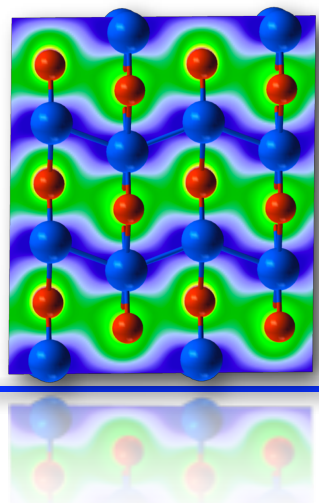# Formation of a Two-Dimensional Electron Gas in a Dense **Lithium**-**Beryllium** Alloy

Richard G. Hennig, Ji Feng, Neil W. Ashcroft and Roald Hoffmann

Do Li and Be form alloys?   What are their electronic structures? Can they have higher superconducting temperatures than pure Li and Be?
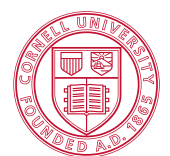
- Li and Be form intermetallic compounds under pressure

- Larger core of Li and smaller core of Be push valence electron density into 2D electron gas

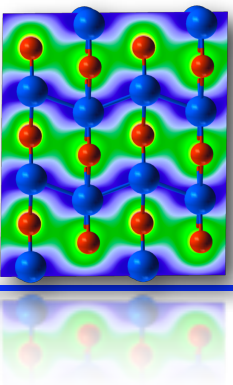- Possible enhancement of T_c through increased density of states
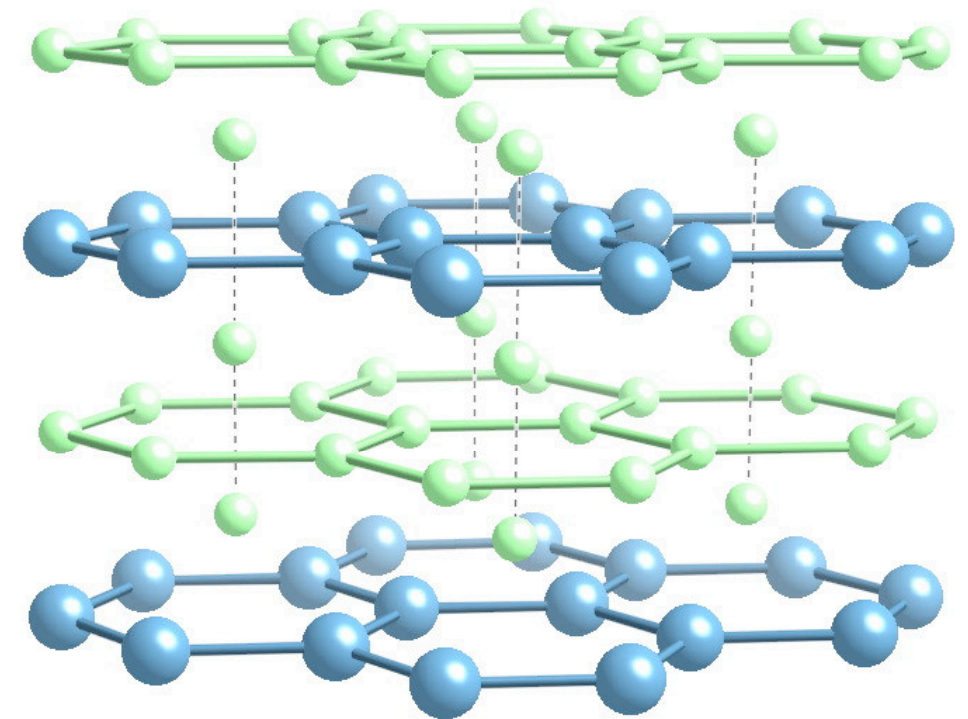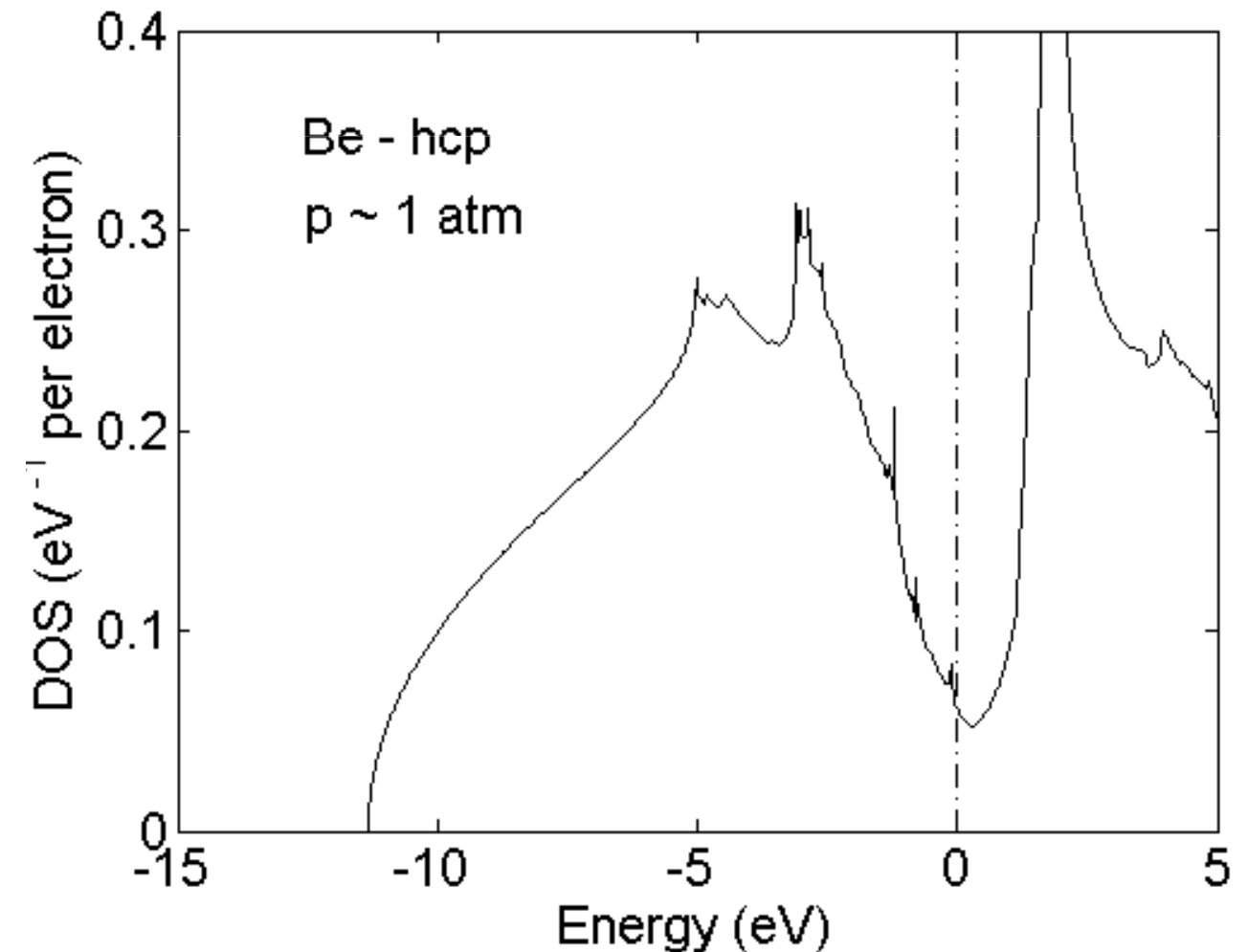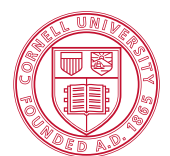
The Beryllium Story

