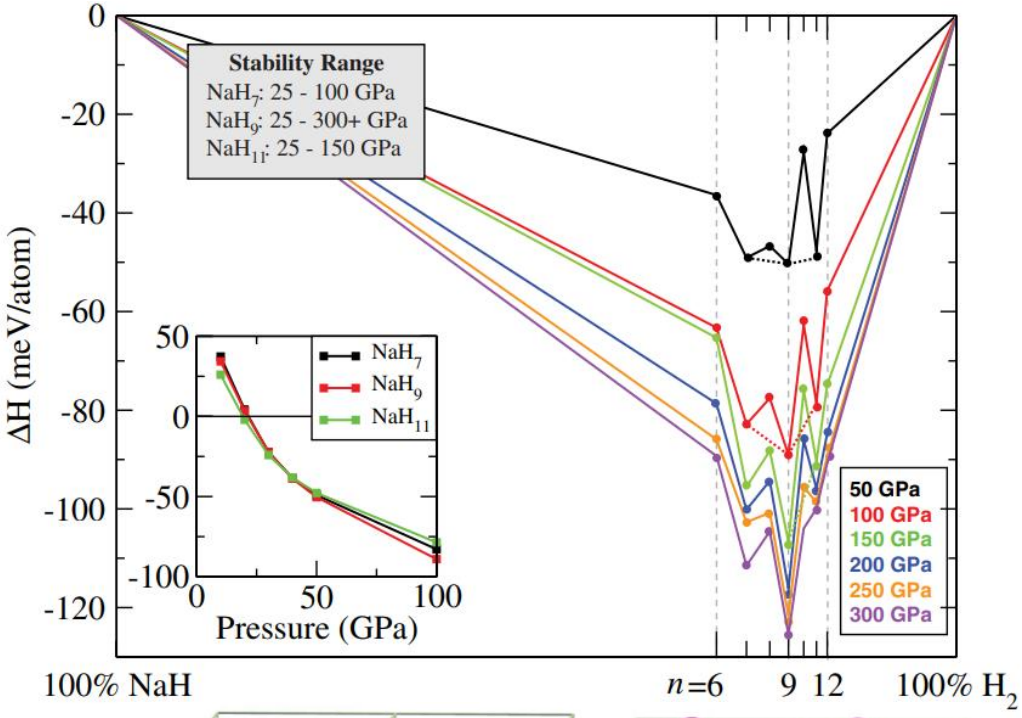
ABSTRACT

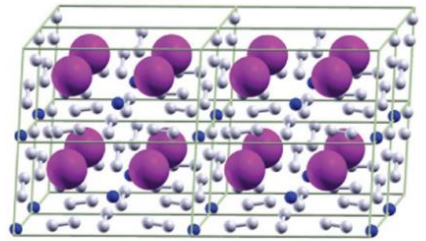
The implementation and testing of XTALOPT, an evolutionary algorithm for crystal structure prediction, is outlined. We present our new periodic displacement (ripple) operator which is ideally suited to extended systems. It is demonstrated that hybrid operators, which combine two pure operators, reduce the number of duplicate structures in the search. This allows for better exploration of the potential energy surface of the system in question, while simultaneously zooming in on the most promising regions. A continuous workflow, which makes better use of computational resources as compared to traditional generation based algorithms, is employed. Various parameters in XTALOPT are optimized using a novel benchmarking scheme. XTALOPT is available under the GNU Public License, has been interfaced with various codes commonly used to study extended systems, and has an easy to use, intuitive graphical interface.

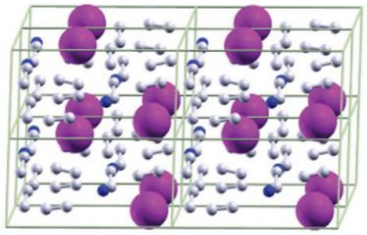
**Program summary**

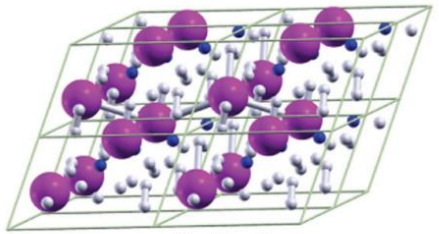
*Program title:* XTALOPT
*Catalogue identifier:* AEGX_v1_0
*Program summary URL:* http://cpc.cs.qub.ac.uk/summaries/AEGX_v1_0.html
*Program obtainable from:* CPC Program Library, Queen's University, Belfast, N. Ireland
*Licensing provisions:* GPL v2.1 or later [1]
*No. of lines in distributed program, including test data, etc.:* 36 849
*No. of bytes in distributed program, including test data, etc.:* 1 149 399
*Distribution format:* tar.gz
*Programming language:* C++
*Computer:* PCs, workstations, or clusters
*Operating system:* Linux
*Classification:* 7.7
*External routines:* QT [2], OpenBabel [3], AVOGADRO [4], SPGLIB [8] and one of: VASP [5], PWSCF [6], GULP [7].
*Nature of problem:* Predicting the crystal structure of a system from its stoichiometry alone remains a grand challenge in computational materials science, chemistry, and physics.
*Solution method:* Evolutionary algorithms are stochastic search techniques which use concepts from biological evolution in order to locate the global minimum on their potential energy surface. Our evolutionary algorithm, XTALOPT, is freely available to the scientific community for use and collaboration under the GNU Public License.
*Running time:* User dependent. The program runs until stopped by the user.
*References:*

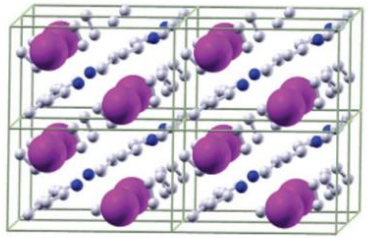
[1] http://www.gnu.org/licenses/gpl.html.
[2] http://www.trolltech.com/.
[3] http://openbabel.org/.
[4] http://avogadro.openmolecules.net.
[5] http://cms.mpi.univie.ac.at/vasp.
[6] http://www.quantum-espresso.org.
[7] https://www.ivec.org/gulp.



