Predicting high pressure crystal structures in the Earth's interior with density functional theory

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Earth as a laboratory sample
• Compositionally complex
• Inhomogeneous pressure and temperature
  ⇒ Multiple phases

How did it form & evolve?
How does it work today?
• Response to thermal and mechanical forces depends on material properties at extreme conditions

Taken by the Apollo 8 astronauts as they became the first humans to circumnavigate the Moon.
Pressure and Temperature

Extreme conditions

<table>
<thead>
<tr>
<th></th>
<th>Pressure</th>
<th>Temperature</th>
<th>Earth’s core</th>
<th>Diamond-anvil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmosphere</td>
<td>$10^{-4}$ GPa</td>
<td>300 K</td>
<td>100–400 GPa</td>
<td>360 GPa</td>
</tr>
<tr>
<td>Pencil</td>
<td>0.1 GPa</td>
<td>1800 K</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- 360 GPa (approximately 180 tons x 20)

- 1 cm$^2$
Composition and Crystal Structure

Plagioclase (plg); Spinel (sp); Wadsleyite (wa); Ringwoodite (ri); Akimotoite (ak); Mg-perovskite (mgpv); Ca-perovskite (capv); Ferropericlase (fp)

What Do We Need to Know?

Crystal structure
• New phases under pressure and at high temperatures
• Equation of state
  ‣ $E(V, T) \Rightarrow \rho(p, T)$
• Transition pressures and temperatures

Elastic properties
• Earthquakes allow the measurement of longitudinal and shear wave velocities
• Discontinuity at core-mantle boundary
• Smaller discontinuities near surface

Electronic properties
• Band gap affects thermal transport
Structure Discovery

Observation in nature

• Meteor impacts
• Problems:
  ‣ Post-mortem observation
  ‣ Difficult to extract transition pressures

Laboratory experiments

• Diamond-anvil cell compression
• Shock experiments
• Problems:
  ‣ High energy barriers, metastability, experimental times
  ‣ Difficult to extract transition

Example: Stishovite

• First discovered in the lab, later found in meteor crater
Energies and properties of different crystal phases

- Method of choice: *Density-functional theory*
- Nobel prize in chemistry 1998 for Walter Kohn
- Most widely used “first principles” method for solids and molecules
- Accurate quantum mechanical description of
  - Structural energies
  - Elastic properties
- Not accurate enough for band gaps

Structure search methods

- *Random search method*

- *Evolutionary algorithms*
Density Functional Theory

Hohenberg-Kohn Theorems (1964)

The ground state energy of a quantum system is given by its electron density $\rho(r)$.

\[
\begin{align*}
V_{\text{ext}}(r) & \leftrightarrow \rho_0(r) \\
\Psi_i(r_1, \ldots r_N) & \Rightarrow \Psi_0(r_1, \ldots r_N)
\end{align*}
\]

Kohn-Sham Equations

Mapping the many-body system on a system of non-interacting electrons leads to a set of single-particle equations for the electrons moving in an effective potential with an unknown exchange-correlation functional.
Climbing “Jacob’s ladder” to heaven of chemical accuracy (Perdew et al. PRL 2003)

Comparison to experiment or quantum chemistry

Difficulties:
- Experimental energies of defects
- Quantum chemistry methods for solids

Benchmark calculations by quantum Monte Carlo
Computational Structure Predictions

Computational structure prediction based on optimization

• Stable crystal structure $\Rightarrow$ Lowest free energy
• Minimize the free energy
• Non-trivial for the following reasons:
  ‣ High-dimensional search space
  ‣ Rough free energy surface, i.e. sensitive to small changes
  ‣ Representation of structures by unit cells leads to redundancies
  ‣ Accurate \textit{ab-initio} free energy calculations are computationally expensive

• Only limited success of conventional optimization methods
  ‣ Simulated annealing
  ‣ Metadynamics
  ‣ Minima hopping

• New optimization methods:
  ‣ \textit{Random search} and \textit{evolutionary algorithms}
Random Search Method

Generate a population of random structures and relax them:
• Choose random unit cell translation vectors
• Renormalize the volume to a reasonable range of values
• Choose random atomic positions within the cell

May constrain the initial positions:
• Fix the initial positions of some of the atoms (e.g., defect)
• Insert molecules randomly (rather than atoms)
• Choose a particular space group

Relax population of random structures
• Use accurate density functional methods
• Increase accuracy during optimization
Do Be and Li form alloys? What is their electronic structure? Can they have higher superconducting temperatures than pure Be and Li?