Elemental beryllium

- Highest Debye temperature of all metallic elements: $\Theta_D = 1{,}100$ K

- Superconducting transition temperature of only $T_c = 26$ mK

- BCS theory of supeconductivity

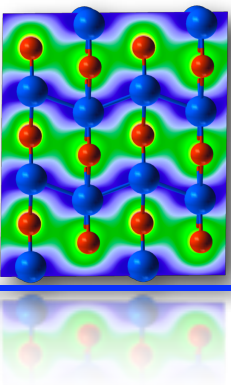$$T_c = 1.13 \cdot \theta_D \exp\left(-\frac{1}{g_0 \cdot V}\right)$$

- Low density of states at Fermi level leads to low T_c

Be - hcp
p ~ 1 atm

DOS (eV^{-1} per electron) vs Energy (eV)

Beryllium is barely a metal.

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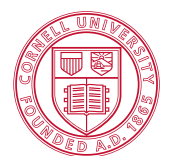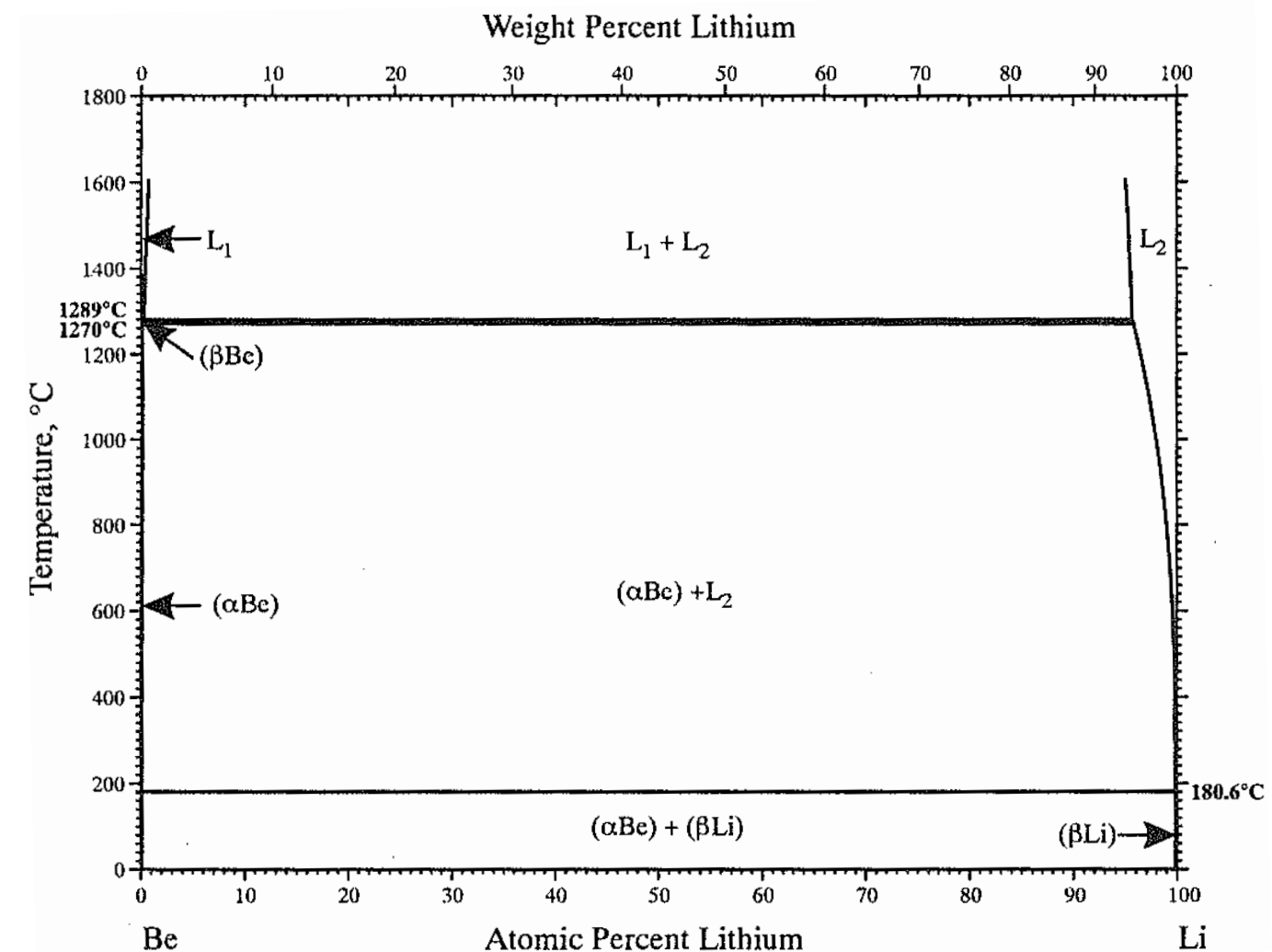June, 2008 • Urbana-Champaign, Illinois
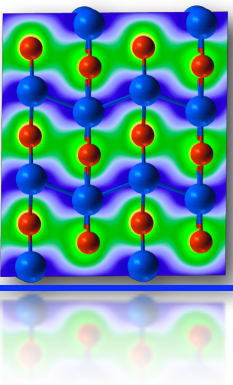
Alloying to improve T_c

Alloying with light elements – Lithium

- Light, metallic, electropositive

- However, Li and Be do not mix
  or form any intermetallic compounds
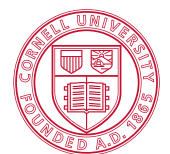
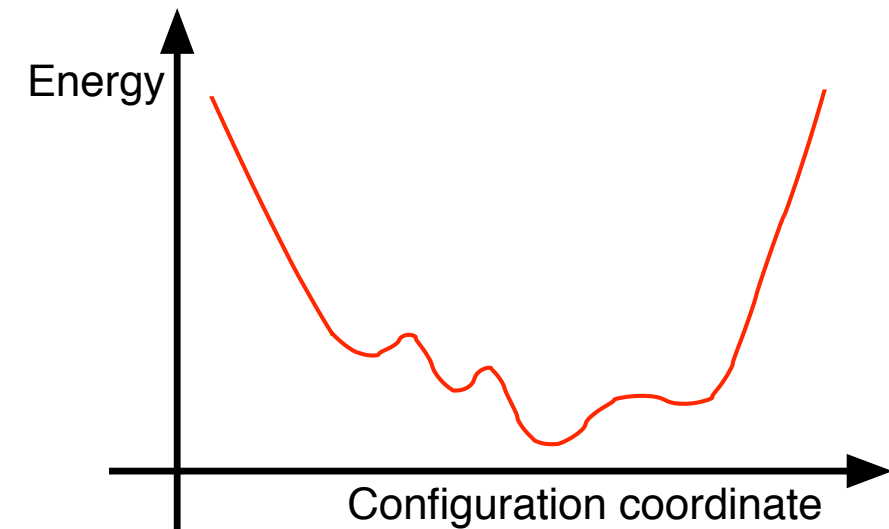**Can pressure lead
to compound formation?**