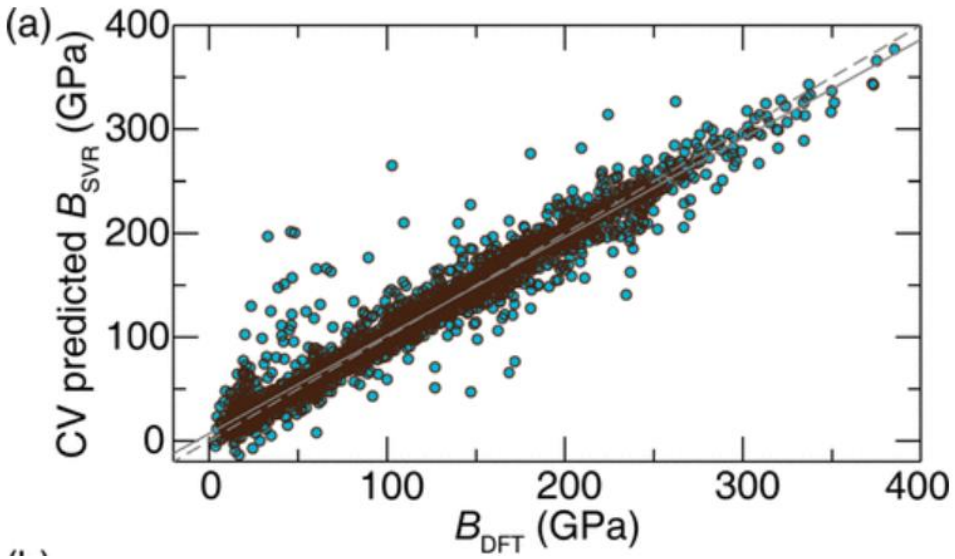


NaH$_9$; *Pm*

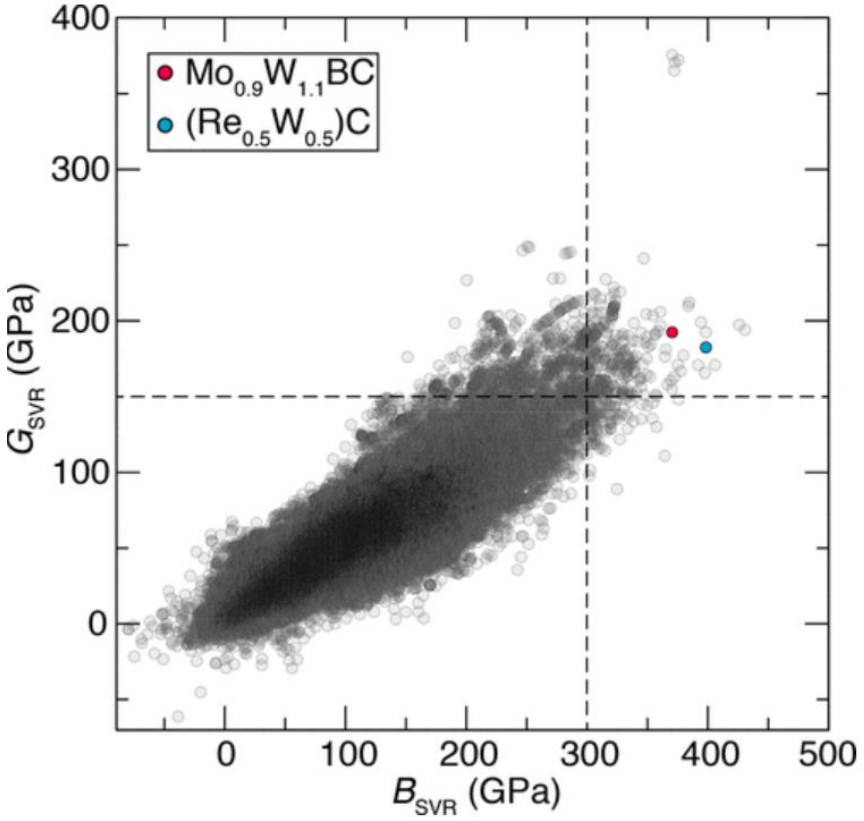

NaH$_9$; *Cmc*2$_1$

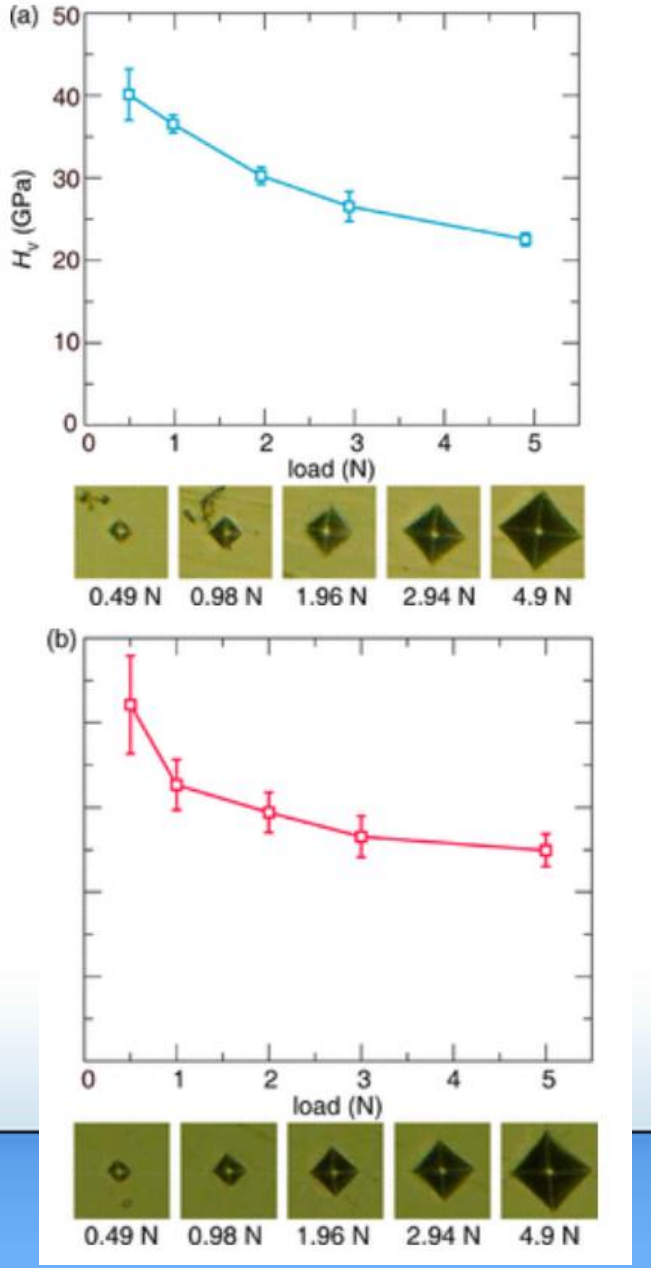

NaH$_7$; *Cc*


NaH$_{11}$; *P*1

# Predicting Materials with Stellar Properties



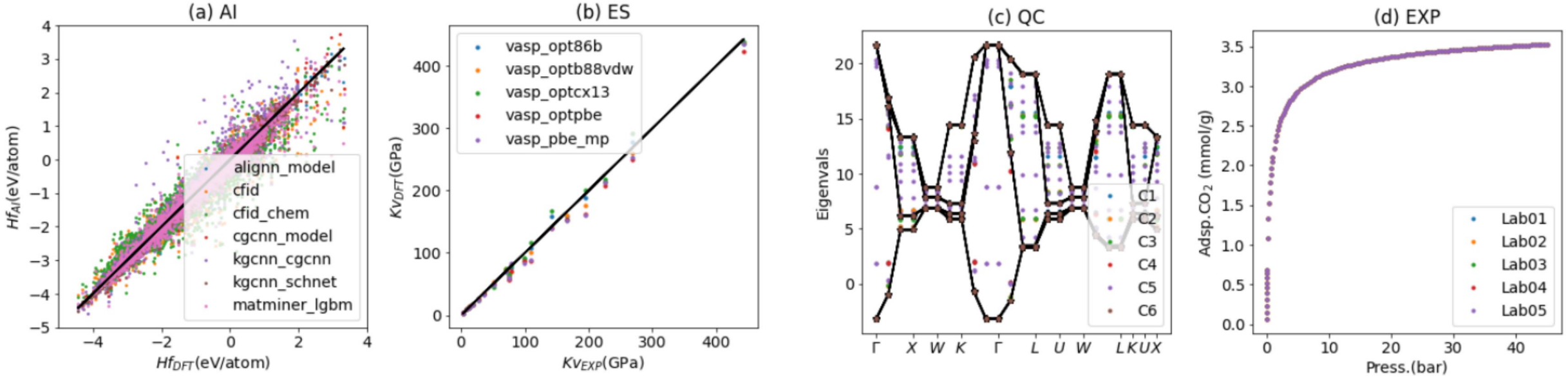






A. Tehrani, T.D. Sparks, J. Brgoch, et al. JACS 140, 9844 (2018)

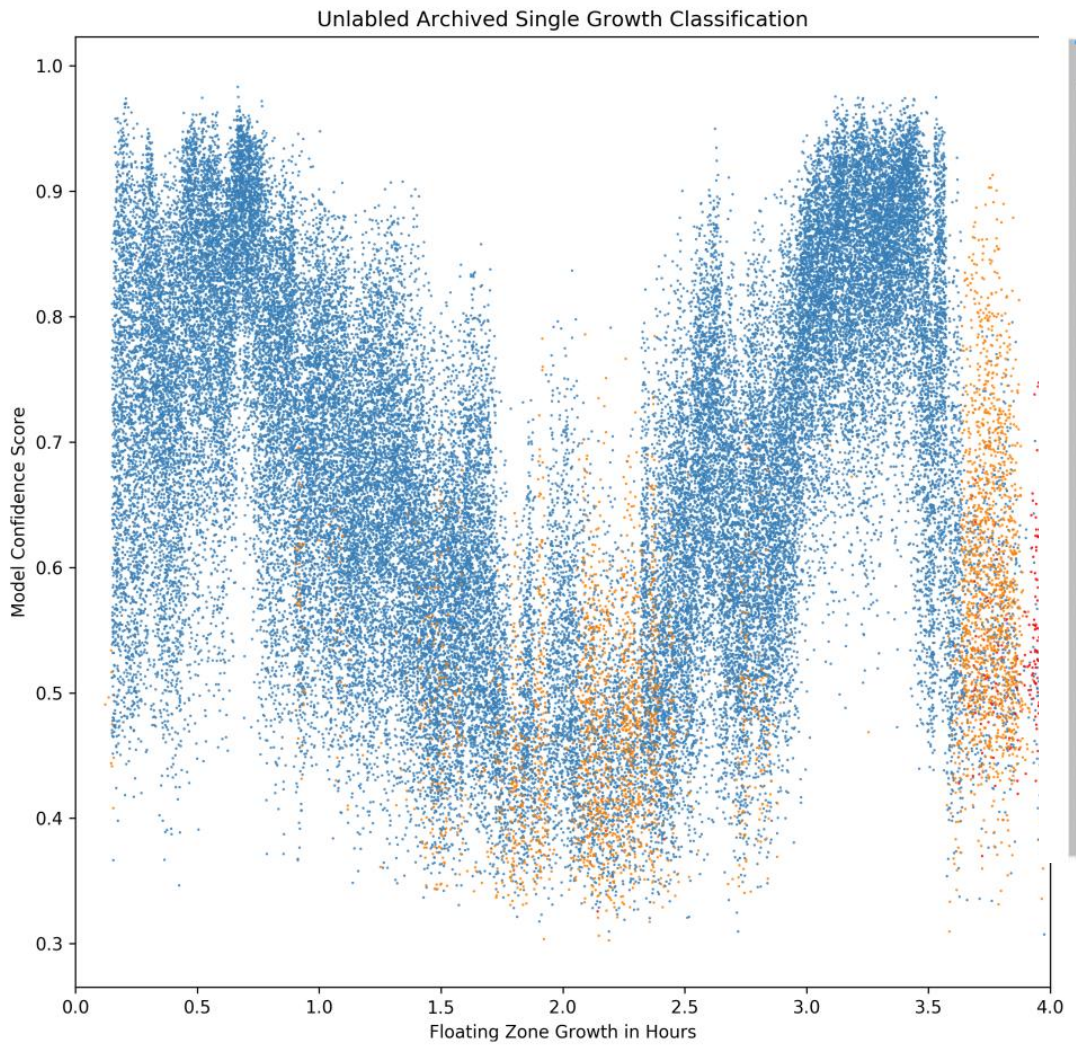
# Importance of Ecosystem and Validation

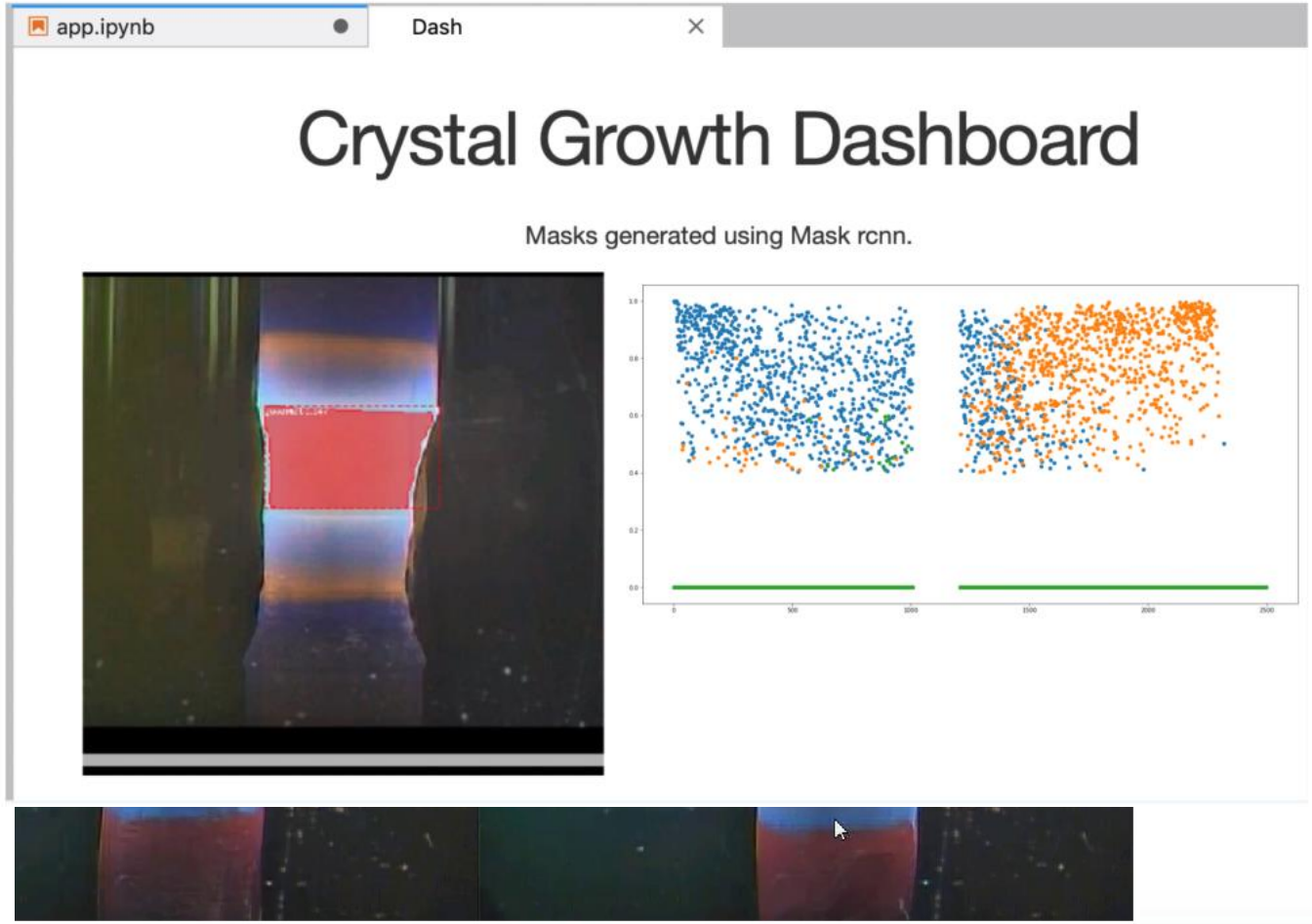



## Large Scale Benchmark of Materials Design Methods


Kamal Choudhary[1, a)] Daniel Wines[1] Kangming Li[2] Kevin F. Garrity[1] Vishu Gupta[3] Aldo H. Romero[4] Jaron T. Krogel[5] Kayahan Saritas[5] Addis Fuhr[6] Panchapakesan Ganesh[6] Paul R. C. Kent[7] Keqiang Yan[8] Yuchao Lin[8] Shuiwang Ji[8] Ben Blaiszik[9] Patrick Reiser[10] Pascal Friederich[11, 10] Ankit Agrawal[3] Pratyush Tiwary[12] Eric Beyerle[12] Peter Minch[13] Trevor David Rhone[13] Ichiro Takeuchi[14] Robert B. Wexler[15] Arun Mannodi-Kanakkithodi[16] Elif Ertekin[17, 18] Avanish Mishra[19] Nithin Mathew[19] Sterling G. Baird[20] Mitchell Wood[21] Andrew Dale Rohskopf[21] Jason Hattrick-Simpers[2] Shih-Han Wang[22] Luke E. K. Achenie[22] Hongliang Xin[22] Maureen Williams[1] Adam J. Biacchi[23] and Francesca Tavazza[1]

