Aalto University
School of Chemical
Engineering

Functional Inorganic Materials
Lecture 2:
Computational Materials Design

Fall 2022

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Lecture Exercise 2 is a MyCourses Quiz

Contents

- Short introduction to atomic-level materials modelling and computational materials design
  - Density Functional Theory (DFT)
- Materials discovery and design by high-throughput screening
  - Crystal structure databases
  - Computational databases
- Crystal structure prediction
  - Evolutionary algorithms
- Practical examples of computational materials design coming in the lectures related to thermal conductivity and thermoelectricity

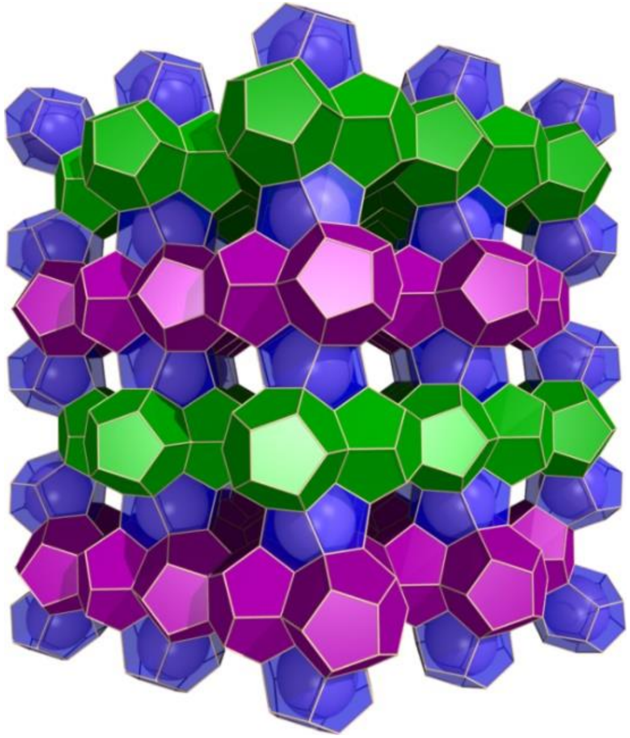
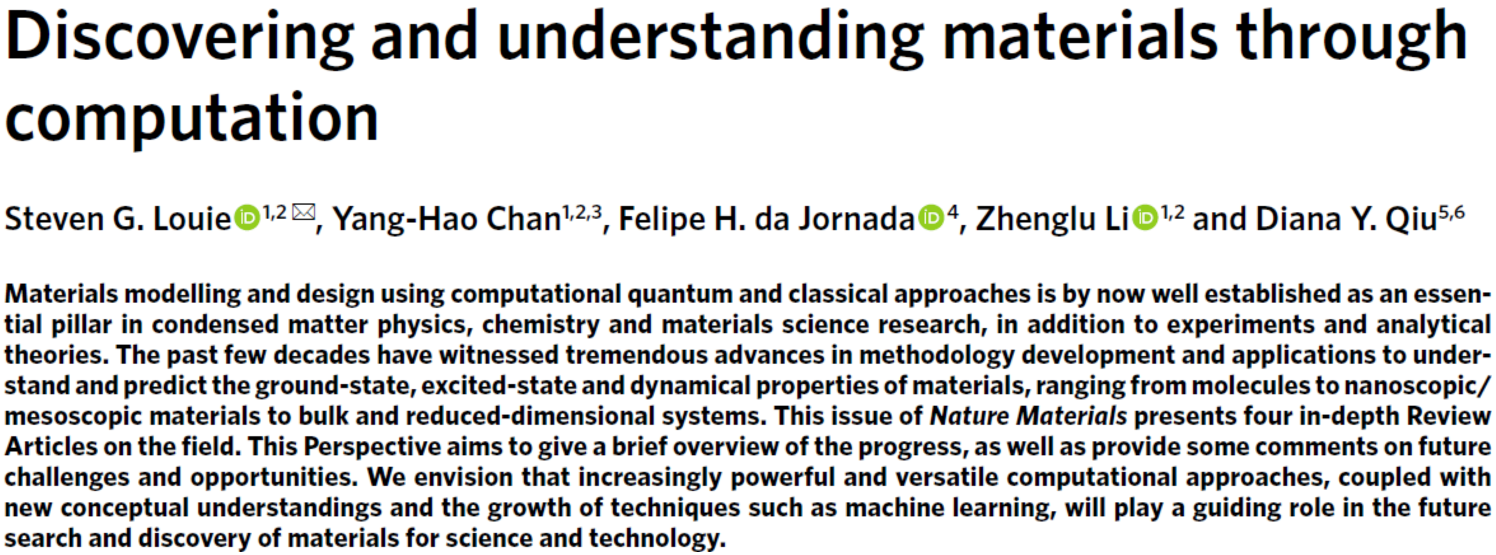


Figure: AJK

Recent literature overviews

Nature Materials **2021**, *20*, 728–735. https://doi.org/10.1038/s41563-021-01015-1

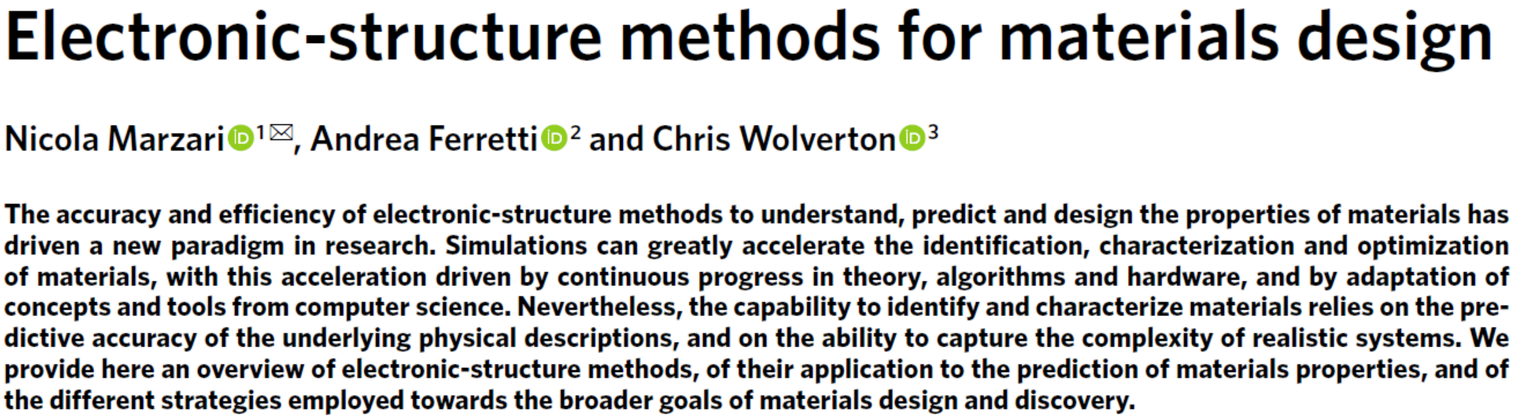


Discovering and understanding materials through computation

Steven G. Louie[1,2] ✉, Yang-Hao Chan[1,2,3], Felipe H. da Jornada[4], Zhenglu Li[1,2] and Diana Y. Qiu[5,6]

Materials modelling and design using computational quantum and classical approaches is by now well established as an essential pillar in condensed matter physics, chemistry and materials science research, in addition to experiments and analytical theories. The past few decades have witnessed tremendous advances in methodology development and applications to understand and predict the ground-state, excited-state and dynamical properties of materials, ranging from molecules to nanoscopic/mesoscopic materials to bulk and reduced-dimensional systems. This issue of *Nature Materials* presents four in-depth Review Articles on the field. This Perspective aims to give a brief overview of the progress, as well as provide some comments on future challenges and opportunities. We envision that increasingly powerful and versatile computational approaches, coupled with new conceptual understandings and the growth of techniques such as machine learning, will play a guiding role in the future search and discovery of materials for science and technology.