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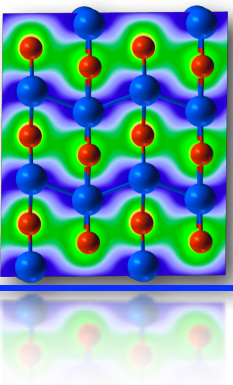
Computational Structure Predictions

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 *ab-initio* free energy calculations are computationally expensive

- Only limited success of conventional optimization methods
  - Simulated annealing, Metadynamics, Minima hopping

- Recent advances in optimization methods:
  - *Random search* (Pickard & Needs) $\Rightarrow$ Used in this work
  - *Evolutionary algorithms* (Oganov)

Energy

Configuration coordinate

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Random Search Method

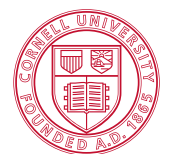## Generate a population of random structures and relax them:

- Choose random unit cell translation vectors
- Renormalize the volume to a reasonable range of values
- Choose random atomic positions within the cell
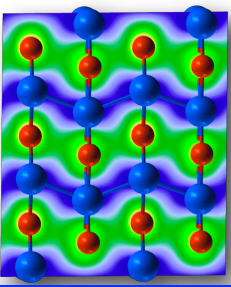
May constrain the initial positions:

- 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

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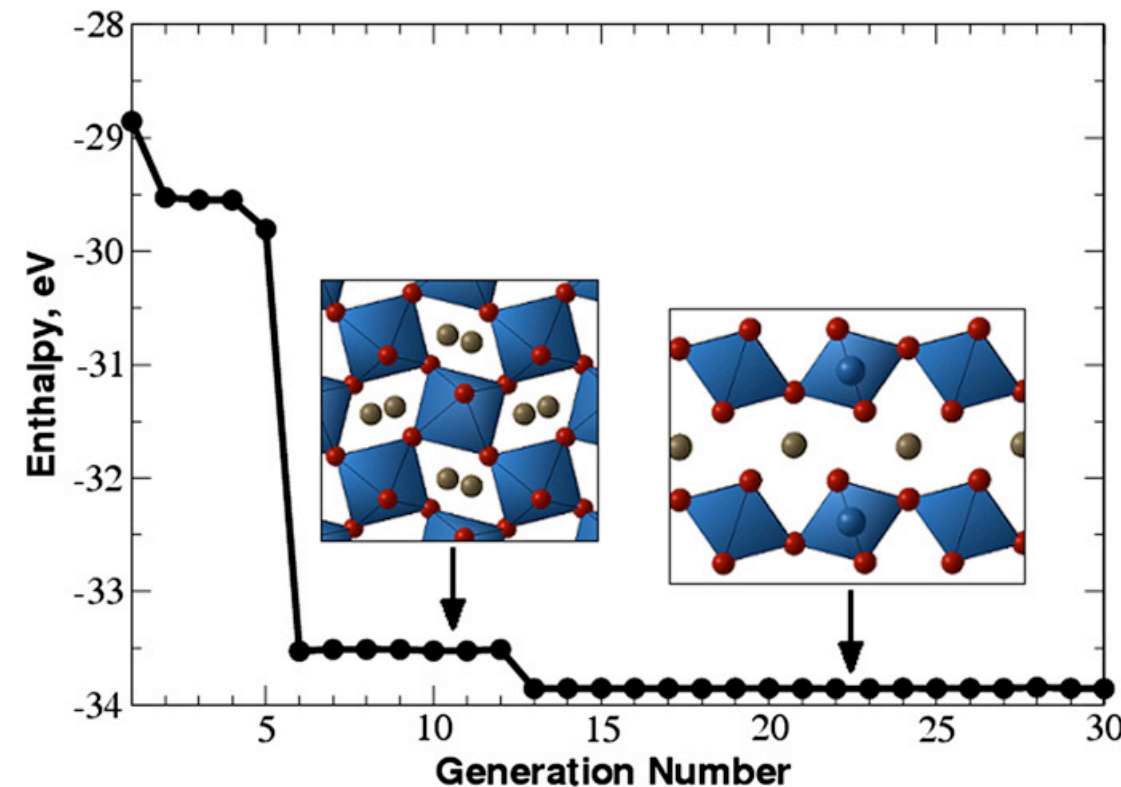
Evolutionary Algorithms

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.
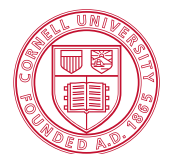
Evaluation function: Ab initio free energy

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

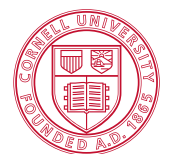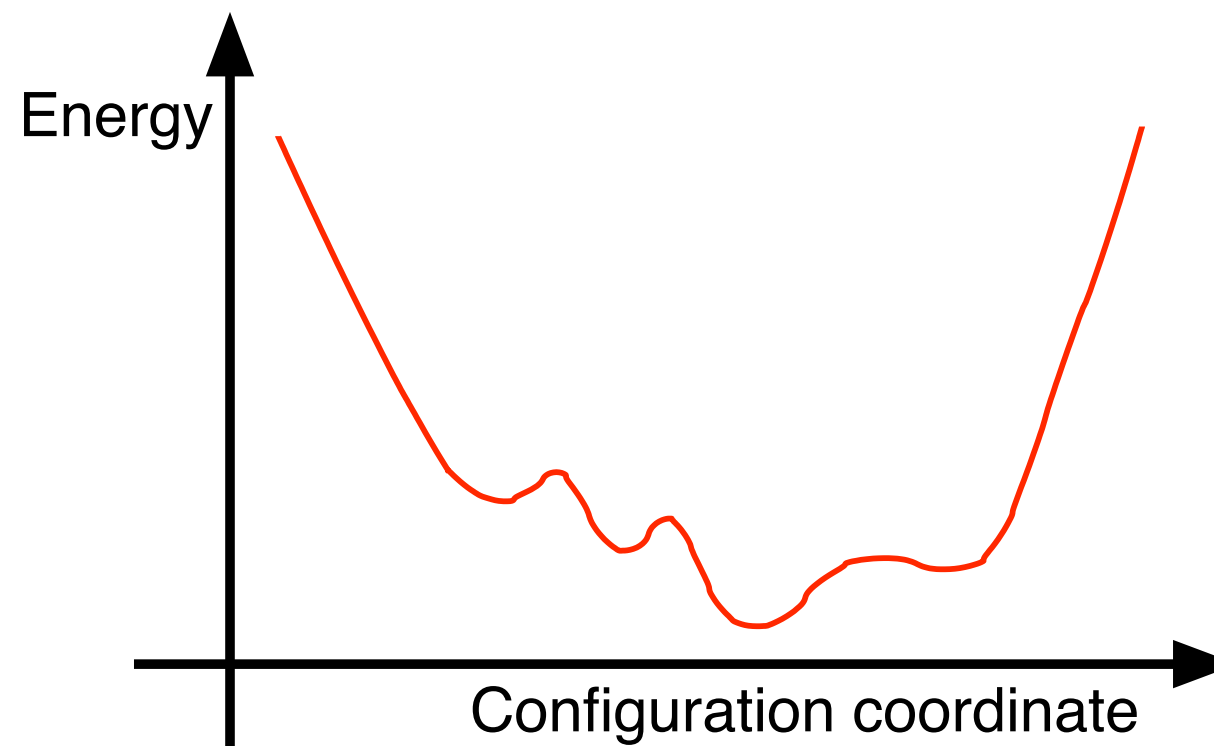C. W. Glass, A. R. Oganov, N. Hansen, Comp. Phys. Comm. (2006)