# Improving Success of Growth Attempts



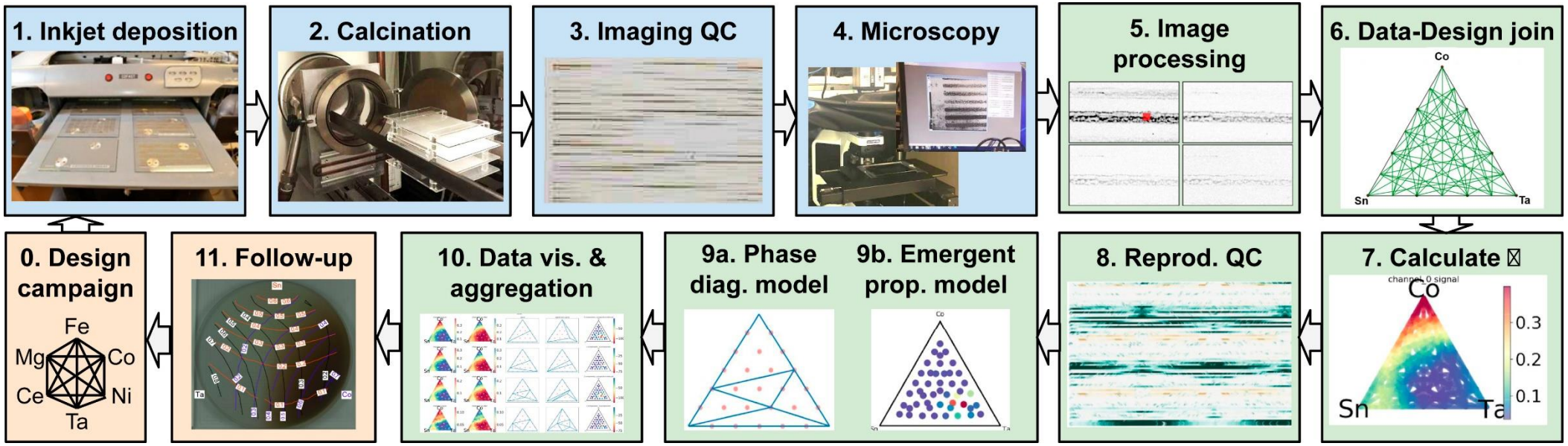



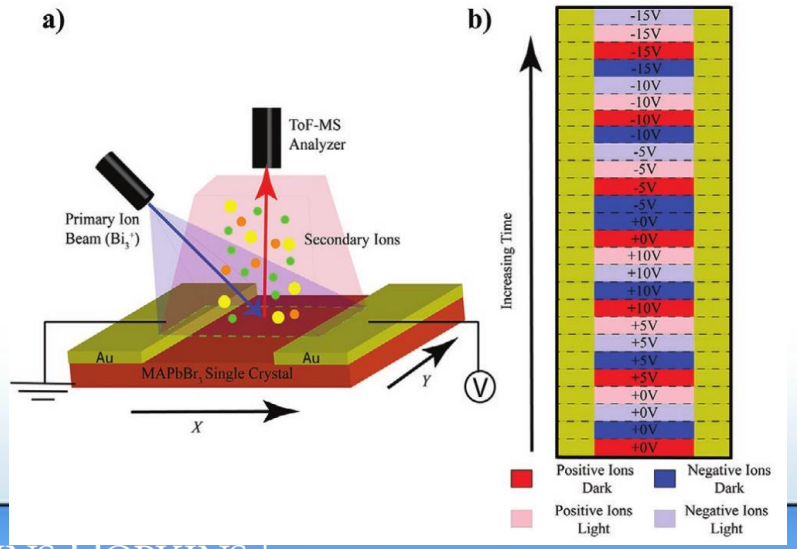

Op ry via

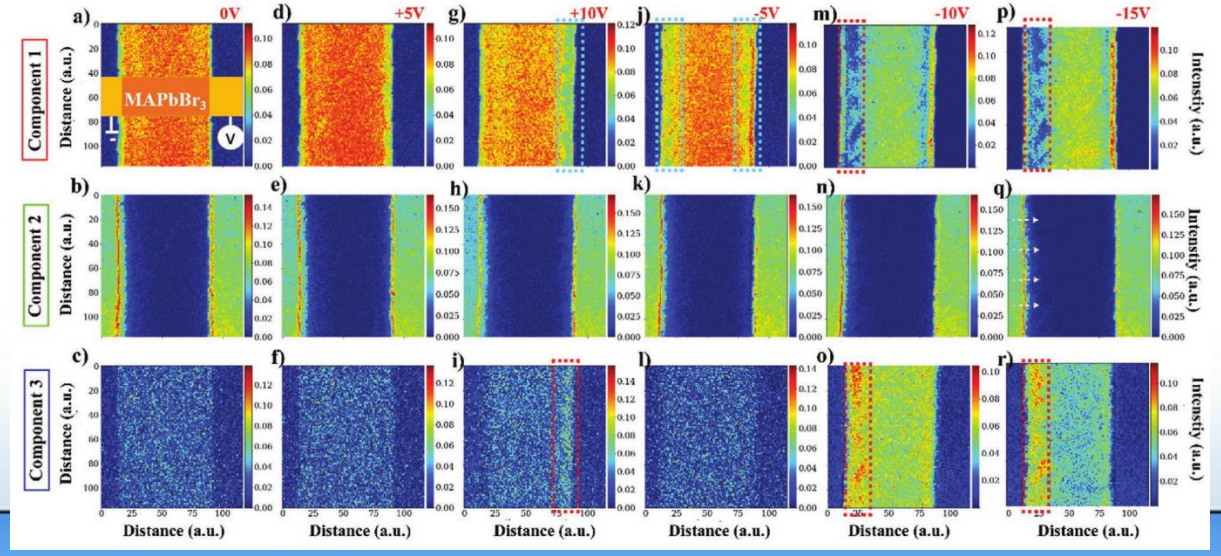
## Deep Neural Net Instance Segmentation

Nicholas Carey · W. Adam Phelan · Ali Rachidi · Connor Krill · Pheobe Appel · Jessica Zahn · Matthew Hudes · Brian Schuster · Tyrel M. McQueen · David Elbert

# High-Throughput Experiment + Theory






L. Yang, et al. PNAS 118, e2106042118 (2021) and K. Higgins, M. Ahmadi, et al. Adv. Funct. Mater. 30, 2001995 (2020)

# What about superconductors?

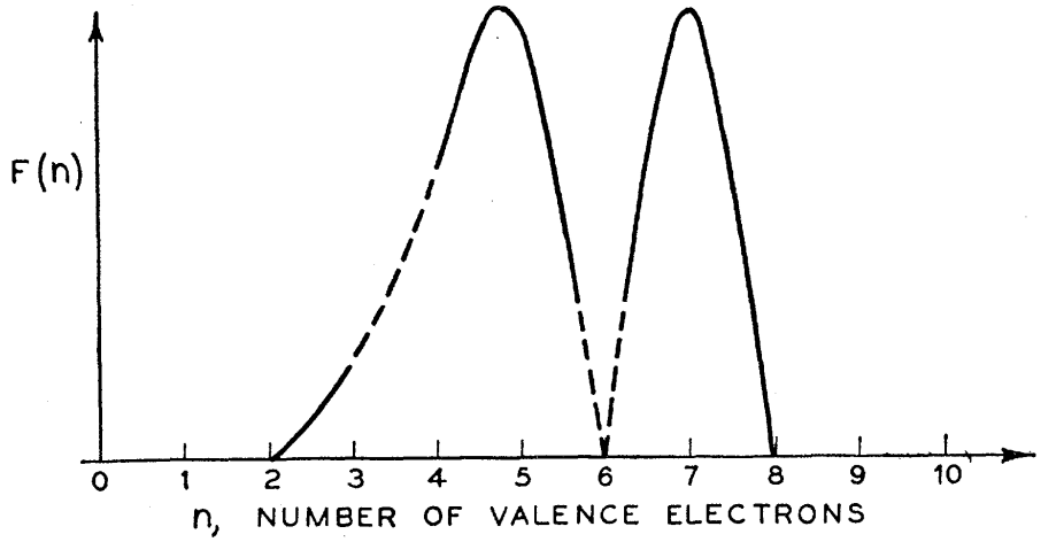



FIG. 1. Variation of superconducting transition temperature with number of valence electrons per atom.

AL REVIEW VOLUME 97, NUMBER 1 1955 JANUARY

## Empirical Relation between Superconductivity and the Number of Valence Electrons per Atom

B. T. MATTHIAS
*Bell Telephone Laboratories, Inc., Murray Hill, New Jersey*
(Received September 28, 1954)

The relation between the transition temperature of a superconductor and its number of valence electrons/atom has been investigated. Optimum conditions for the occurrence of superconductivity seem to exist for 5 and 7 valence electrons/atom.