Nature Materials **2021**, *20*, 736–749. https://doi.org/10.1038/s41563-021-01013-3



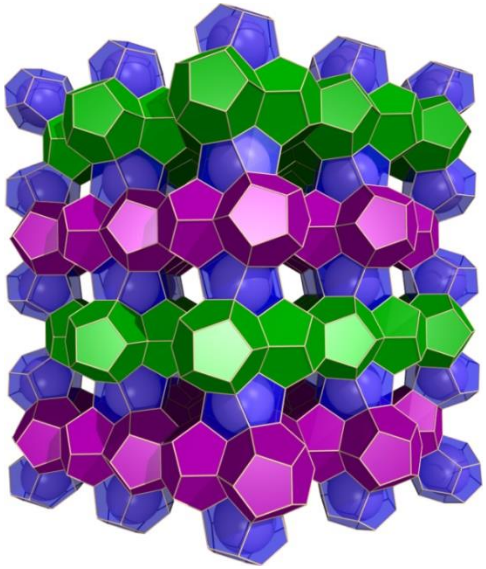
Electronic-structure methods for materials design

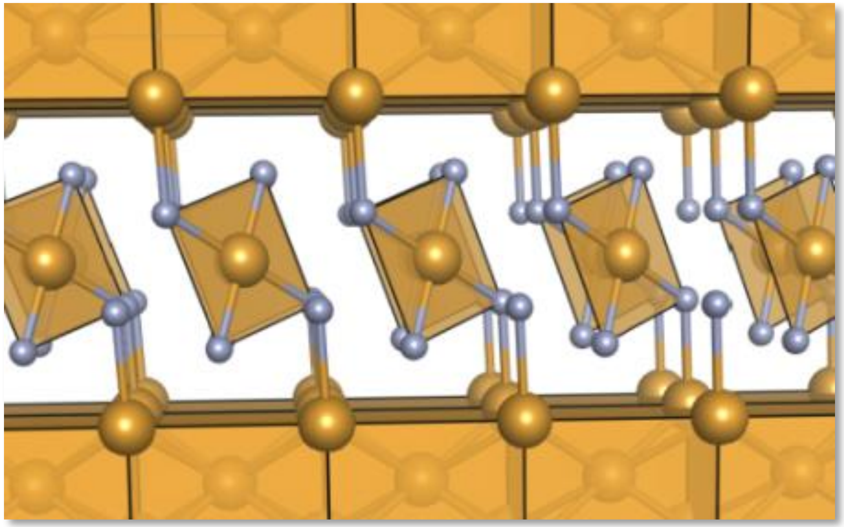
Nicola Marzari[1] ✉, Andrea Ferretti[2] and Chris Wolverton[3]

The accuracy and efficiency of electronic-structure methods to understand, predict and design the properties of materials has driven a new paradigm in research. Simulations can greatly accelerate the identification, characterization and optimization of materials, with this acceleration driven by continuous progress in theory, algorithms and hardware, and by adaptation of concepts and tools from computer science. Nevertheless, the capability to identify and characterize materials relies on the predictive accuracy of the underlying physical descriptions, and on the ability to capture the complexity of realistic systems. We provide here an overview of electronic-structure methods, of their application to the prediction of materials properties, and of the different strategies employed towards the broader goals of materials design and discovery.

Goals of atomic-level materials modelling

- **Goal 1**: Explain experimentally observed properties of molecules and materials
- **Goal 2**: Predict the structures and properties of new molecules and materials
  - Reduce the amount of experimental work and provide new ideas for experimental work
- The predictive power of the modern materials modelling techniques enables **computational materials design**
  - Most effective in close collaboration with experimental work

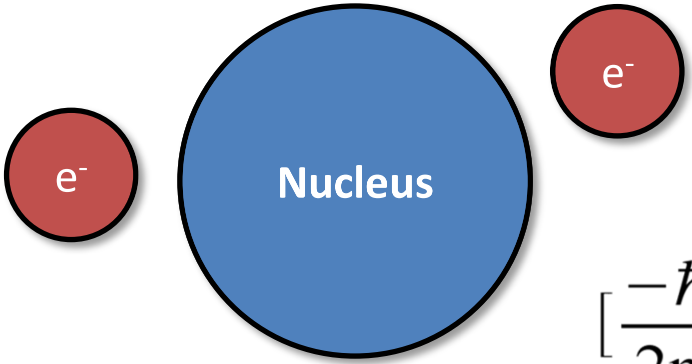




Quantum chemical methods

- In principle, quantum mechanics provides the mathematical machinery to describe all chemical phenomena exactly.
- We can study chemical systems at the level of individual electrons. However, in practice, exact solutions are not feasible.
- We need approximate methods and computational power.
- Understanding the limitations of the approximations is a crucial skill for any computational chemist.

$$F_e = \frac{k q_1 q_2}{r^2}$$



$$\left[\frac{-\hbar^2}{2m}\nabla^2 + V\right]\Psi = i\hbar\frac{\partial}{\partial t}\Psi$$

Density Functional Theory (DFT)

- Computational methodology based on **quantum chemistry**.
- Most used quantum chemical approach already for over 20 years.
  - Nowadays it is more and more common to have DFT calculations as part of experimental papers
- **No system-dependent parametrization** required (*ab initio* / first principles).
- For the purposes of this lecture, we can consider DFT as a black box:

Atomic-level structure (unit cell and coordinates)

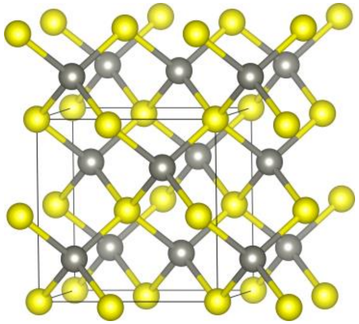
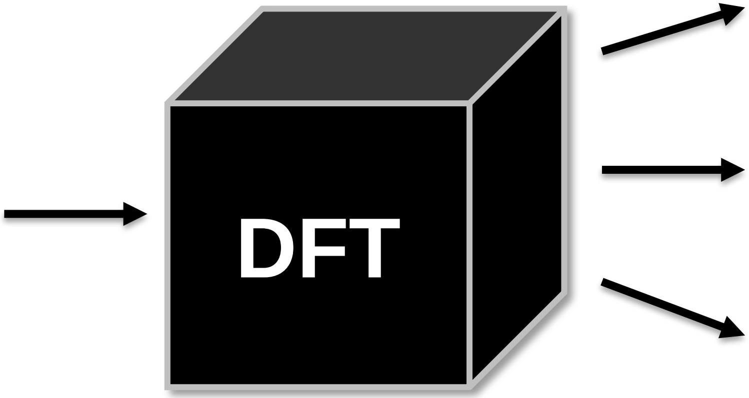


Figure: AJK



Total energy of the system

Optimized geometry

Properties (for example, spectra, thermal conductivity, …)

A structure model of the material is always needed to predict its properties

Examples of material properties that can be predicted with DFT

Electronic structure

Electronic band structure

Electronic density of states

Magnetic ground states and magnetic ordering

Thermal properties

Enthalpy and entropy

Gibbs Free Energy

Heat capacity

Thermal expansion

Spectroscopic

Infrared, Raman, inelastic neutron scattering

Solid-state NMR

UV-Vis

X-R *e.g.*
X)

Lecture 12

Mössbauer

Dielectric

Dielectric constant

Refractive index

Polarizability

Second-harmonic generation

Spontaneous polarization (ferroelectricity)

Physical properties

Elastic moduli

Piezoelectric moduli

Pyroelectric moduli

Photoelastic moduli

Lectures 9 and 10

Transport

Electronic transport (conductivity, thermopower)

Phonon transport (thermal conductivity)

Thermoelectric properties

Lectures 7 and 8

Structure-property correlations

If you want to understand function, study structure

– Francis Crick

- Ideally, structure-property correlations can be discovered by a brute-force approach:
  - Take a large set of crystal structures (10^2–10^5 crystal structures)
  - Predict the target property for all of them
  - Derive structure-property correlations from data (*e.g.* certain valence electron count or bonding situation leads in desired electronic properties)
  - Based on the correlation, predict new material compositions for experiments

- How to obtain that large set of crystal structures?
  1. Take a known crystal structure and vary the elemental composition (the next slide has an example for the perovskite structure ABO_3)
  2. Screen known crystal structures from crystal structure databases
  3. Crystal structure prediction

Screening hypothetical perovskites

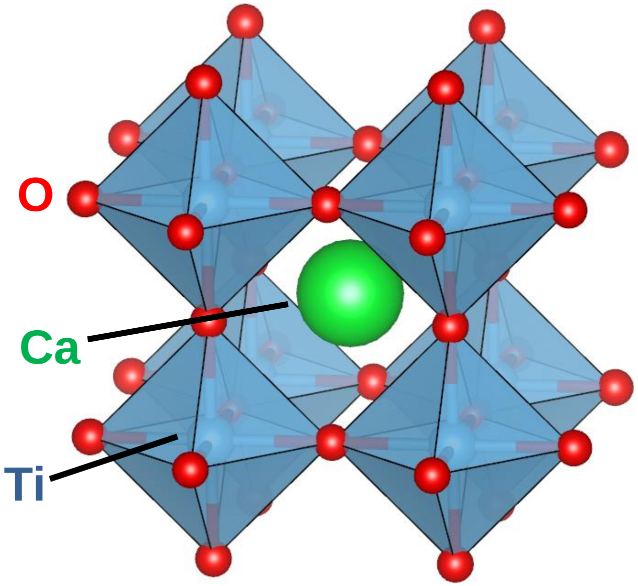
The geometric blueprint of perovskites

Marina R. Filip[a,1] and Feliciano Giustino[a,b,1,2]

PNAS, **2018**, *115*, 5397-5402, https://doi.org/10.1073/pnas.1719179115

- Approximately 2,000 perovskites are currently known.
- How many perovskites are left to discover?
- By subsituting ions with known ionic radii into the perovskite crystal structure, the authors count 3,658,527 hypothetical compounds
- They revisit the century-old model proposed by Goldschmidt to predict the formability of perovskites
- They demonstrate that the nonrattling rule postulated by Goldschmidt can predict the stability of perovskites with a success rate of 80%.
- Using this approach, they predict the existence of **90,000** so far unknown perovskites.