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Comparison of Search Methods
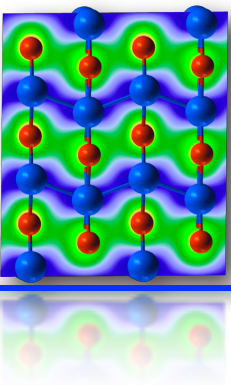
Random search	Evolutionary algorithm
• Simple to program	• More complex rules
• Successful for small unit cells	• Successful for structures with large unit cells and structural motifs
• Increasingly more difficult for large structures	
• SiH_4, $LiBe$, H_2O, H, N	• $CaCO_3$, $MgSiO_3$, CO_2, O, H

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Structure Maps

- Pettifor structure map
  of A-B ordered alloy

- Adapted from Villars *et al*.

- Advantage: Fast, simple

- Disadvantage:
  Structures have to be known

Structure Prediction and Search Algorithm
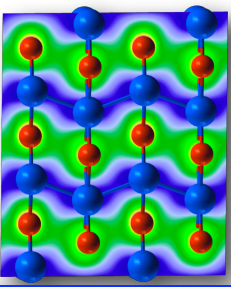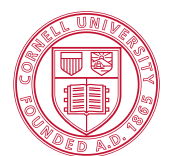
- Do we understand the structures of intermetallics?
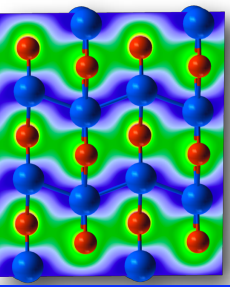
- Can we predict the structure of compounds?

Be_4Li, Be_3Li, Be_2Li, Be_3Li_2, $BeLi$, Be_2Li_3, $BeLi_2$, $BeLi_3$, $BeLi_4$

p → Be_mLi_n

MgB_2

Structure Search Algorithm

$GaLi_2$

$H_f < 0$?
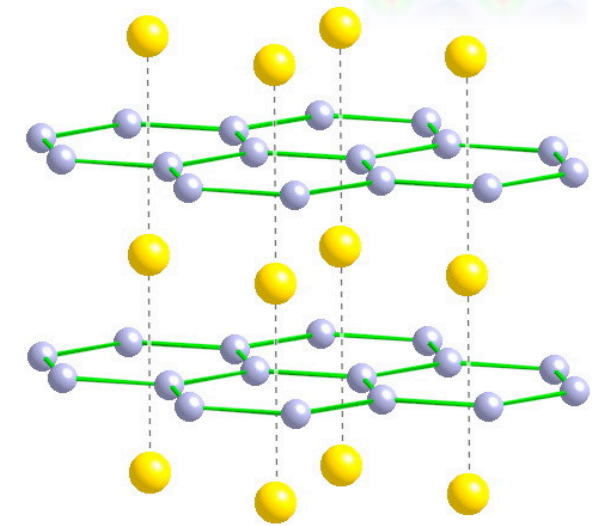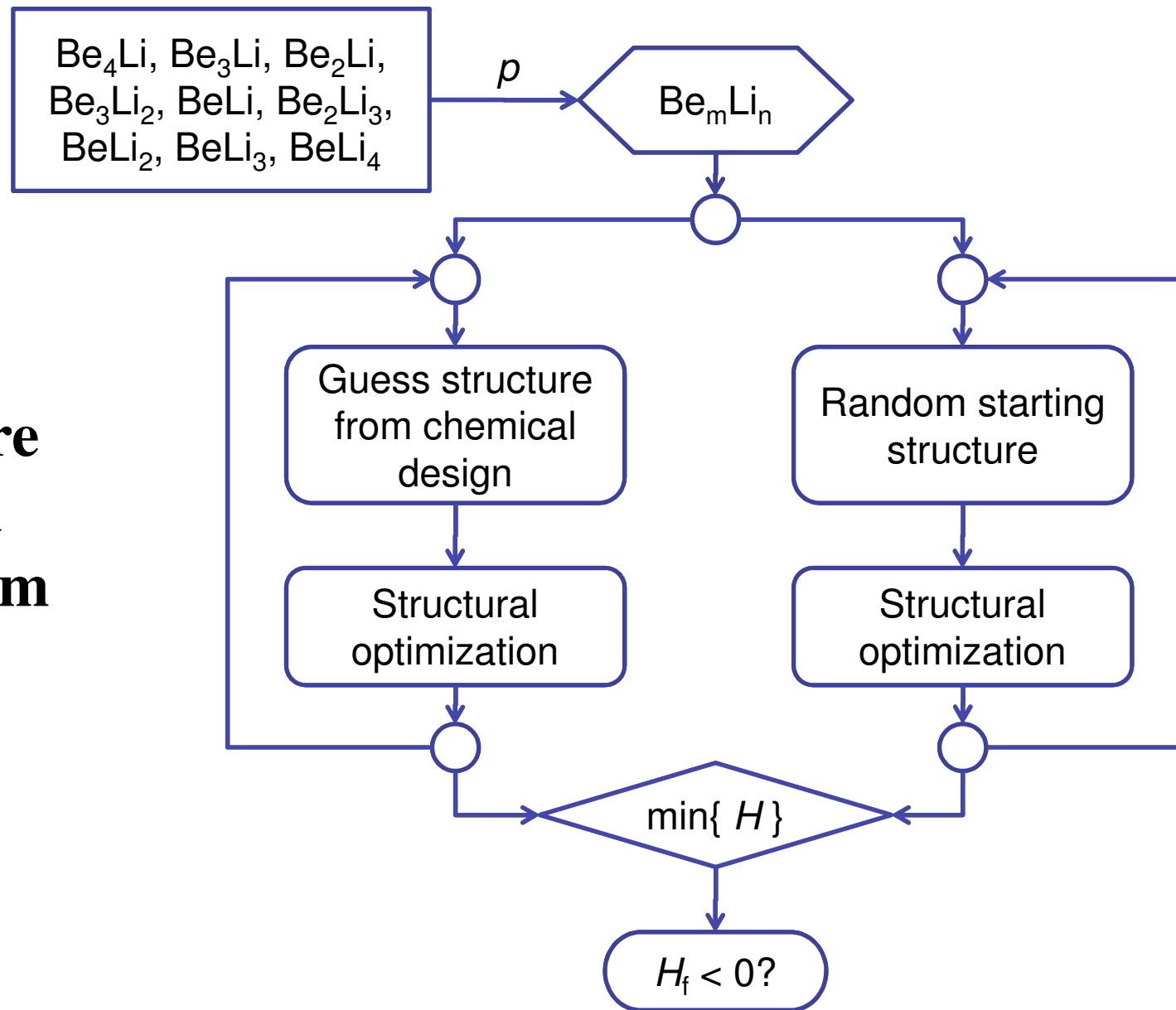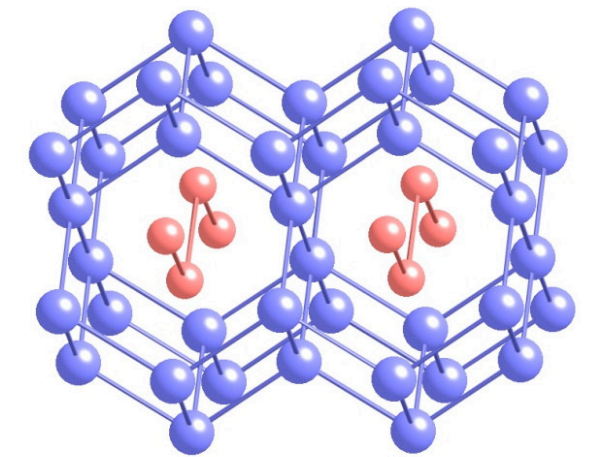
Computational Details