# What about superconductors?

EVIEW B VOLUME 37, NUMBER 4 1 FEB

## Quantum structural diagrams and high-$T_c$ superconductivity

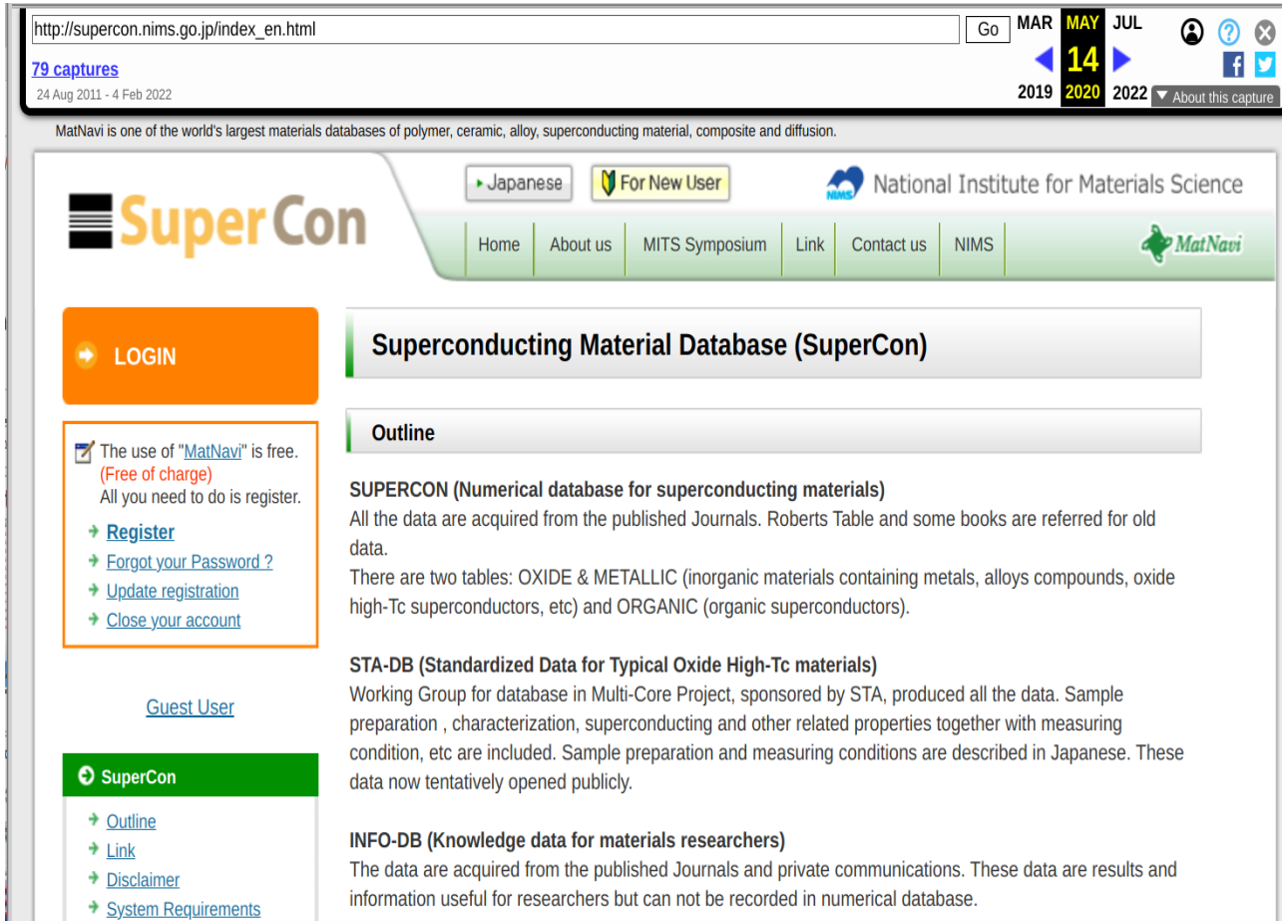
P. Villars* and J. C. Phillips
*AT&T Bell Laboratories, Murray Hill, New Jersey 07974*
(Received 21 September 1987)

Using golden coordinates we have successfully isolated the sixty known superconductors with $T_c > 10$ K into three small volumes which occupy about 1% of elemental configuration space. Two volumes contain the familiar NbN and $Nb_3Ge$ materials, but the third volume contains both the Chevrel sulfide and Bednorz-Müller-Chu oxide materials. Compounds in the third volume with formulas near $YBa_2Cu_3O_7$ are suggested as promising candidates for new high-$T_c$ superconductors.

| | Cr* | Mn* | Rh* | Fe | Co | Ni | Cu | Ag | Au | Zn | Cd | Hg |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Li | | Cl F | Cl N | F Cl | F Cl | O Cl | O F | Cl | S Br Cl N | N O | N O | |
| Na | | I Cl | I Cl Se | F I | F Se I | O Se I | O Te F Se | Cl Se Te | S Br Cl Se | N Te O Se | N Te O Se | Se |
| K | | | | F | F | O | O F | Cl | S Br Cl | N O | N | |
| Rb | I | | | F | F | O | O F | Cl | S Br Cl | N O | N | |
| Cs | | | | F I | F | O | O F | Cl | S Br Cl | N O | | |
| Be | F | F | O P | F | O F | O F | N O | N O | N S O | N O | N O | N O |
| Mg | F Br Cl | Cl Br | Cl Br | F Br Cl | O Cl F Br | O Br Cl | N O | S | S | N O | N O | |
| Ca | I Br | I Cl | I | F Cl I | O I F | O I | N O | | | N O | N O | |
| Sr | | | | F | O F | O | N O | | S | N O | N | |
| Ba | | | | F Br | O F | O | N O | | S | N O | N | |

FIG. 2. A tableau of promising pseudoternary (quaternary) candidates for high-$T_c$ superconductors with compositions paralleling $YBa_2Cu_3O_7$. The restrictions imposed on the golden coordinates $\overline{N_v}$, $\overline{\Delta X}$, and $\overline{\Delta R}$ used to derive this tableau are described in the text. The compositions have the general formula $([2s+f]/3)_3(p,d)_3p_7$ where $f$=Y, La, or a rare earth. The $s$ elements are listed in the ordinate. On the abcissas are the $p,d$ elements. Because of similar coordinates the Mn* column includes Re, Ru, and Os, the Rh* column includes Ir, Pd, and Pt, and the Cr* column includes Mo, W, O, S, Se, and Te.

# What about superconductors?




## Exploration of new superconductors and functional materials, and fabrication of superconducting tapes and wires of iron pnictides


**Hideo Hosono[1,2,3], Keiichi Tanabe[4], Eiji Takayama-Muromachi[5], Hiroshi Kageyama[6], Shoji Yamanaka[7], Hiroaki Kumakura[5], Minoru Nohara[8], Hidenori Hiramatsu[2,3] and Satoru Fujitsu[3]**

[1] Frontier Research Center, Tokyo Institute of Technology, Yokohama 226-8503, Japan
[2] Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama 226-8503, Japan
[3] Materials Research Center for Element Strategy, Tokyo Institute of Technology, Yokohama 226-8503, Japan
[4] Superconductivity Research Laboratory, International Superconductivity Technology Center (ISTEC), 2-11-19 Minowa-cho, Kohoku-ku, Yokohama, Kanagawa 223-0051, Japan
[5] National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan
[6] Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan
[7] Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan
[8] Department of Physics, Okayama University, Okayama 700-8530, Japan

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Received 2 April 2015
Accepted for publication 28 April 2015
Published 8 May 2015



**Abstract**

This review shows the highlights of a 4-year-long research project supported by the Japanese Government to explore new superconducting materials and relevant functional materials. The project found several tens of new superconductors by examining ~1000 materials, each of which was chosen by Japanese experts with a background in solid state chemistry. This review summarizes the major achievements of the project in newly found superconducting materials, and the fabrication wires and tapes of iron-based superconductors; it incorporates a list of ~700 unsuccessful materials examined for superconductivity in the project. In addition, described are new functional materials and functionalities discovered during the project.