Figure: AJK



Perovskite $CaTiO_3$ (*Pm*-3*m*)
Generally ABO_3

Materials discovery and design by high-throughput screening

Crystal structure databases

- ICSD (Inorganic Crystal Structure Database)
  - Crystal structures of inorganic compounds (No C-C **and** C-H bonds)
  - Over 260 000 structures (2022-09-07)
  - http://libproxy.aalto.fi/login?url=https://icsd.fiz-karlsruhe.de/

- COD (Crystallography Open Database)
  - Inorganic, organic, metal-organic compounds, and minerals
  - Excludes biopolymers, which are covered by RCSB PDB (Protein Data Bank)
  - Over 490 000 structures (2022-09-07)
  - ***Open access*** database, available at http://www.crystallography.net/

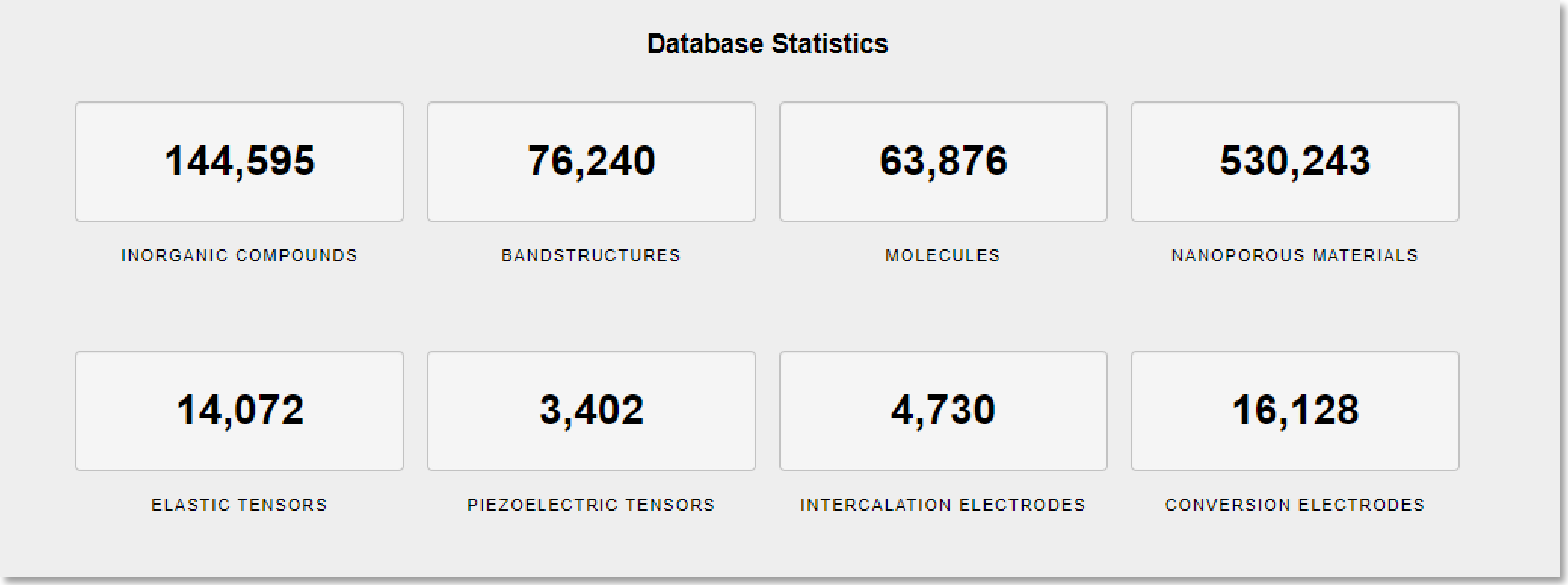
- CSD (Cambridge Structural Database)
  - Small-molecule organic and metal-organic crystal structures
  - Over 1 212 000 structures (2022-09-07)
  - https://www.ccdc.cam.ac.uk/structures/ (only from campus or with Aalto VPN)

High-throughput screening of experimental databases

- There are several large-scale research consortia that have created “high-throughput screening” methodology for carrying out DFT calculations on the experimentally known crystal structures
  - Their results are publicly available in the Internet as searchable databases
- Not a trivial effort due to several reasons:
  - **Supercomputers** are needed for DFT calculations on 10^5 crystal structures
  - Everything must be carefully **automated** (too much work for humans)
  - Crystal structure data is not always perfect (**disorder, vacancies**), so many crystal structures cannot be used as such
  - Materials can have **magnetic order**, which is not included in the crystal structure data
  - **WARNING:** while DFT generally performs well, not all data in the computational databases is 100% correct!
- Let’s study **Materials Project**, a computational materials database as an example
  - Another similar databased is AFLOW: http://aflowlib.org/

Materials Project (1)

- https://materialsproject.org
- Electronic structure and various physical properties for each material
- Includes both experimentally known (ICSD) and hypothetical materials
- Free to use, but search requires sign-in
  - Also possible to access materials directly via Google (see the next slide)



Database Statistics

144,595	**76,240**	**63,876**	**530,243**
INORGANIC COMPOUNDS	BANDSTRUCTURES	MOLECULES	NANOPOROUS MATERIALS
14,072	**3,402**	**4,730**	**16,128**
ELASTIC TENSORS	PIEZOELECTRIC TENSORS	INTERCALATION ELECTRODES	CONVERSION ELECTRODES

Materials Project (2)

- The easiest way to access a single material is to google it:
  - Google: *materials project ZnO*
- For example: ZnO ($P6_3mc$): https://materialsproject.org/materials/mp-2133/
  - Look at crystal structure, band structure (band gap underestimated by DFT!), vibrations (phonons)

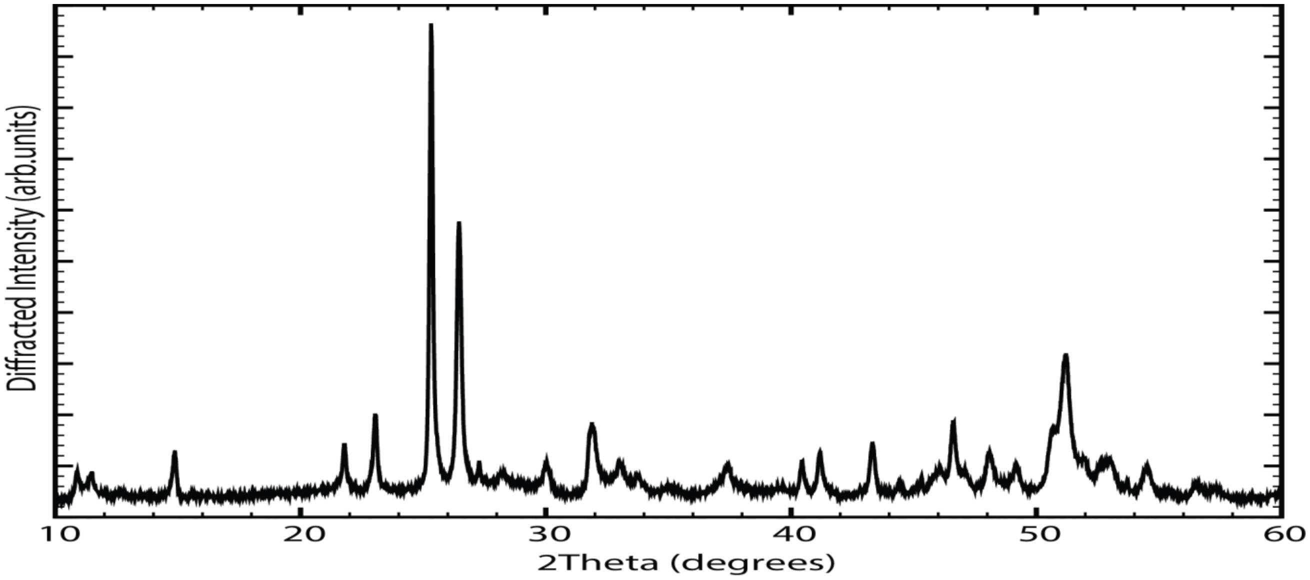
- Example 2: Search by composition V and Pt only (requires login)
  - https://materialsproject.org/materials
  - Go to VPt_8 ($I4/mmm$) https://materialsproject.org/materials/mp-1079997/
  - Study *Thermodynamic Stability* (Phase diagram at 0 K)

- Example 3: Synthesis explorer (requires login)
  - https://materialsproject.org/synthesis
  - Search for example for $SrTiO_3$
  - The search will return synthesis recipes extracted from literature.