Density functional theory (VASP)

- Generalized gradient approximation (PBE)

- Plane-wave basis and PAW potentials

- Optimization of all parameters (atom positions and lattice vectors) at given pressure

Random structural search

- Use 20 – 50 starting structures for each selected pressure, composition and cell size

  - Pressure range: 0 – 200 GPa

  - Compositions: $Be_{1-x}Li_x$ x = 0, 20, 25, 33, 40, 50, 60, 66, 75, 100 %

  - Cell size: Up to 15 atoms per primitive cell

- Symmetry identification using **ISOTROPY** (Stokes & Hatch, BYU)

- Check energy of **higher symmetry** structures

- **Phonon dispersion** calculation to confirm mechanical stability

Use of petascale computing for structure searches
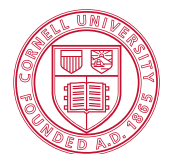
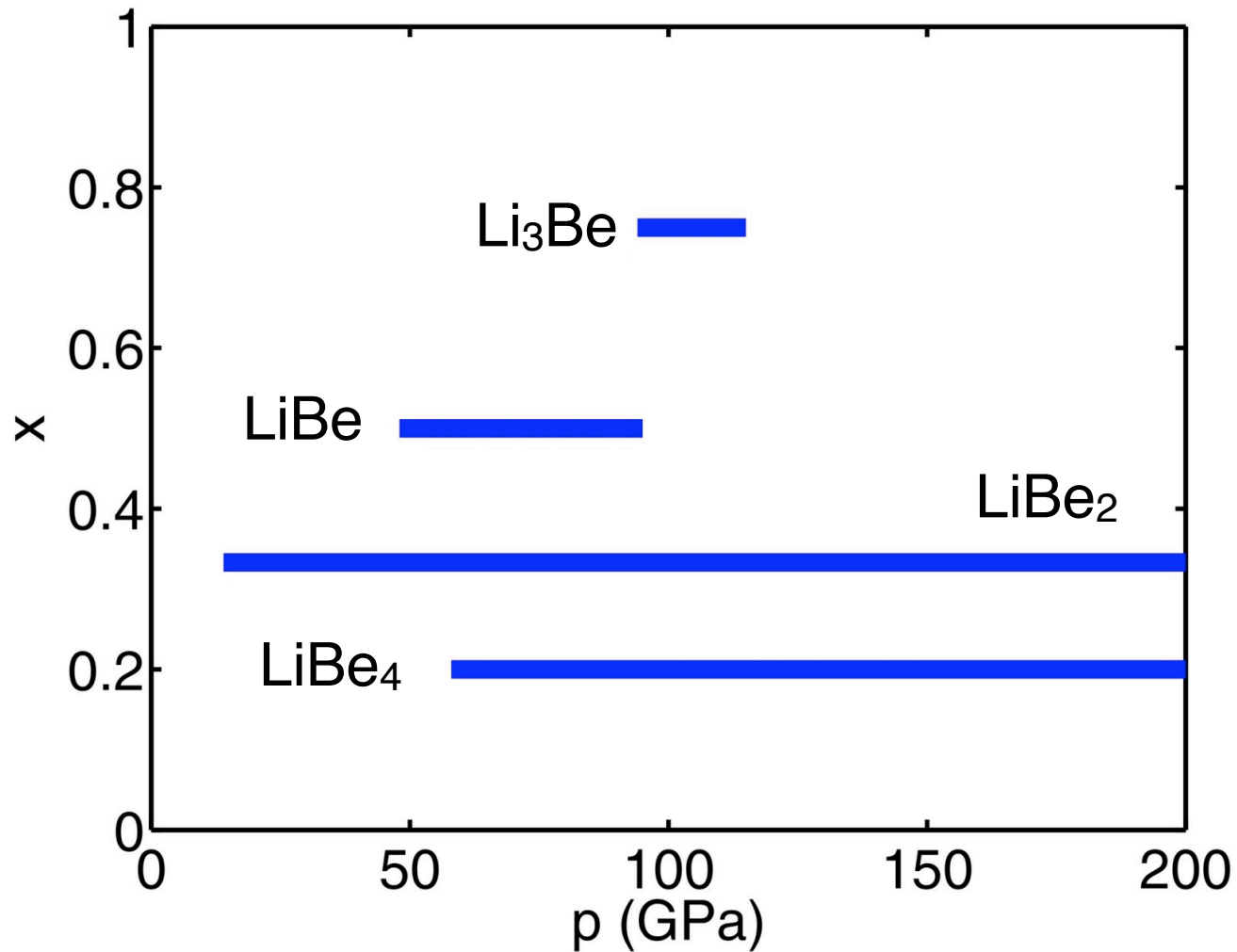# Enthalpy of Formation of Li-Be Compounds
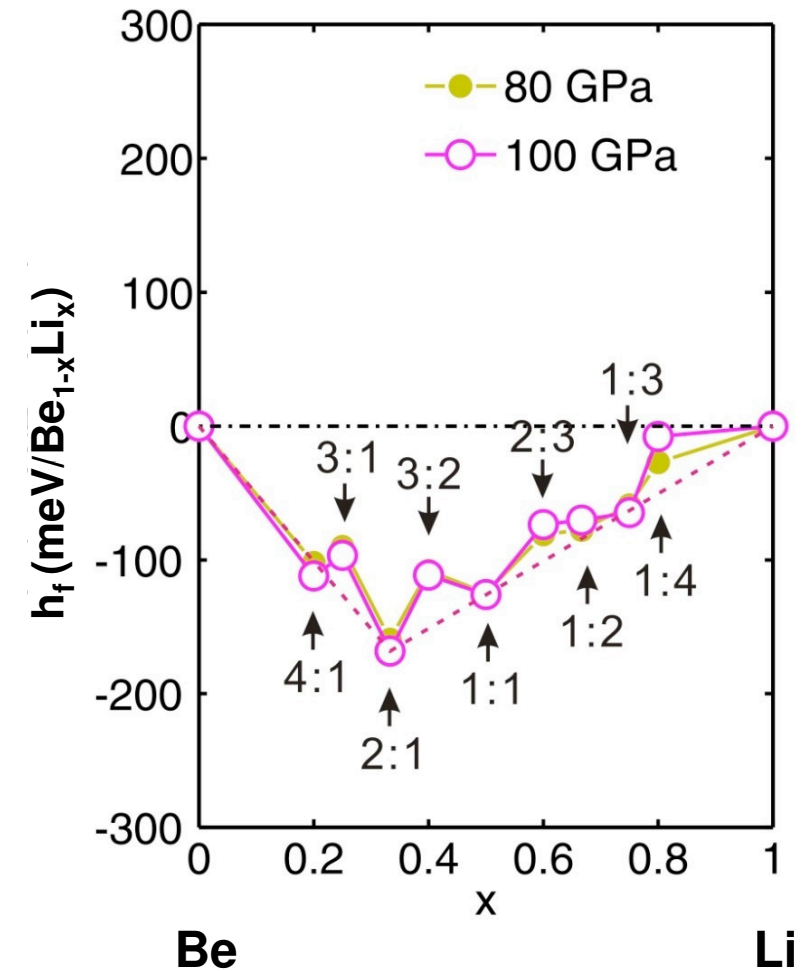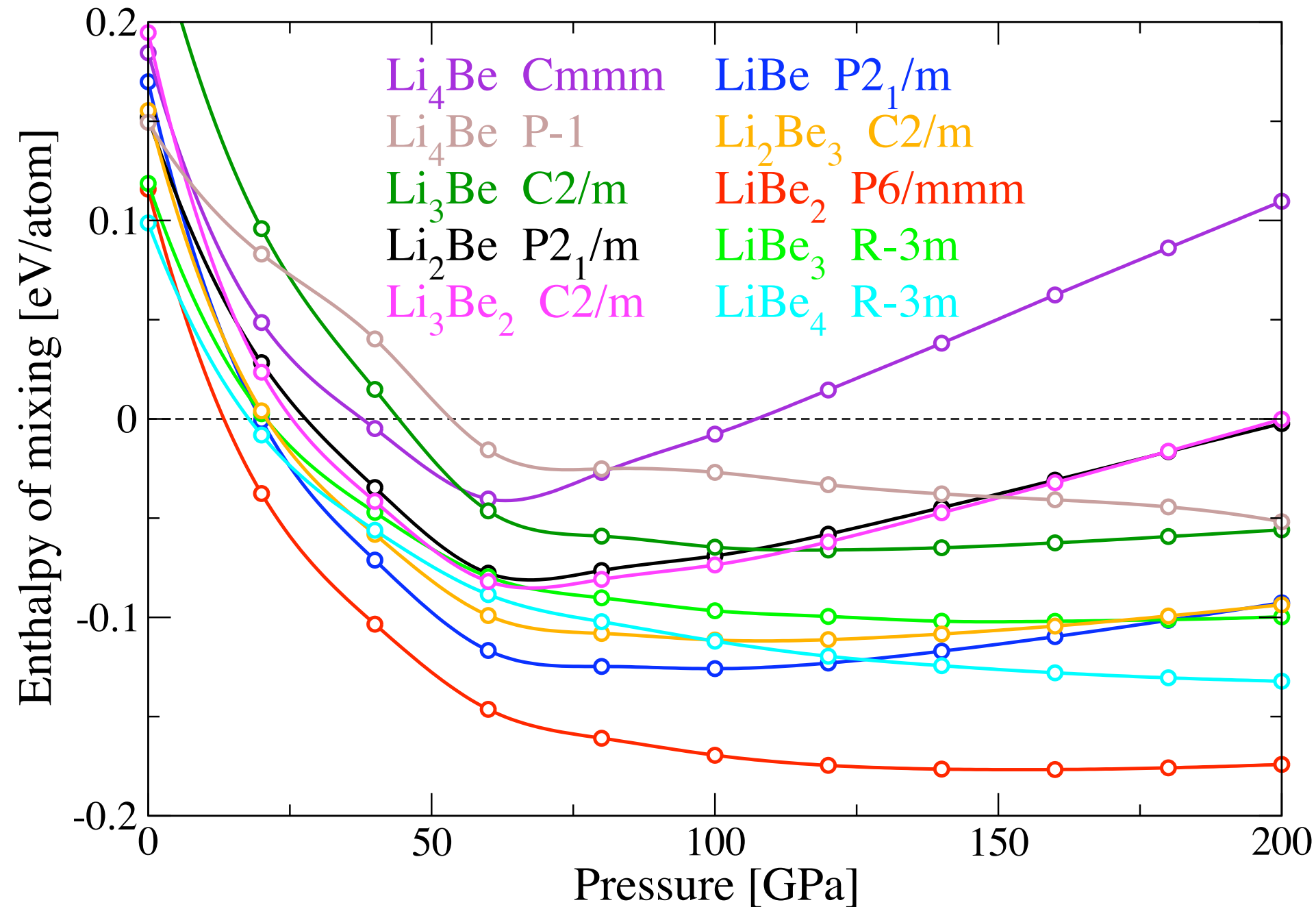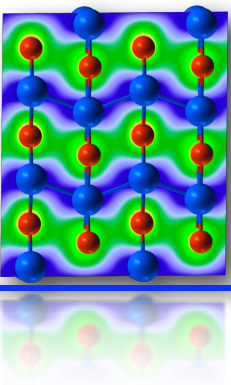