# Deep learning model for finding new superconductors

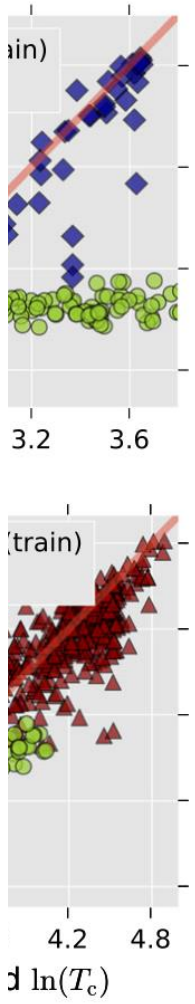
Tomohiko Konno,[1,*] Hodaka Kurokawa,[2,†] Fuyuki Nabeshima,[2] Yuki Sakishita,[2] Ryo Ogawa,[2] Iwao Hosako,[1] and Atsutaka Maeda[2]

[1]*National Institute of Information and Communications Technology, 4-2-1 Nukui-Kitamachi, Koganei, Tokyo 184-8795, Japan*

[2]*The University of Tokyo, 7 Chome-3-1 Hongo, Bunkyo City, Tokyo 113-8654, Japan*

(Received 2 December 2019; accepted 3 December 2020; published 12 January 2021)

Exploration of new superconductors still relies on the experience and intuition of experts, and is largely a process of experimental trial and error. In one study, only 3% of the candidate materials showed superconductivity [Hosono *et al.*, Sci. Technol. Adv. Mater. 16, (2015)]. Here, we report a deep learning model for finding new superconductors. We introduced the method named "reading periodic table" that represented the periodic table in a way that allows deep learning to learn to read the periodic table and to learn the law of elements for the purpose of discovering novel superconductors which are outside the training data. It is recognized that it is difficult for deep learning to predict something outside the training data. Although we used only the chemical composition of materials as information, we obtained an $R^2$ value of 0.92 for predicting $T_c$ for materials in a database of superconductors. We also introduced the method named "garbage-in" to create synthetic data of nonsuperconductors that do not exist. Nonsuperconductors are not reported, but the data must be required for deep learning to distinguish between superconductors and nonsuperconductors. We obtained three remarkable results. The deep learning can predict superconductivity for a material with a precision of 62%, which shows the usefulness of the model; it found the recently discovered superconductor $CaBi_2$ and another one $Hf_{0.5}Nb_{0.2}V_2Zr_{0.3}$, neither of which is in the superconductor database; and it found Fe-based high-temperature superconductors (discovered in 2008) from the training data before 2008. These results open the way for the discovery of new high-temperature superconductor families. The candidate materials list, data, and method are openly available on the Internet.



# Lets Tackle One Hard Problem at a Time

I want a s.c. with…

$T_c$ > 350 K

$J_c$ > 2000 A/m$^2$

$H_{c2}$ > 30 T

At 1 atm pressure

No toxic elements

AI/ML Magic

Make compound XYZQ with the W structure.
To so by first making XY, then … , after that…

What is the $T_c$ of (or is it s.c.)?

$Ba_{0.6}K_{0.4}BiO_3$

AI/ML Magic

$T_c$ = 35 K

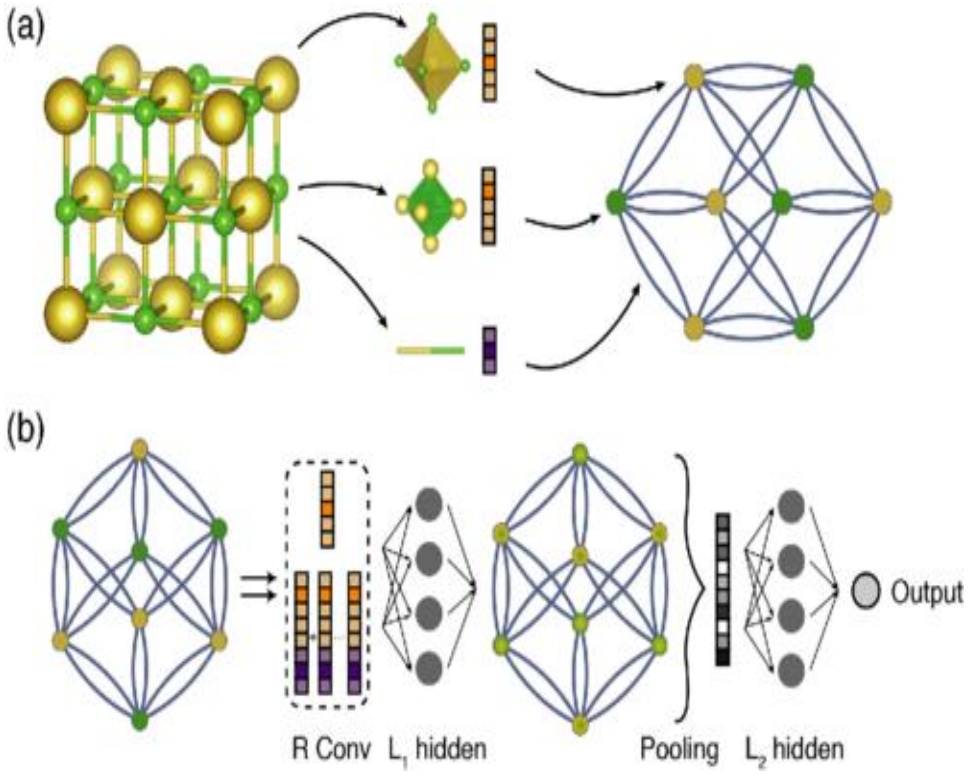
What is the $T_c$ of (or is it s.c.)?

$Ba_{0.6}K_{0.4}BiO_3$ in the perovskite structure with a statistical mix of Ba/K

AI/ML Magic?