Crystal Structure Prediction

Reasons to use crystal structure prediction

1. Crystal structure of a material is unknown and single crystals are not available for X-ray diffraction (XRD)
2. Powder XRD not solvable without initial structure model
3. XRD dataset not complete enough (often the case for thin films)
4. Impossible to obtain experimental XRD data (e.g. geochemistry)
5. Predicting the structure and existence of a material before synthesis



Crystal structure prediction methods (1)

One of the continuing scandals in the physical sciences is that it remains in general impossible to predict the structure of even the simplest crystalline solids from a knowledge of their chemical composition

– Sir John Maddox (*Nature* **1988**, *335*, 201)

- Given a chemical composition such as $SrTiO_3$, what is the thermodynamically most stable crystal structure?
- This is a global optimization problem
- Quantum chemical methods can very robustly find local minima, but the global optimization of a crystal structure is a daunting problem

Crystal structure prediction methods (2)

- Potential energy surfaces of materials are complex and multidimensional
- Finding the global energy minimum is not feasible by brute-force methods
- As an example, take a cubic unit cell with volume *V* and *N* identical atoms.
  - Assume that the atoms may occupy discrete positions with resolution δ = 1 Å.
  - The number of distinct crystal structures (*C*) becomes:

$$C = \frac{1}{(V/\delta^3)} \frac{(V/\delta^3)!}{[(V/\delta^3)-N]!\,N!}$$

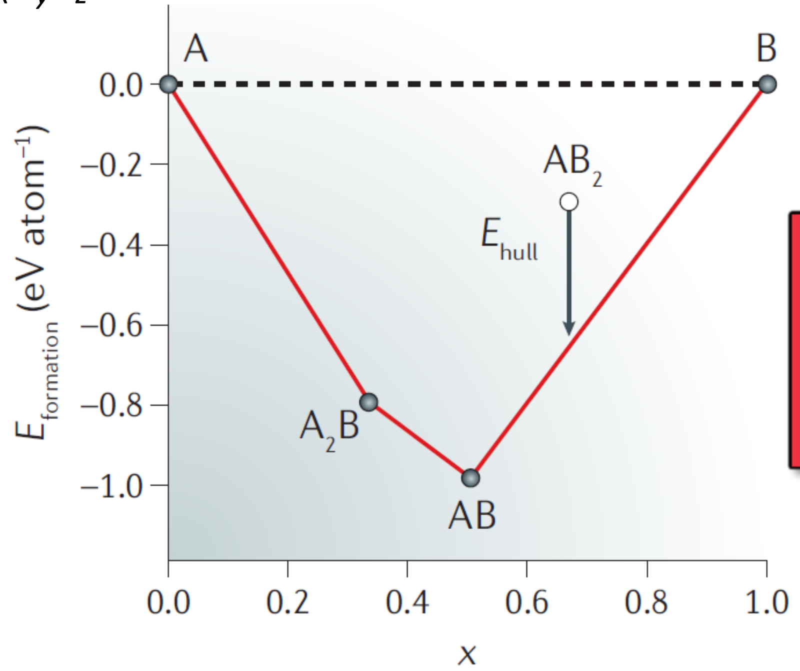
  - Already for $N \approx$ 10-20 atoms, the number of distinct structures *C* would be ~10^N

Simple projection of a complex potential energy surface

A. R. Oganov, C. W. Glass, *J. Chem. Phys.* **2006**, *124*, 244704.
A. R. Oganov, A. O. Lyakhov, M. Valle *Acc. Chem. Res.* **2011**, *44*, 227.

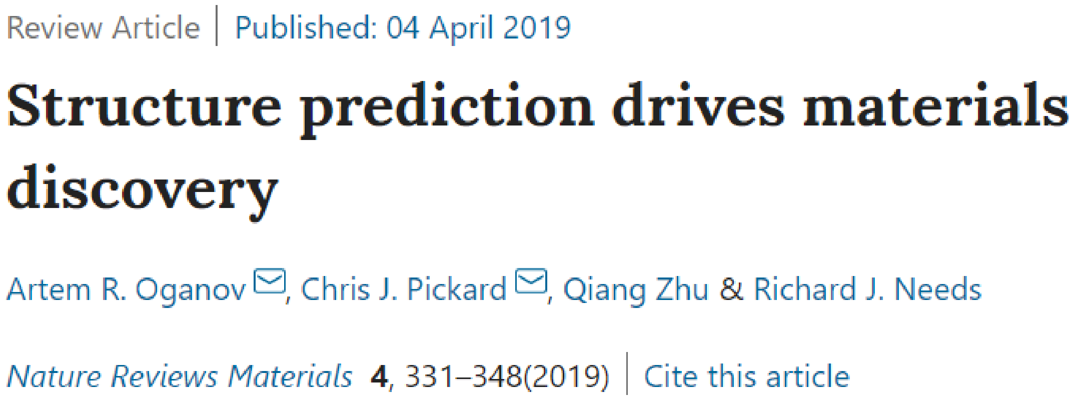
Crystal structure prediction methods (3)

- Start from known structure types (+ ”chemical intuition”)
- Screen all known structure types (database mining)
- The above strategies are limited to known structure types
- Discovering new materials requires an exploration of all possible stoichiometries for a given chemical system
  (AB, AB_x, A_xB_y, $A_xB_yC_z$…)



Convex hull plot for binary compound A_xB_y

Crystal structure prediction methods (4)



Review Article | Published: 04 April 2019

Structure prediction drives materials discovery

Artem R. Oganov ✉, Chris J. Pickard ✉, Qiang Zhu & Richard J. Needs

Nature Reviews Materials **4**, 331–348(2019) | Cite this article

- Examples of crystal structure prediction methods used nowadays:
  - Simulated annealing
  - Basin hopping
  - Minima hopping
  - Particle swarm optimization
  - Genetic and evolutionary algorithms

Codes for crystal structure prediction

- There is a large number of codes for crystal structure prediction, both for inorganic and organic materials.
- Some of them are freely available, some not.
  - AIRSS (inorganic)
  - CALYPSO (inorganic)
  - CrySPY (inorganic)
  - DMaCRYS (organic)
  - GASP (inorganic)
  - Gator (organic)
  - GraCe (organic)
  - MAISE (inorganic)
  - Molpak (organic)
  - uPack (organic)
  - USPEX (inorganic and organic)
  - Xtalopt (inorganic)

In addition, local optimizations need to be carried out within the crystal structure prediction algorithm (global optimization). Most common approach: DFT or so-called parametrized force fields.

Evolutionary crystal structure prediction with USPEX

USPEX Computational
Materials
Discovery

USPEX: Universal Structure Predictor: Evolutionary Xtallography

USPEX Computational
Materials
Discovery

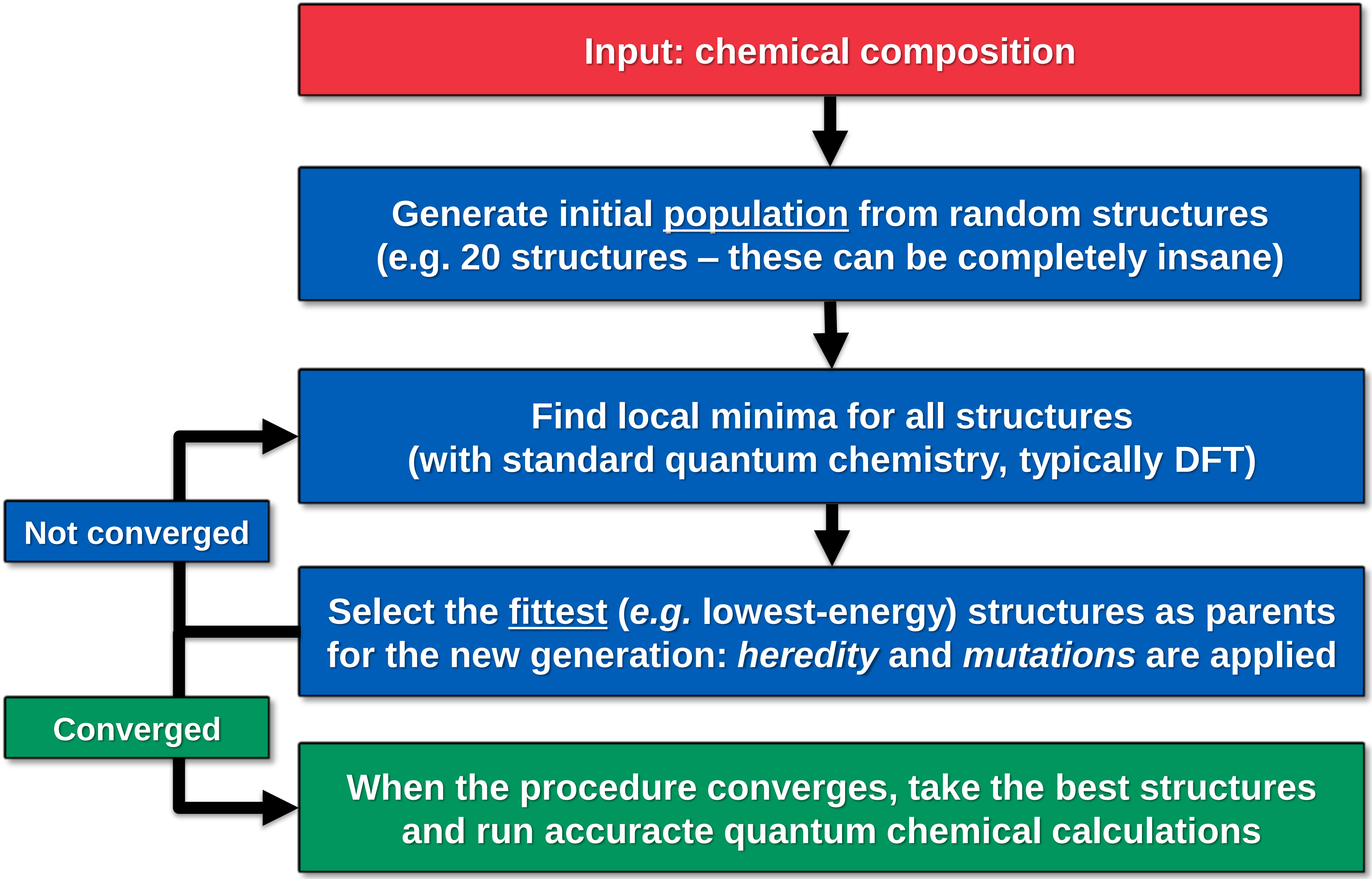
https://uspex-team.org/

1. Oganov, A. R.; Glass, G. W., Crystal structure prediction using ab initio evolutionary techniques: Principles and applications, *J. Chem. Phys.* **2006**, *124*, 244704.
2. Glass, C. W.; Oganov, A. R.; Hansen, N., USPEX – Evolutionary crystal structure prediction, *Comp. Phys. Commun.* **2006**, *175*, 713.
3. Oganov, A. R.; Lyakhov, A. O.; Valle, M., How Evolutionary Crystal Structure Prediction Works - and Why, *Acc. Chem. Res.* **2011**, *44*, 227.
4. Lyakhov, A. O.; Oganov, A. R.; Stokes, H. T.; Zhu, Q., New developments in evolutionary structure prediction algorithm USPEX, *Comp. Phys. Commun.* **2013**, *184*, 1172.