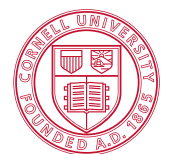**Stability increases with pressure dramatically at low pressures**
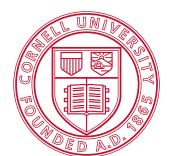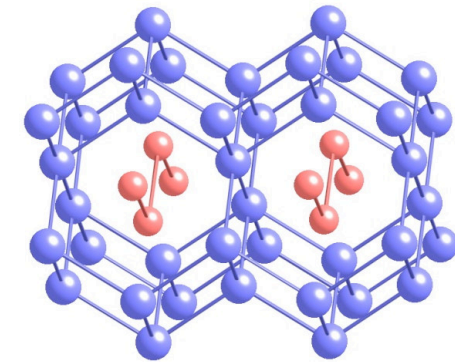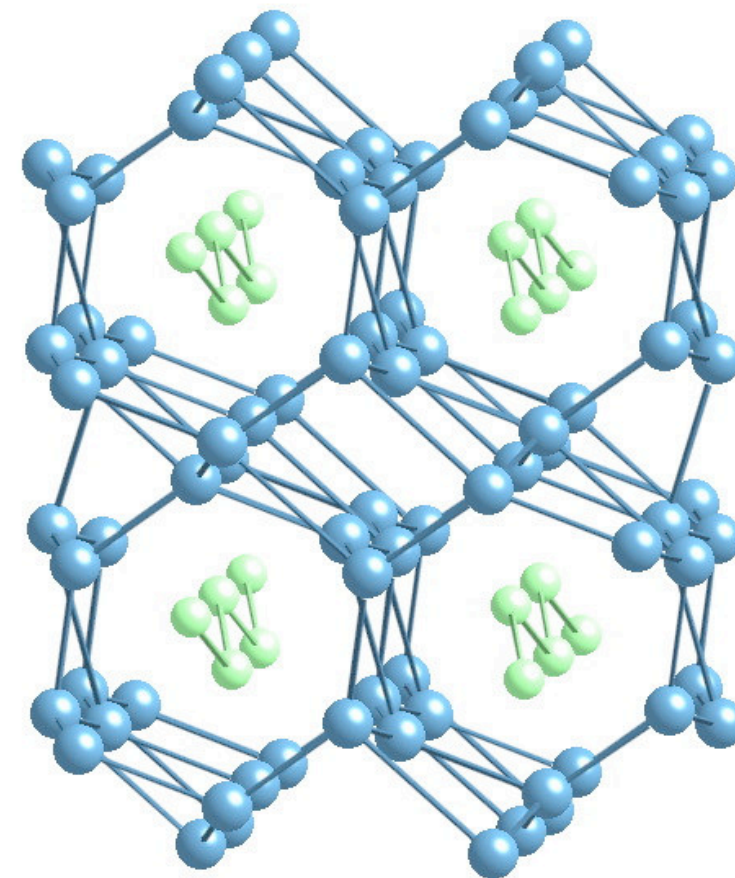
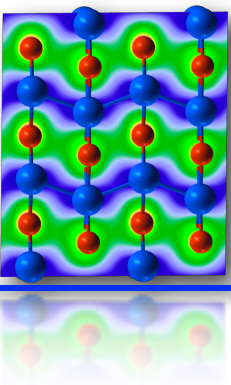# Li-Be Phasediagram under Pressure
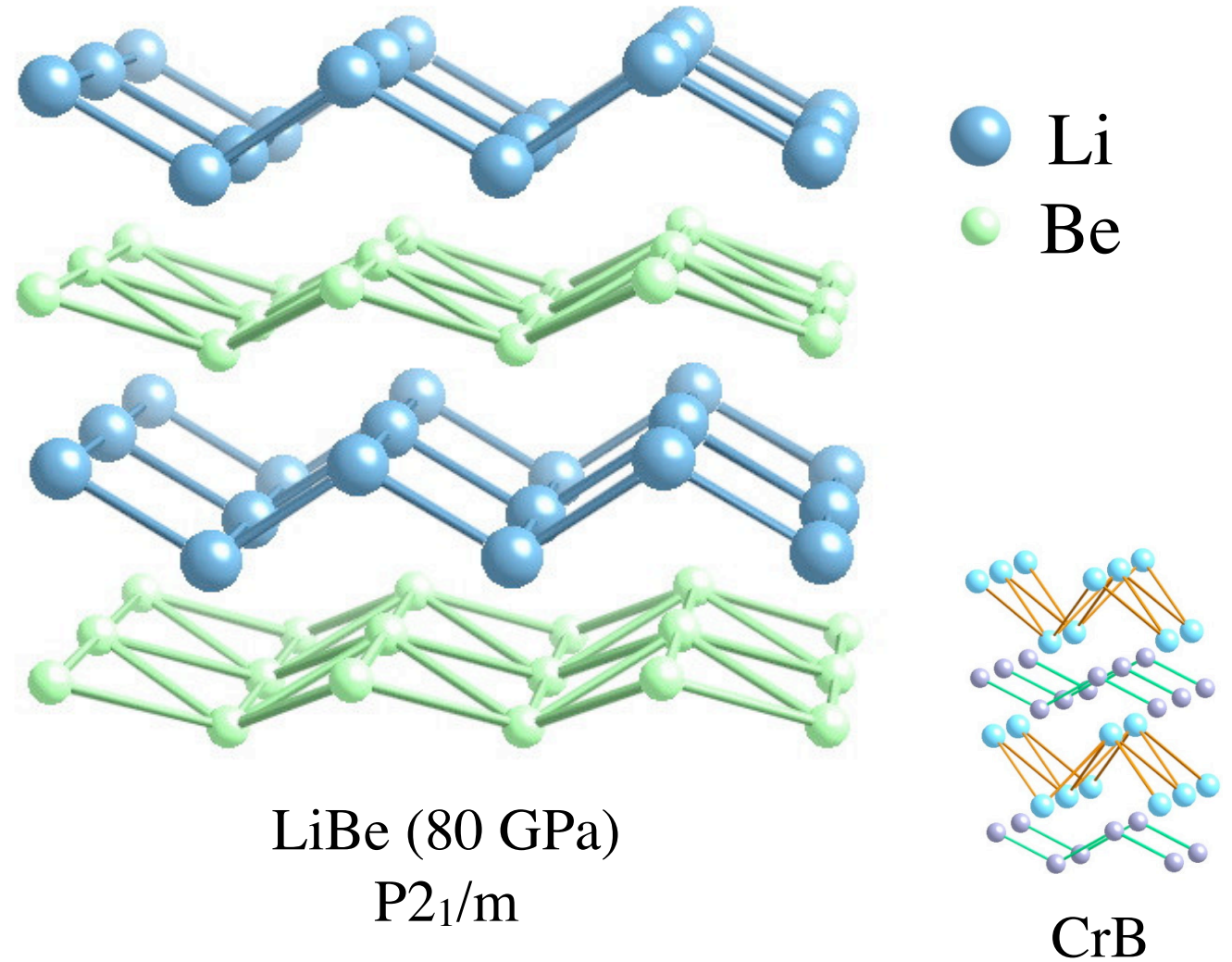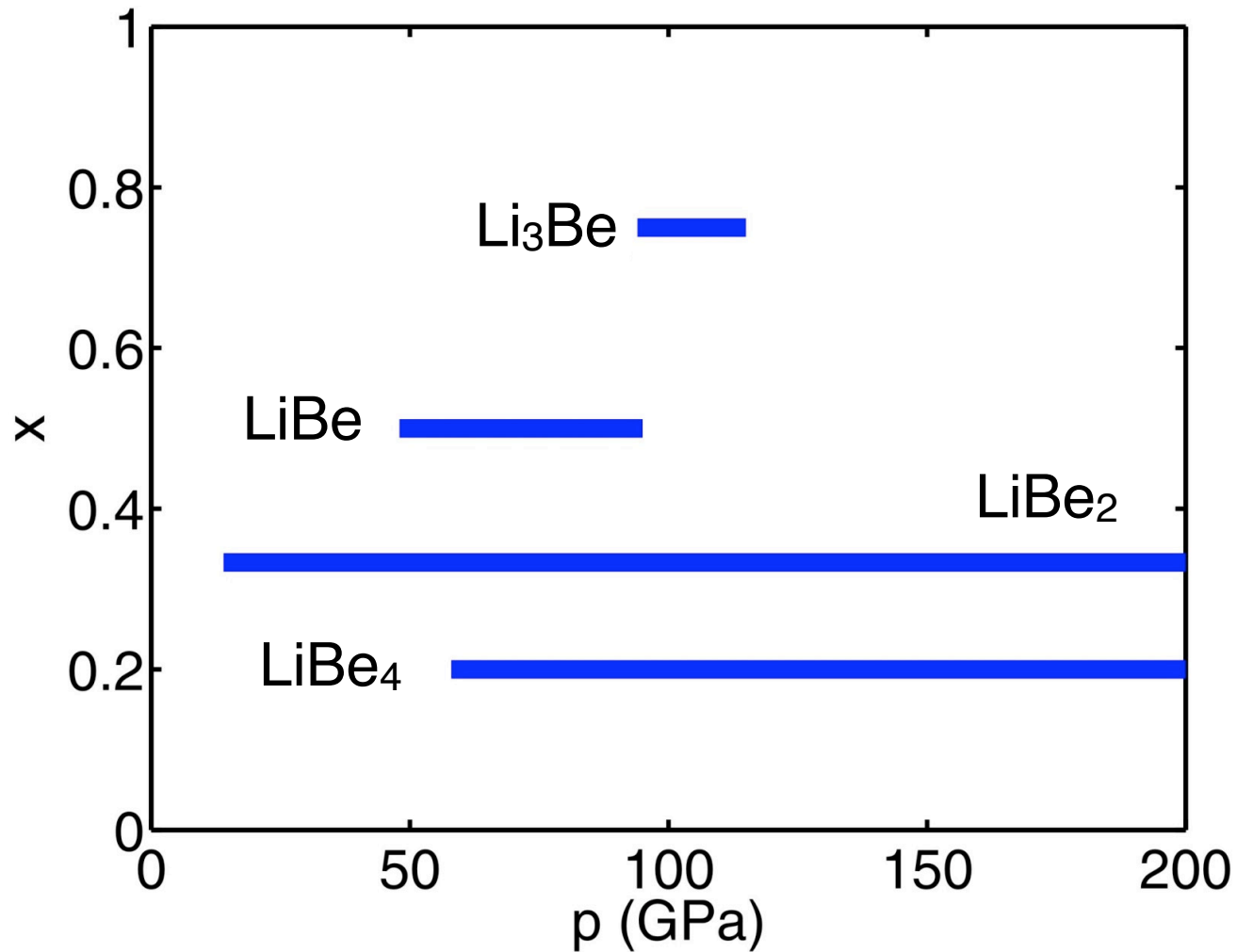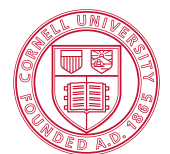
Stability ranges