Elemental beryllium

- Highest Debye temperature of all metallic elements: $\Theta_D = 1100$ K
- Superconducting transition temperature of only $T_c = 26$ mK
- Because Be is barely a metal

Improve $T_c$ by alloying

- BCS formula $T_c = 1.13 \cdot \theta_D \exp \left( -\frac{1}{g_0 \cdot V} \right)$
- Alloying with light elements: Light, metallic, electropositive
Structural Search Algorithm

\[ \text{Be}_4\text{Li}, \text{Be}_3\text{Li}, \text{Be}_2\text{Li}, \text{Be}_3\text{Li}_2, \text{BeLi}, \text{Be}_2\text{Li}_3, \text{BeLi}_2, \text{BeLi}_3, \text{BeLi}_4 \]

\[ p \]

\[ \text{Be}_{m}\text{Li}_n \]

\[ \text{Guess structure from chemical design} \]

\[ \text{Structural optimization} \]

\[ \min \{ H \} \]

\[ H_f < 0? \]

\[ \text{Random starting structure} \]

\[ \text{Structural optimization} \]
Computational Detail

Density functional theory
• Generalized gradient approximation (PBE)
• Plane-wave basis and PAW potentials
• Optimization of all parameters

Random structural search
• Use 20 – 50 starting structures at each selected pressure and composition
• Pressure range 0 – 200 GPa
• Symmetry identification using ISOTROPY (Stokes & Hatch, BYU)
• Check energy of higher symmetry structures
• Choice of compositions:
  Be$_{1-x}$Li$_x$  \( x = 0, 20, 25, 33, 40, 50, 60, 66, 75, 100 \% \)
Results for Enthalpy of Formation

Stability increases with pressure dramatically at low pressures
Phase Diagram of LiBe under Pressure

Stability ranges

Four novel BeLi phases become stable under pressure

BeLi₃, BeLi, Be₂Li, Be₄Li
Fermi Density of States

- Beryllium’s DOS at the Fermi level is nearly constant over entire pressure range: $g(\varepsilon_F) = 0.04 \text{ eV}^{-1}$ per valence electron

<table>
<thead>
<tr>
<th>80 GPa</th>
<th>Be$_4$Li R-3m</th>
<th>Be$_2$Li P6/mmm</th>
<th>BeLi P2$_1$/m</th>
</tr>
</thead>
<tbody>
<tr>
<td>$g(\varepsilon_F)$ in eV$^{-1}$ per valence electron</td>
<td>0.06</td>
<td>0.06</td>
<td>0.12</td>
</tr>
</tbody>
</table>

For a comparable e-ph coupling, $T_c$ would be about 32 K
Do Be and Li form alloys? What is their electronic structure? Can they have higher superconducting temperatures than pure Be and Li?

- Be and Li form intermetallic compounds under pressure.
- Possible enhancement of $T_c$ through increased DOS.
- Larger core of Li and smaller core of Be push valence electron density into 2D electron gas.
- Fascinating high-pressure chemistry of alloys from simple elements.

They used to be called the simple elements.

Evolutionary Algorithms

In evolutionary algorithms a *population* of candidate solutions is evolved over successive iterations of *random variation* and *selection*. Random variation provides the mechanism for discovering new solutions. Selection determines which solutions to maintain as a basis for further exploration.

**Evaluation function**

- Ab initio free energy

**Variation operators**

- Heredity
  - Combining a fraction of each of two structures
  - Use spatially coherent slab to retain structural motifs
- Mutation
  - Random atom displacements and lattice strains
- Permutation
  - Swap pairs of atoms

Iterate until low-energy structure is found
Evolutionary Algorithms – Applications

40-atom cell of MgSiO$_3$ post-perovskite

- Structure search using local optimization of random structures
  - Does not produce correct structure even after 120,000 steps
  - Constant energy distribution $\Rightarrow$ No “learning” during run

- Evolutionary search
  - Stable structure in fewer than 1000 steps
  - Start from similar distribution as in random search
  - Shift to lower energy as result of “learning”

Show movies: http://olivine.ethz.ch/~artem/USPEX.html
## Comparison of Search Methods

<table>
<thead>
<tr>
<th>Random search</th>
<th>Evolutionary algorithm</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Simple to program</td>
<td>• More complex rules</td>
</tr>
<tr>
<td>• Successful for small unit cells</td>
<td>• Successful for structures with large unit cells and structural motifs</td>
</tr>
<tr>
<td>• Increasingly more difficult for large structures</td>
<td></td>
</tr>
<tr>
<td>• SiH₄, LiBe, H₂O, H, N</td>
<td>• CaCO₃, MgSiO₃, CO₂, O, H</td>
</tr>
</tbody>
</table>