Genetic and evolutionary algorithms

- A key concept is the population of individuals
- Genetic algorithms (GA) typically use a binary representation for the individuals ("01001…")
- Binary representation of a crystal structure limits the search to a discretized grid within a pre-determined unit cell.
- In Evolutionary Algorithms (EA), the individuals (crystal structures) are represented with real numbers, corresponding to the lattice parameters and atomic coordinates
- This choice makes the evolutionary variation operations (heredity, mutations) more difficult to implement
- At the same time it greatly increases the efficiency of the global optimization (the search space is continuous, not discrete)

Structure prediction with USPEX



Input: chemical composition

Generate initial population from random structures
(e.g. 20 structures – these can be completely insane)

Find local minima for all structures
(with standard quantum chemistry, typically DFT)

Select the fittest (*e.g.* lowest-energy) structures as parents
for the new generation: *heredity* and *mutations* are applied

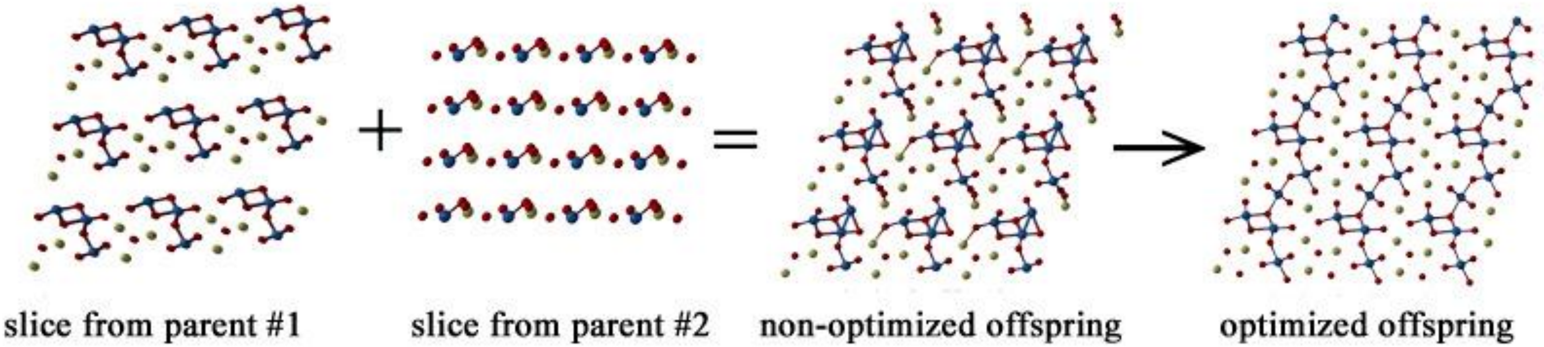
Not converged

Converged

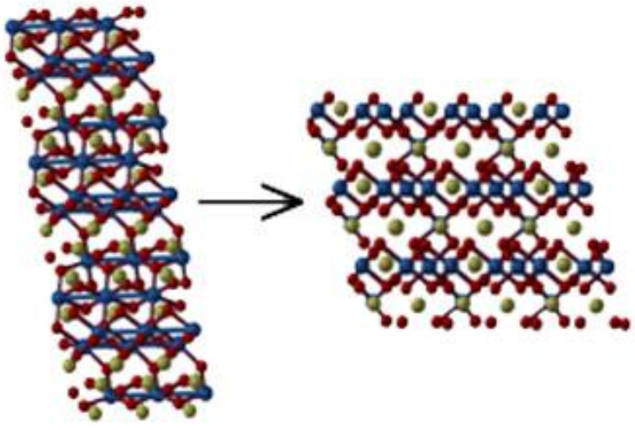
When the procedure converges, take the best structures
and run accuracte quantum chemical calculations

Variation operators in USPEX

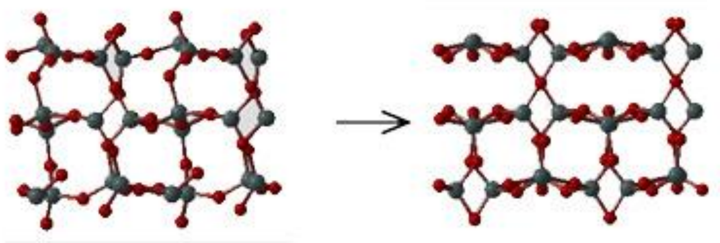
(a) heredity



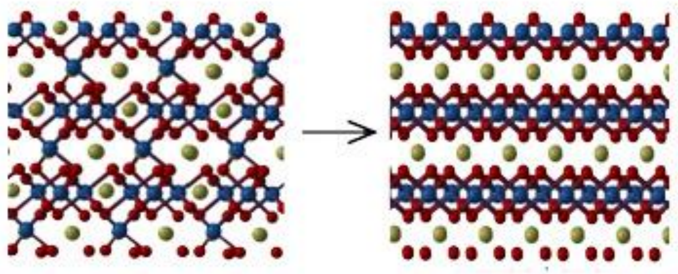
(b) lattice mutation



(c) softmode mutation

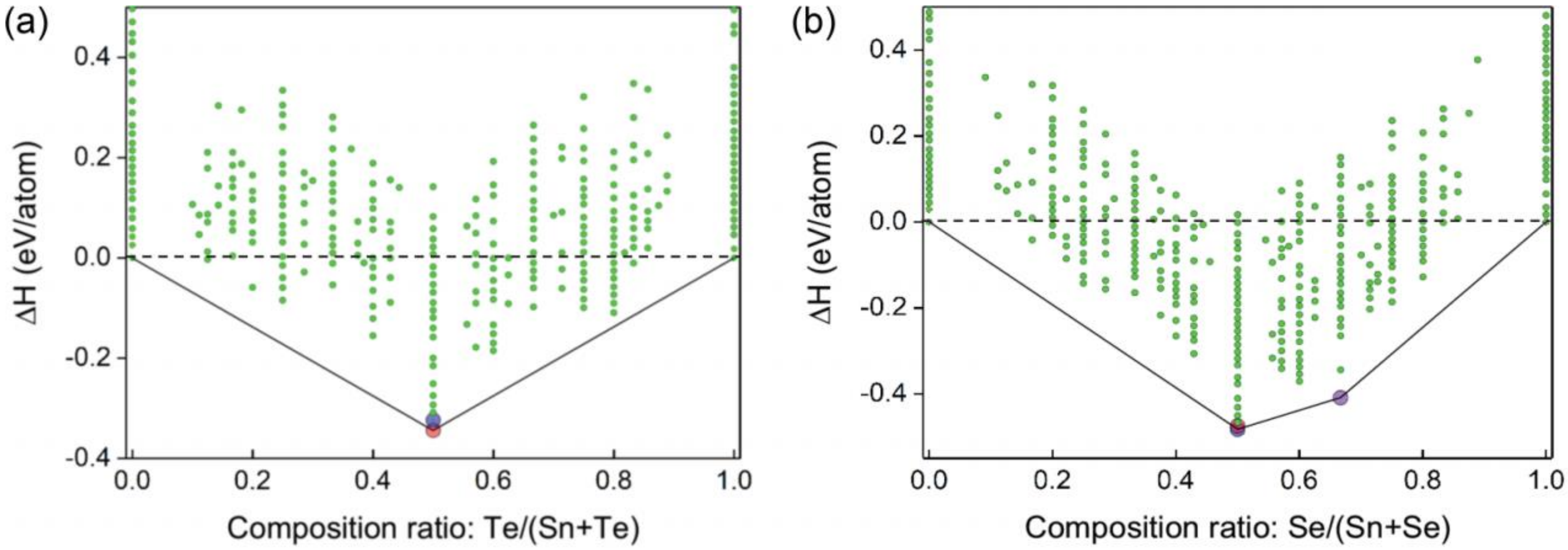


(d) permutation



USPEX in practice

- A typical USPEX run involves thousands of local optimizations
  - Can take hours, days, or even weeks depending on the level of theory and available computational resources
- Typically hundreds or thousands of crystal structures are produced
- The fittest structures typically need to be re-optimized at a higher level of theory
- Analysis of the resulting structures can be time-consuming