$T_c$ = 35 K

# Crystal Structure is Important!



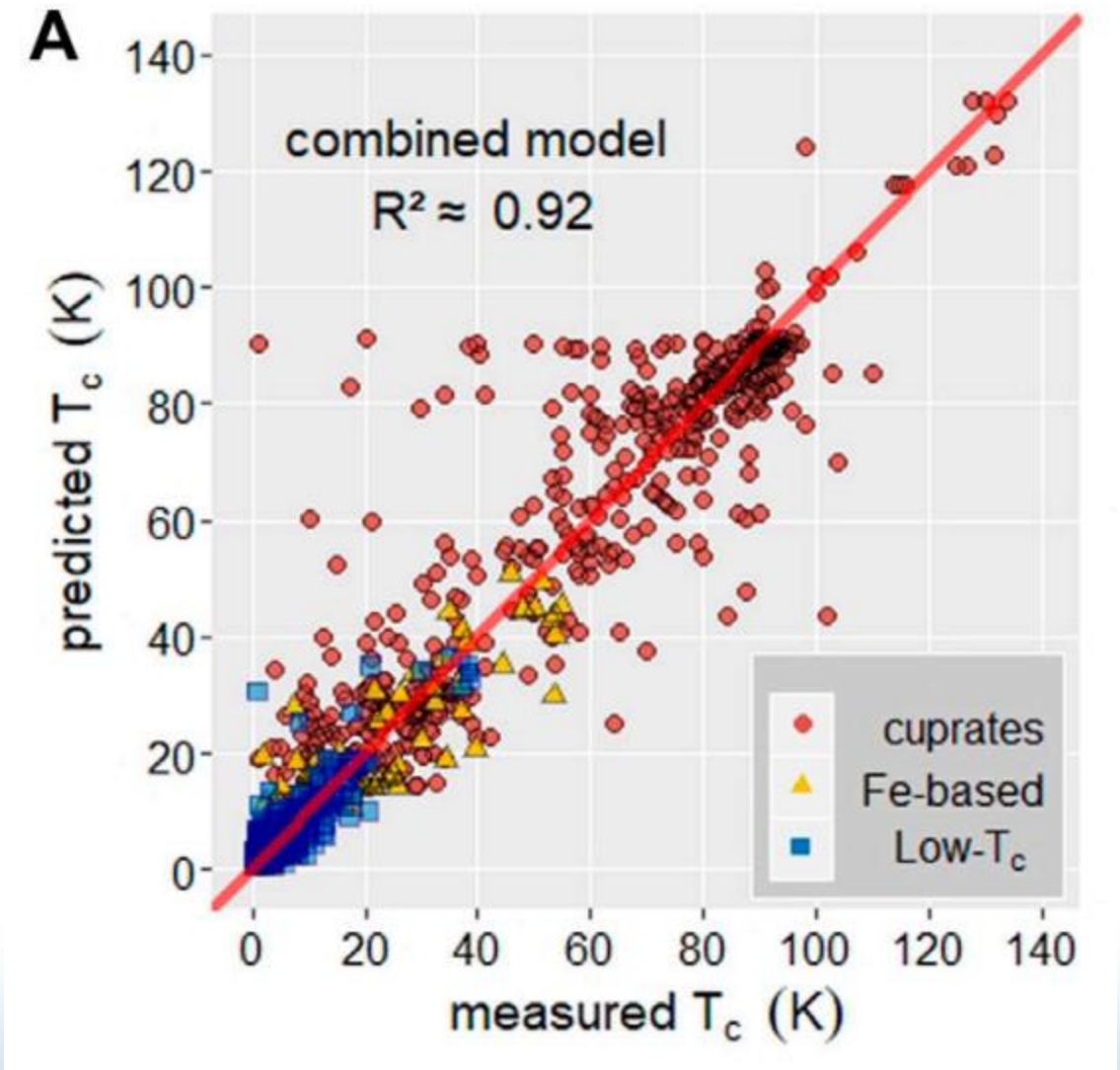

| | composition | pretty_composition | parent_guess | materials_project_id | tc | de |
|---|---|---|---|---|---|---|
| 0 | Au0.9Ga0.1 | Ga0.1Au0.9 | Au | mp-81 | 0.264 | Au |
| 1 | Au0.95Ga0.05 | Ga0.05Au0.95 | Au | mp-81 | 0.032 | Au |
| 2 | Ba0.2La1.8Cu1O4-Y | Ba0.2La1.8Cu1O4 | La2CuO4 | mp-19735 | 29 | Ba |
| 3 | Ba0.1La1.9Ag0.1Cu0.9O4-Y | Ba0.1La1.9Cu0.9Ag0.1O4 | La2CuO4 | mp-19735 | 26 | Ba |
| 4 | Ba0.1La1.9Cu1O4-Y | Ba0.1La1.9Cu1O4 | La2CuO4 | mp-19735 | 19 | Ba |
| 5 | Ba0.15La1.85Cu1O4-Y | Ba0.15La1.85Cu1O4 | La2CuO4 | mp-19735 | 22 | Ba |
| 6 | Ba0.3La1.7Cu1O4-Y | Ba0.3La1.7Cu1O4 | La2CuO4 | mp-19735 | 23 | Ba |
| 7 | Ba0.5La1.5Cu1O4-Y | Ba0.5La1.5Cu1O4 | La2CuO4 | mp-19735 | 23 | Ba |
| 11 | Sr0.1La1.9Cu1O4-Y | Sr0.1La1.9Cu1O4 | La2CuO4 | mp-19735 | 33 | Sr |
| 12 | Sr0.15La1.85Cu1O4-Y | Sr0.15La1.85Cu1O4 | La2CuO4 | mp-19735 | 36 | Sr |
| 13 | Sr0.2La1.8Cu1O4-Y | Sr0.2La1.8Cu1O4 | La2CuO4 | mp-19735 | 31 | Sr |
| 14 | Sr0.3La1.7Cu1O4-Y | Sr0.3La1.7Cu1O4 | La2CuO4 | mp-19735 | 33 | Sr |
| 15 | Ba0.3La1.7Hg0.3Cu0.7O4-Y | Ba0.3La1.7Cu0.7Hg0.3O4 | La2CuO4 | mp-19735 | 26 | Ba |
| 17 | Ba0.1La1.9Ag0.05Cu0.95O4-Y | Ba0.1La1.9Cu0.95Ag0.05O4 | La2CuO4 | mp-19735 | 27 | Ba |
| 18 | Ba0.1La1.9Ag0.1Cu0.9O4-Y | Ba0.1La1.9Cu0.9Ag0.1O4 | La2CuO4 | mp-19735 | 27 | Ba |
| 19 | Ba0.1La1.9Ag0.25Cu0.75O4-Y | Ba0.1La1.9Cu0.75Ag0.25O4 | La2CuO4 | mp-19735 | 26 | Ba |
| 20 | Ba0.1La1.9Ag0.5Cu0.5O4-Y | Ba0.1La1.9Cu0.5Ag0.5O4 | La2CuO4 | mp-19735 | 27 | Ba |
| 21 | Y1Ba1.5Ca0.5Cu3O7-Z | Ba1.5Ca0.5Y1Cu3O7 | Ba2YCu3O7 | mp-20674 | 82 | Y |
| 22 | Ba0.15La1.85Cu1O4-Y | Ba0.15La1.85Cu1O4 | La2CuO4 | mp-19735 | 30 | Ba |
| 23 | La1.85Ba0.15Cu1O4 | Ba0.15La1.85Cu1O4 | La2CuO4 | mp-19735 | 30 | La |
| 24 | La1.85Sr0.15Cu1O4 | Sr0.15La1.85Cu1O4 | La2CuO4 | mp-19735 | 39 | La |
| 25 | In1Sc1Au2 | ScInAu2 | ScInAu2 | mp-30395 | 3.02 | In |



T. Xie & J.C. Grossman, PRL 120, 145301 (2018)

M. Quinn & T.M. McQueen, Front. Elec. Mater. 2, 893797 (2022)

# Results

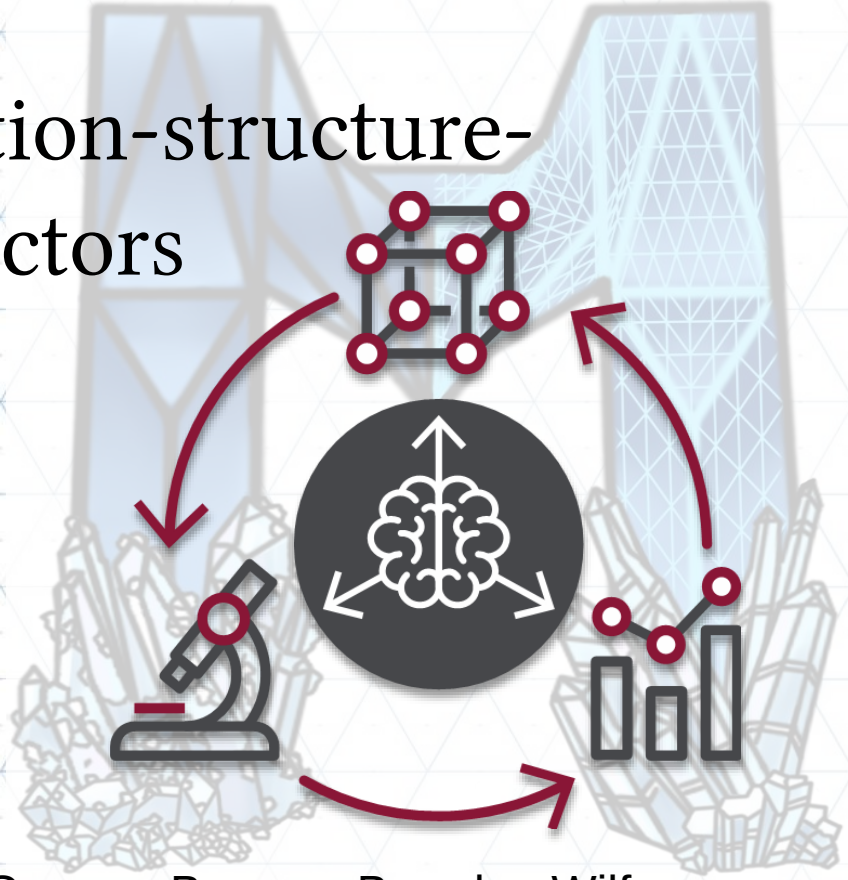



| Composition | Reference No. | $T_{C,\ PRED}$ |
|---|---|---|
| Nickelate | (*n* = 271) | – |
| $MgNiO_2$ | mp-1239335 | 30 |
| $CaNiO_2$ | mp-1147749 | 44 |
| $BaNiO_2$ | mp-1147749 | 74 |
| $SrNdNiO_4$ | mp-1217981 | 31 |
| $Ba_3NiO_4$ | mp-27957 | 76 |
| $YBa_2Ni_3O_8$ | mvc-1132 | 76 |
| – | – | – |
| Palladate | (*n* = 28) | |
| $Ba_2Pd_2O_5$ | mp-984976 | 26 |
| $BaY_2PdO_5$ | mp-9656 | 29 |
| $BaLn_2PdO_5$ | – | – |
| (Ln = Ho, | mp-9785, | 38 |
| Tb, | mp-9760, | 28 |
| Tm, | mp-1187634, | 25 |
| Nd) | mp-8514 | 23 |
| – | – | – |
| Ruthenium-Oxide | (*n* = 158) | |
| $Ba_2RuO_4$ | mp-1025337 | 31 |
| $Sr_2Y_{1.5}Ce_{0.5}RuCu_2O_{10}$ | mp-1218787 | 38 |
| $Sr_2CeYRuCu_2O_{10}$ | mp-1218854 | 32 |
| $Sr_2EuCeRuCu_2O_{10}$ | mp-1218883 | 31 |
| $Sr_2La_2RuCuO_8$ | mp-1218695 | 30 |
| $Ba_2PRuO_$ | mp-12729 | 30-72 |