Locating the global minimum of a potential energy surface depends on the number of energy evaluations. “Accurate” methods such as first principles DFT are required.
Elastic Properties of Minerals

Elastic constant calculations

• Energy change due to strain of unit cell

\[
\begin{pmatrix}
    a_1' \\
    a_2' \\
    a_3'
\end{pmatrix}
= \begin{pmatrix}
    a_1 \\
    a_2 \\
    a_3
\end{pmatrix} \cdot (1 + \epsilon)
\]

\[
\epsilon = \begin{pmatrix}
    e_1 & e_6/2 & e_5/2 \\
    e_6/2 & e_2 & e_4/2 \\
    e_5/2 & e_4/2 & e_3
\end{pmatrix}
\]

\[
E(e_i) = E_0 - p(V) \cdot \Delta V + V \cdot \sum_{i=1}^{6} \sum_{j=1}^{6} C_{ij} e_i e_j/2 + O[e_i^3]
\]

• Volume conserving strains preferred

• Alternative approach: Linear response theory
Quantum Monte Carlo is a highly-accurate many-body simulation method. Large parallel computers allowed first QMC calculation of elastic constants (8,000 processors). Softening of elastic constant \(\Rightarrow\) phase transition.

Silicates make up 80% of the Earth's mantle. Seismic analysis shows jumps in wave velocity due to structural changes in silicates with pressure.

K. Driver, J. Wilkins, R. G. Hennig, C. J. Umrigar, R. Cohen
Electronic Properties of Minerals

Minerals under pressure

- Bandgap affects radiative thermal transport
- Metal/insulator transitions affects Earth’s magnetic field
Example of metallic band structure: Cu

- Copper: Band structure calculated with Wien2k
- Nearly free electron s-band dominates at low and high energies
- Electron near diffraction conditions have different effective mass
- Hybridization between nearly-free s and atomic-like d orbitals at intermediate energies
- Necking of Fermi surface in [111] directions ⇒ Hume-Rothery stabilization
The bandgap problem of DFT

Example: Bandstructure of InAs

- LDA, no gap: -0.42 eV
- PBE, no gap: -0.13 eV
- B3LYP 20%, gap: 0.54 eV

- Experimental bandgap: 0.41 eV

**Band gap problem: LDA and GGA yield a metallic ground state!**

- Practical solution: **Hybrid functionals** B3LYP & HSE (0.39 eV)
- Better solution: **GW approximation or QMC methods**
GWA calculation of band structures

- Density functional methods provide a fast way of getting band structures
- However many functionals suffer from the **band gap problem**
- More accurate method: **GW approximation**
  - Based on electronic Green’s function
  - Many-body correction of DFT quasiparticle energies
  - Accurate band structures
  - Computationally more demanding than DFT, implemented in abinit

Aulbur et al.
**Calculations of Mineral Properties**

**Summary: What can we calculate with which method?**

<table>
<thead>
<tr>
<th>Property</th>
<th>DFT</th>
<th>GWA</th>
<th>QMC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structures</td>
<td>yes</td>
<td>no</td>
<td>not done</td>
</tr>
<tr>
<td>Transition press.</td>
<td>yes¹</td>
<td>no</td>
<td>accurate</td>
</tr>
<tr>
<td>Elastic const.</td>
<td>yes</td>
<td>no</td>
<td>accurate</td>
</tr>
<tr>
<td>Band gap</td>
<td>not always accurate¹</td>
<td>very accurate</td>
<td>accurate</td>
</tr>
<tr>
<td>Effective mass</td>
<td>yes</td>
<td>yes</td>
<td>no</td>
</tr>
<tr>
<td>Transition levels</td>
<td>yes</td>
<td>very accurate</td>
<td>not done</td>
</tr>
<tr>
<td>Defect energies</td>
<td>not always accurate¹</td>
<td>no</td>
<td>accurate</td>
</tr>
<tr>
<td>Barriers</td>
<td>not always accurate¹</td>
<td>no</td>
<td>accurate</td>
</tr>
</tbody>
</table>

¹ Improved accuracy for hybrid functionals
Computational methods can accurately predict new high pressure crystal structures and their properties.

Density functional methods are usually accurate for crystal structure, transition pressures, elastic properties and phonons.

Electronic structures may require methods beyond DFT such as GW.

Sánchez-Lavega Cont. Phys. 2006