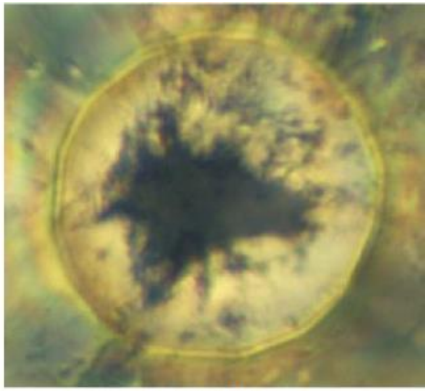


Some examples of convex hulls for tin chalcogenides

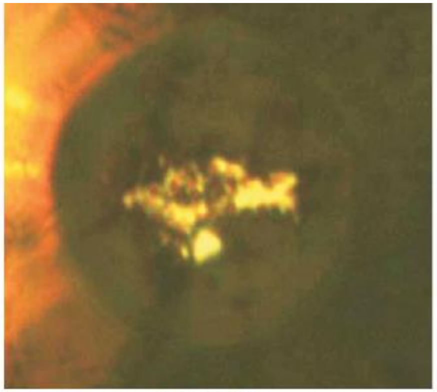
Transparent dense sodium

NATURE|Vol 458|12 March 2009 **LETTERS**

Yanming Ma[1,2], Mikhail Eremets[3], Artem R. Oganov[2,4]†, Yu Xie[1], Ivan Trojan[3], Sergey Medvedev[3], Andriy O. Lyakhov[2]†, Mario Valle[5] & Vitali Prakapenka[6]



156 GPa

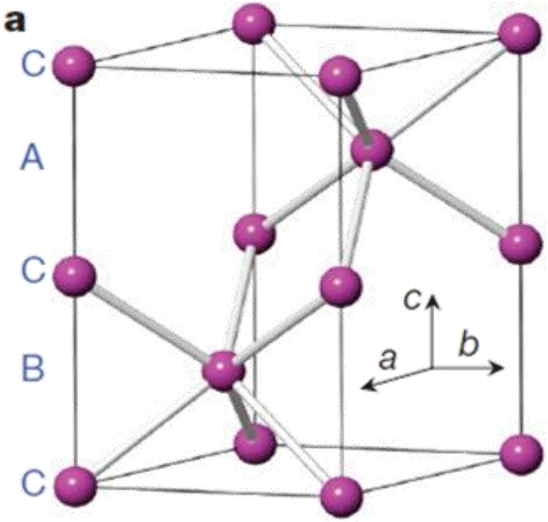


199 GPa

Na-Na distance decreases from
3.72 Å to **1.89 Å**

Na 3s valence electrons are pushed to the interstitial space

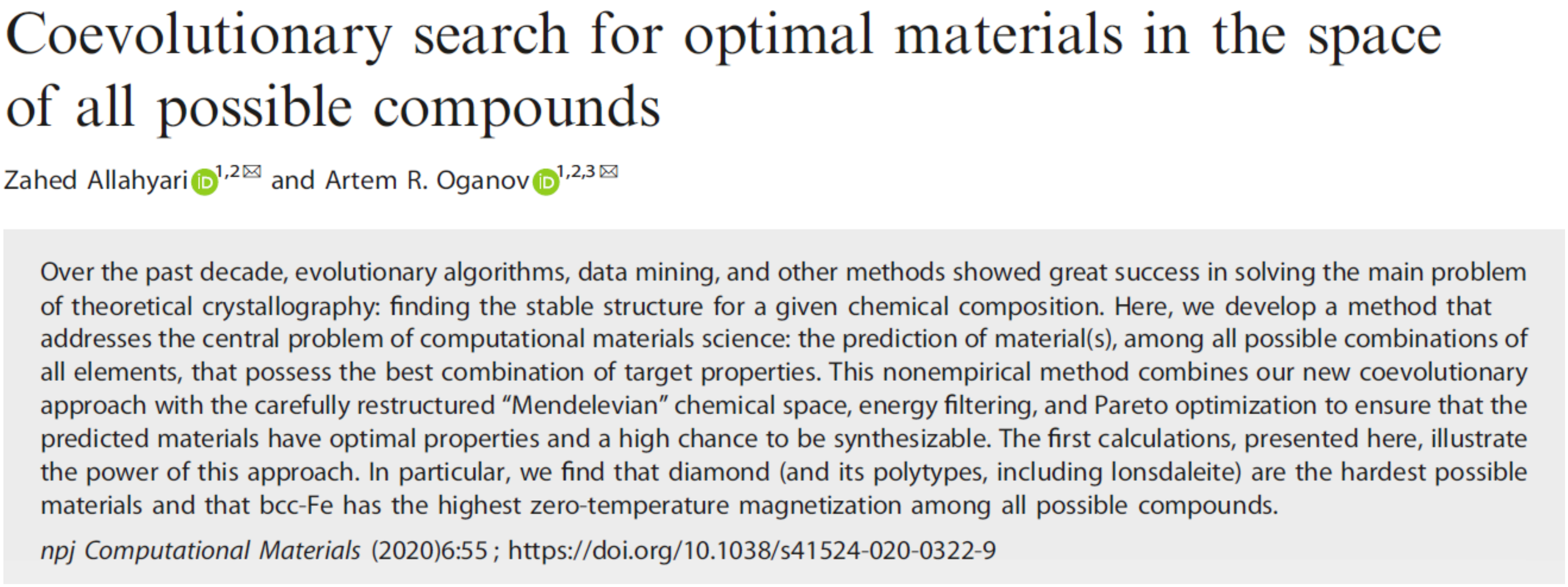
Na metal transforms to optically transparent ”self-salt” (Na^+ / interstitial e^-)



Structure of Na-*hP*4 (*P*6_3*/mmc*) predicted by USPEX

Predicting materials with optimal properties

Example: search for thermodynamically stable materials that have the highest possible **hardness**



Coevolutionary search for optimal materials in the space of all possible compounds

Zahed Allahyari[1,2] and Artem R. Oganov[1,2,3]

Over the past decade, evolutionary algorithms, data mining, and other methods showed great success in solving the main problem of theoretical crystallography: finding the stable structure for a given chemical composition. Here, we develop a method that addresses the central problem of computational materials science: the prediction of material(s), among all possible combinations of all elements, that possess the best combination of target properties. This nonempirical method combines our new coevolutionary approach with the carefully restructured “Mendelevian” chemical space, energy filtering, and Pareto optimization to ensure that the predicted materials have optimal properties and a high chance to be synthesizable. The first calculations, presented here, illustrate the power of this approach. In particular, we find that diamond (and its polytypes, including lonsdaleite) are the hardest possible materials and that bcc-Fe has the highest zero-temperature magnetization among all possible compounds.

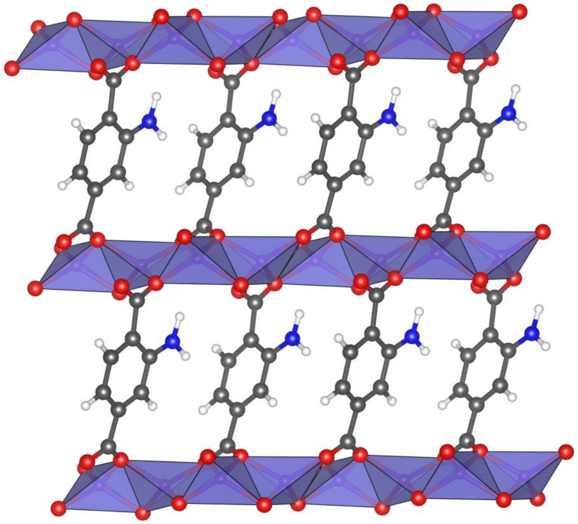
npj Computational Materials (2020)6:55 ; https://doi.org/10.1038/s41524-020-0322-9

Summary on crystal structure prediction for inorganic materials

- Crystal structure prediction is a powerful tool for
  - Complementing experimental studies, where inadequate data is available for structure solution
  - Prediction of new materials before any experiments
- Evolutionary crystal structure prediction algorithms such as USPEX are among the most powerful methods

- Crystal structure prediction is still computationally relatively expensive
- A major development direction is the global optimization of both the **structure** and **properties** at the same time
  - Hardness, optical properties, thermoelectricity, …
- Incorporating **temperature effects** and **entropic effects** in the prediction algorithms is still a major challenge