JOHNS HOPKINS APPLIED PHYSICS LABORATORY

TMS 2022 @ Anaheim, CA 02/28/2022

# Closed-loop Discovery of the Composition-structure-properties Relationships of Superconductors



February 28, 2022

PI: Christopher Stiles

MITHRIL

APL Team: Nam Q. Le, Alexander New, Janna Domenico, Eddie Gienger, Christine Piatko, Ian McCue, Kyle P. McElroy, Justin D. Rokisky, Ivelisse M. Cabrera, Tim J. Montalbano, Daniel J. Rose Jr., Mike Pekala, Christopher R. Ratto, Andrew Lennon, Christine Chung, Nina M. Borodin, William A. Paul, Morgana M. Trexler, I-Jeng Wang, Leslie Hamilton

JOHNS HOPKINS UNIVERSITY

In collaboration with the McQueen Group:
Tyrel M. McQueen, Lisa Pogue, Izze Hedrick, Gregory Bassen, Brandon Wilfong

Materials Science — Interdisciplinary (Bilingual) — Machine Learning

# Findings

Rou

Round 2: Rediscovered Superconductor &


Curated Experimental Data and Computations

1

SuperCon

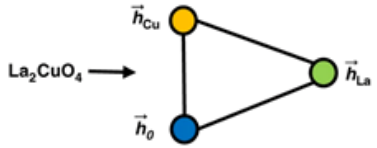
...

| | |
|---|---|
| $Nb_3Sn$ | 18.3 K |
| NbPt | -------- |
| $YBa_2Cu_3O_7$ | 93 K |

...

2

Representation Transform/Mapping (Roost)




Known/Predicted Materials Databases OQMD

3 Training

ML Model

Predicting

4 Predictions

...

$NaFeAs$

$CuRh_2S_4$

$SrFe_2As_2$

$HfNCl$

...

5 Synthesizability Estimation

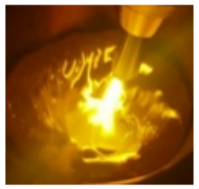
The Materials Project

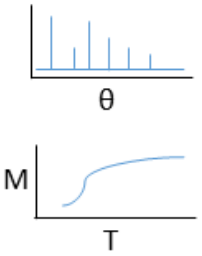
Expert Guidance

6 Materials Downselection

Stable enough?
Nearby phases?
Likely Wrong?
Least Certain?
...

7 Synthesize






Measure

Discoveries

...

NaFeAs

$CsFe_2Se_3$

"$ZrNiIn_4$"

...

Machine/Computational

Human/Experimental

=4.7 K

Round
Superco

[1]CNRS, UMI

(Received 9 June 2017; published 27 July 2017)



npj Computational Materials (2023)

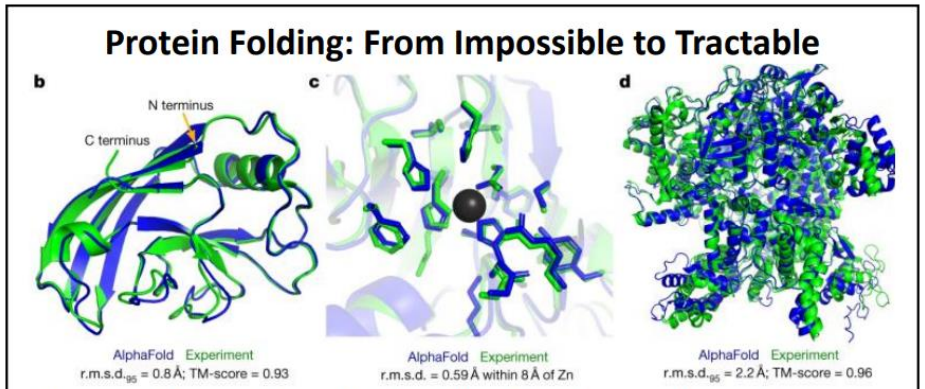
# Some Open Challenges

"AI/ML methods and data science are not black magic, nor are they a panacea."

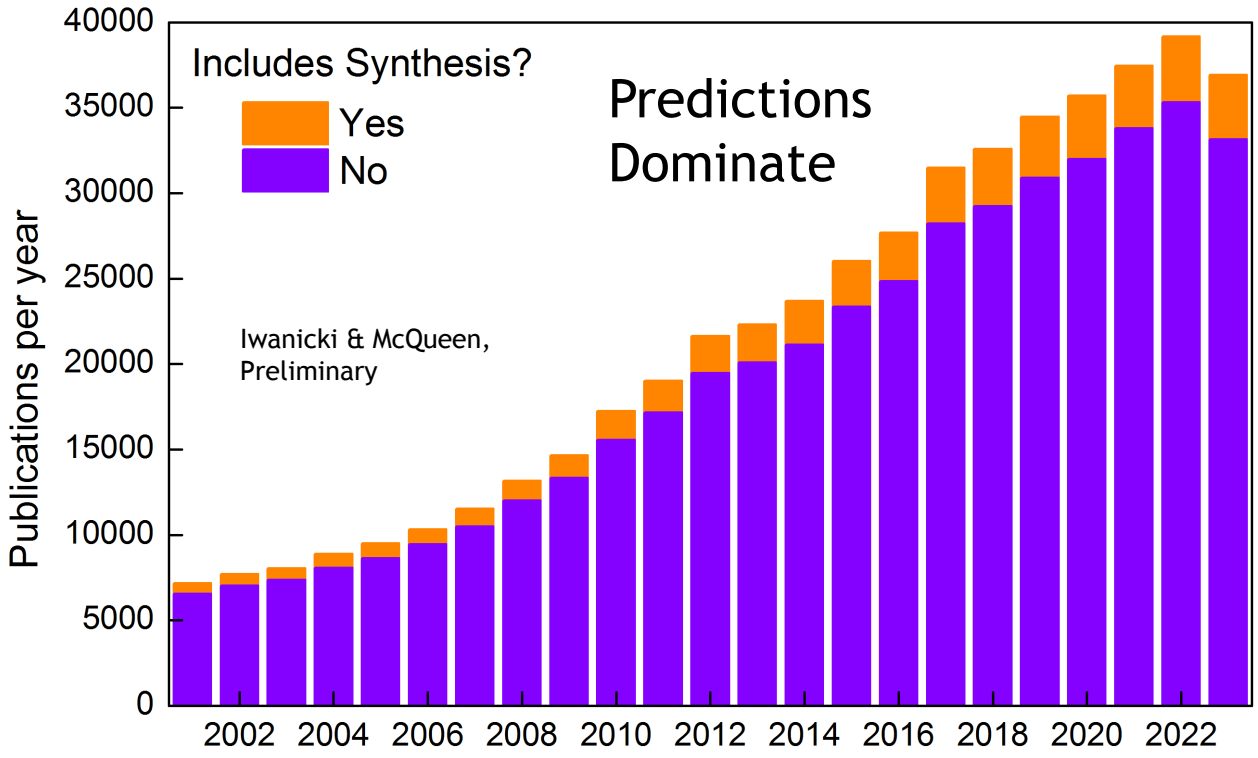
"AI/ML methods have not, to date, moved the needle in actually preparing predicted materials, leading to unbounded growth in imaginary materials that do not exist in reality."

# Opinions

- What can we, as a community, do to encourage *unbiased/impartial* assessments of results, predictive techniques, etc.?
- How do we address the divergence of # of predictions and # of realizations?




The problem of predicting the structure of a protein from its sequence was a 50 year grand challenge [31]. After years of slow but steady improvements, the field was transformed from 2018 to 2022 with the introduction of AlphaFold, a structure prediction approach combining AI/ML techniques with domain specific knowledge and a large corpus of experimentally determined protein structures. It has demonstrated




**How do we automate while retaining discovery (unexpected observations)?**

# An Accelerated, Data-Driven, Materials Discovery Future

Challenges and opportunities in two dimensional, interfacial, and layered materials to advance science and engineering and impact society

Synthesis of two community forums in January and March 2022.

Four interlocking areas:

- Predict outcomes of actual synthesis conditions
- Achieve AI-assisted and autonomous synthesis
- Develop the data materials science workforce
- Enable data curation and community use

Suggests future activities including:

- Competitive, critical evaluation of phase diagram predictive tools
- Community embrace of citable data released alongside publications

…



https://www.materialsarchive.org/2dilm