Extra slides: USPEX and inorganic-organic coordination polymers

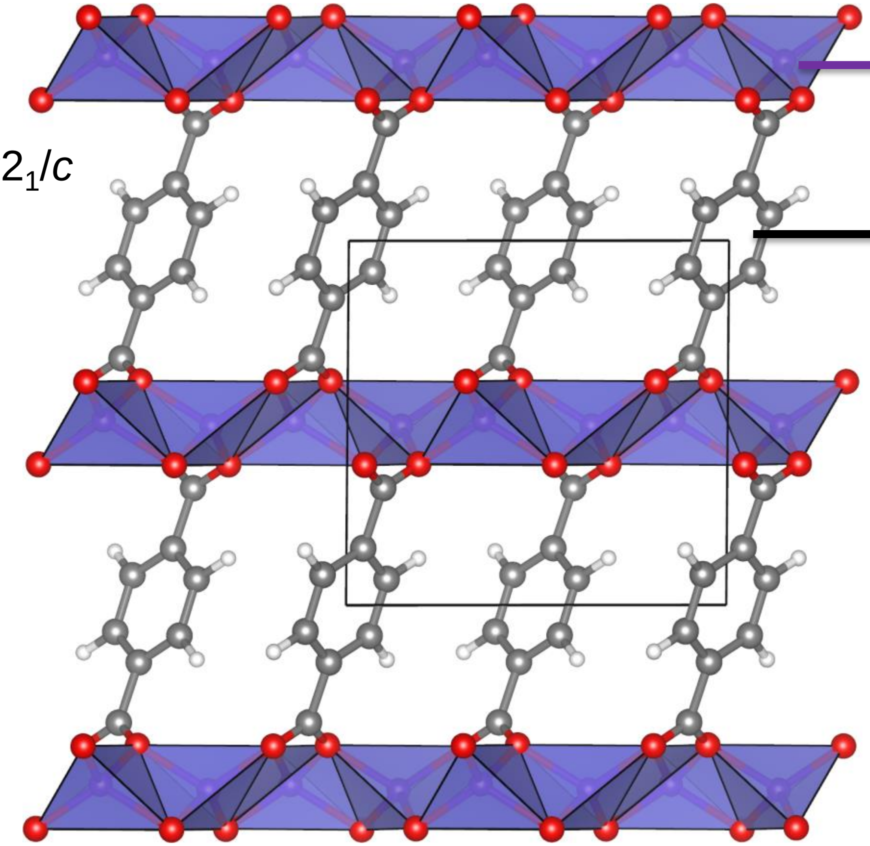


Heiska, J.; Nisula, M.; Rautama, E.-L.; Karttunen, A. J.; Karppinen, M.
Dalton. Trans. **2020**, *49*, 1591–1599.

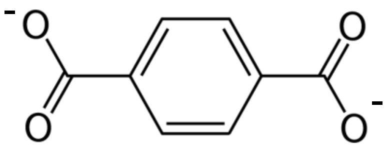
Inorganic-organic coordination polymers

(Metal centers linked by organic ligands)

Li_2TP (dilithium terephthalate)



Li^+ (four-coordinated)



Terephthalate ($C_8H_4O_4^{2-}$)

Synthetized in layer-by-layer fashion with ALD/MLD

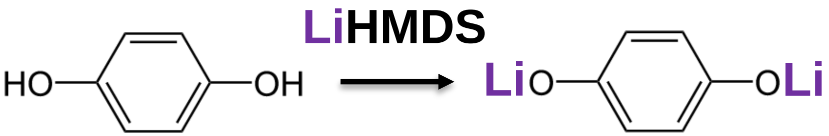
Closely related to Metal-Organic Frameworks (MOF)

Li coordination polymers are applicable as Li-ion thin-film battery materials

M. Nisula, M. Karppinen, *Nano Lett.* **2016**, *16*, 1276.

Dilithium Quinone (Li_2Q)

Hydroquinone + Li

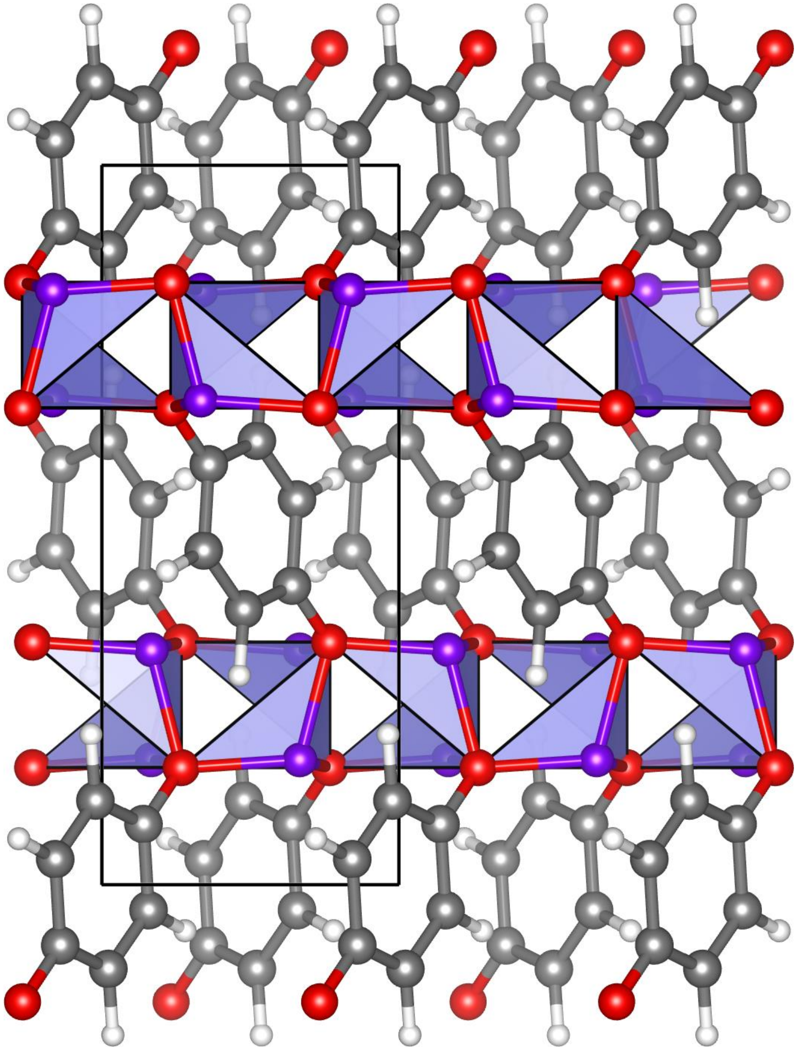


Structure of Li_2Q is not known from previous bulk studies

Structure solution with the help of quantum chemistry (DFT-PBE0)

Na_2Q is known (*$P4_2/ncm$*), but it is not a true minimum for Li_2Q

Symmetry decreases to orthorhombic subgroup *Pccn*

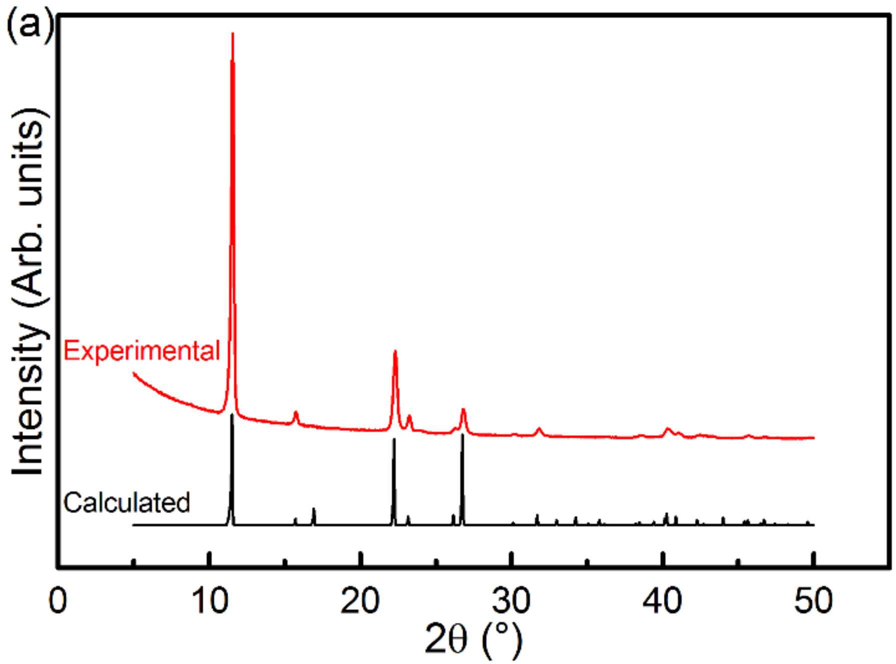


Pccn

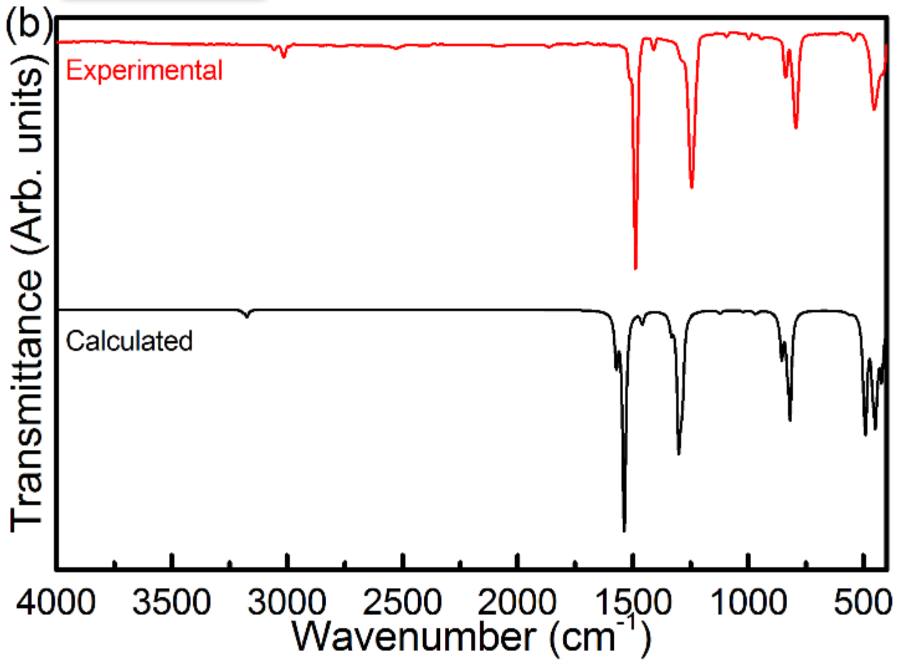
M. Nisula, J. Linnera, A. J. Karttunen, M. Karppinen, *Chem. Eur. J.* **2017**, *23*, 2988.

Li_2Q: Experiment and DFT-PBE0

XRD (1 µm thick film)



IR

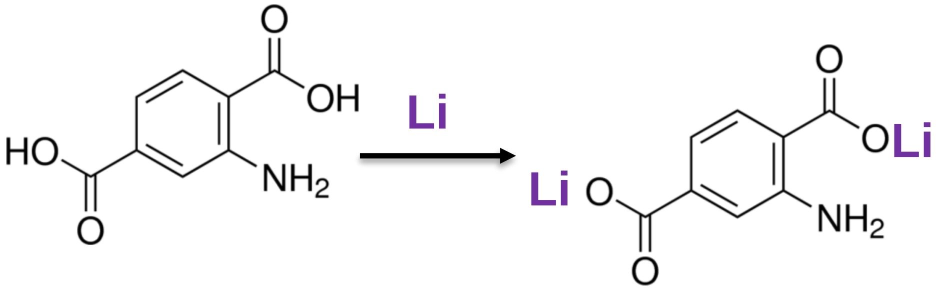


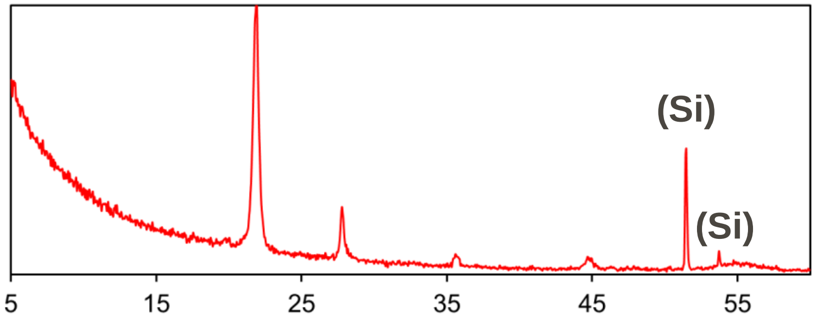
New type of coordination polymer with ALD/MLD!
Has not been synthetized as bulk material

M. Nisula, J. Linnera, A. J. Karttunen, M. Karppinen, *Chem. Eur. J.* **2017**, *23*, 2988.

Dilithium 2-aminoterephthalate ($Li_2TP\text{-}NH_2$)

2-Aminoterephthalic acid ($TPA\text{-}NH_2$) with Li → $Li_2TP\text{-}NH_2$





Grazing-incidence XRD (GIXD)

Bulk structure not known

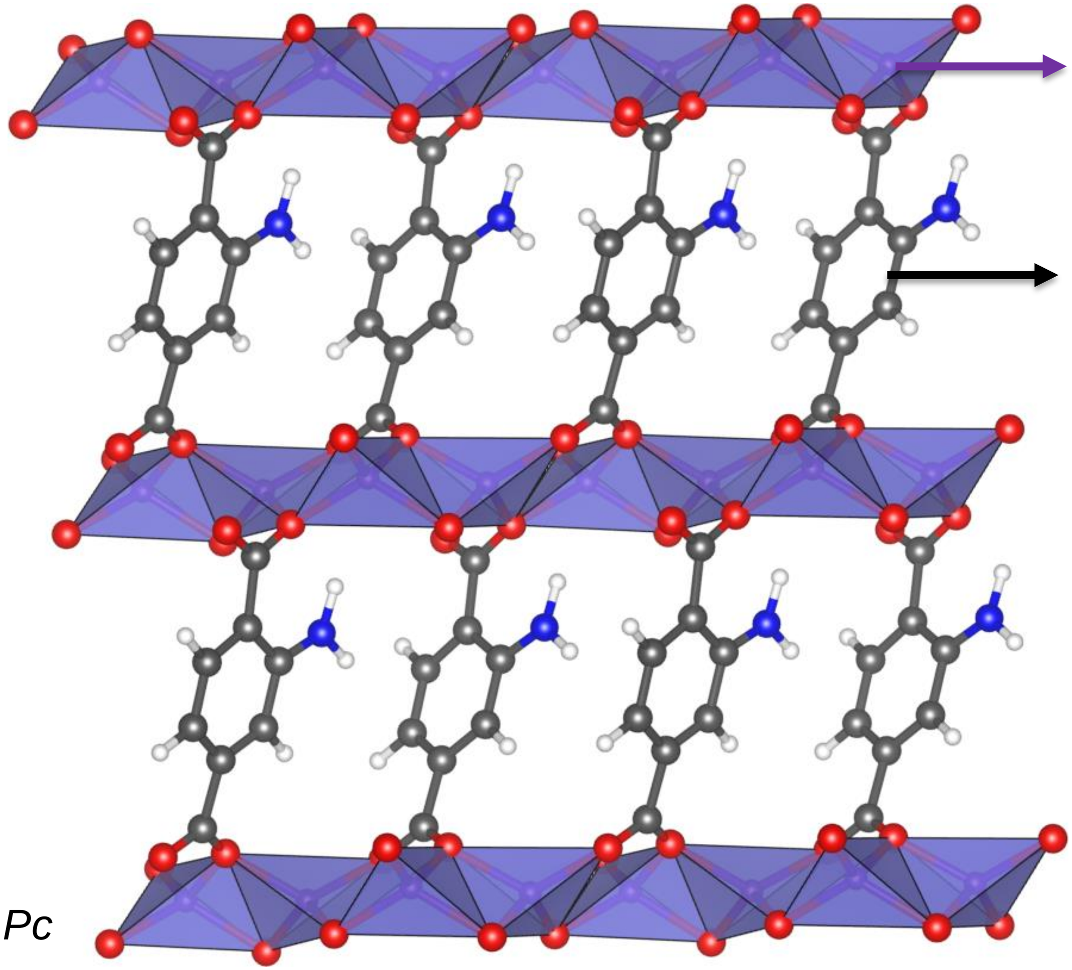
No related bulk stuctures (e.g. for Na)

Structure solution from the GIXD data is not feasible

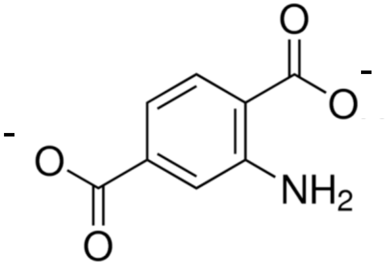
Structure prediction approach needed → USPEX

Heiska, J.; Nisula, M.; Rautama, E.-L.; Karttunen, A. J.; Karppinen, M.
Dalton. Trans. **2020**, *49*, 1591–1599.

Lowest-energy $Li_2TP\text{-}NH_2$ structure predicted by USPEX

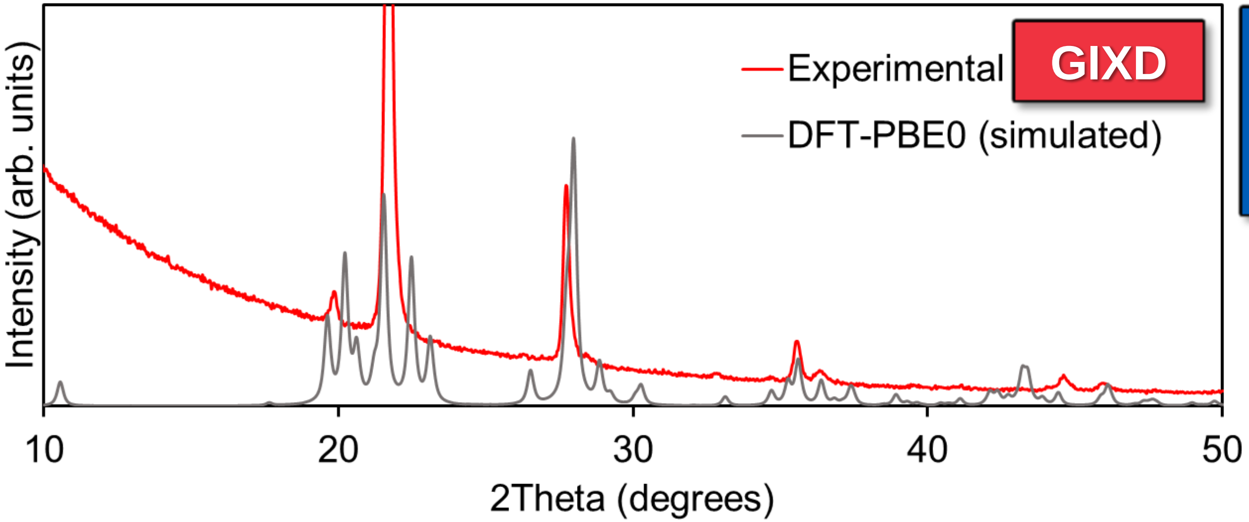

Pc

Li$^+$ (four-coordinated)



Next (closely related) structures ~5 kJ/mol higher in *E*

$Li_2TP\text{-}NH_2$: comparison with experiment



→ Reflections missing from experimental data