Most stable Li₃Be phase

Li₃Be (80 GPa)
C2/m

○ Li
○ Be

GaLi₂

Li-Be Phasediagram under Pressure

Stability ranges

Stability ranges
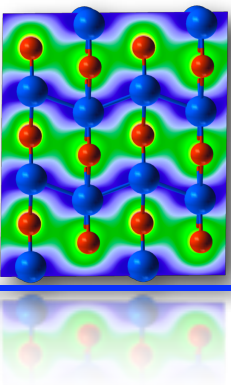
Most stable LiBe phase

Most stable LiBe phase

LiBe (80 GPa)
$P2_1/m$

CrB

- Li
- Be

Li-Be Phasediagram under Pressure
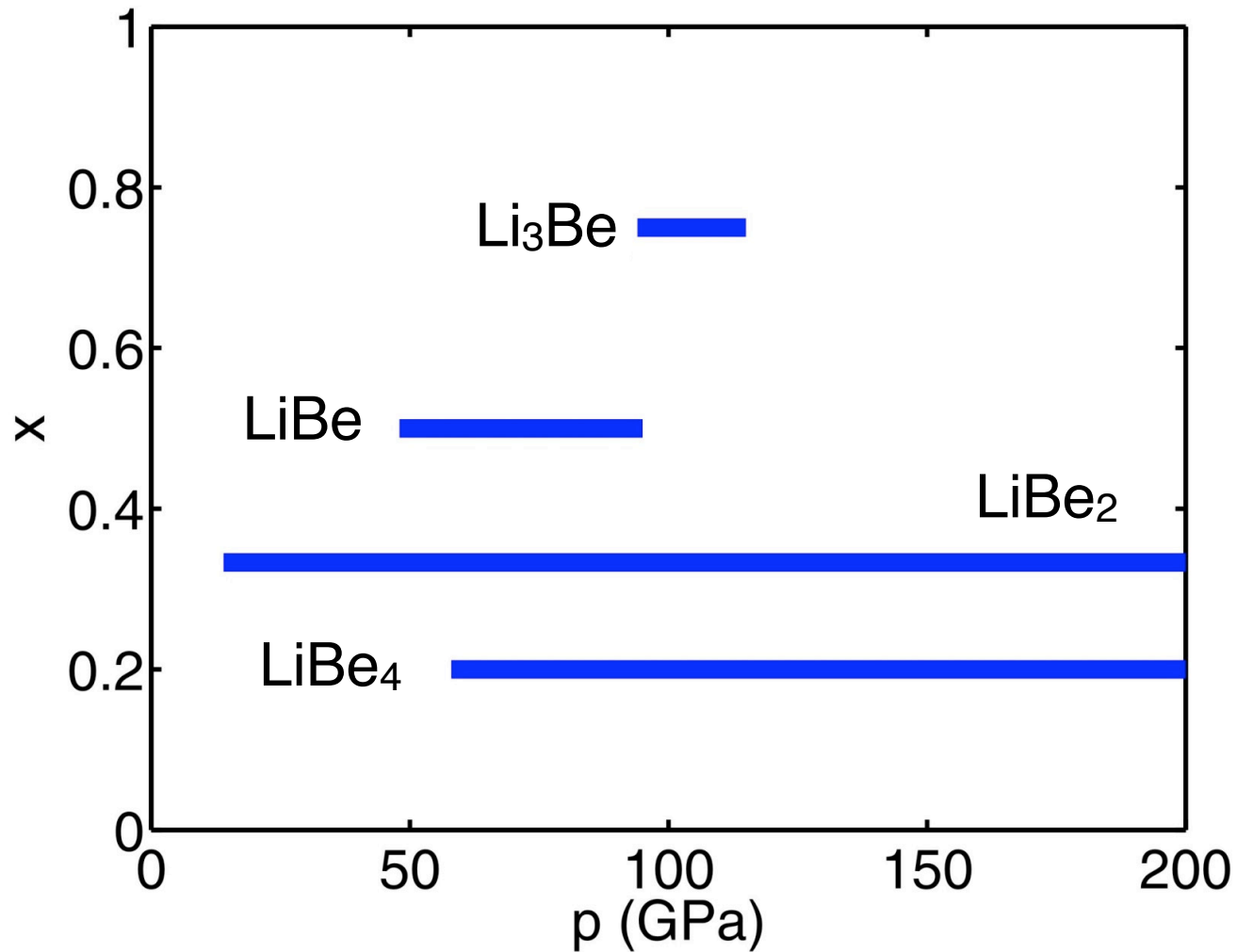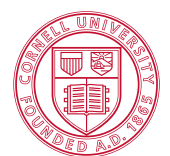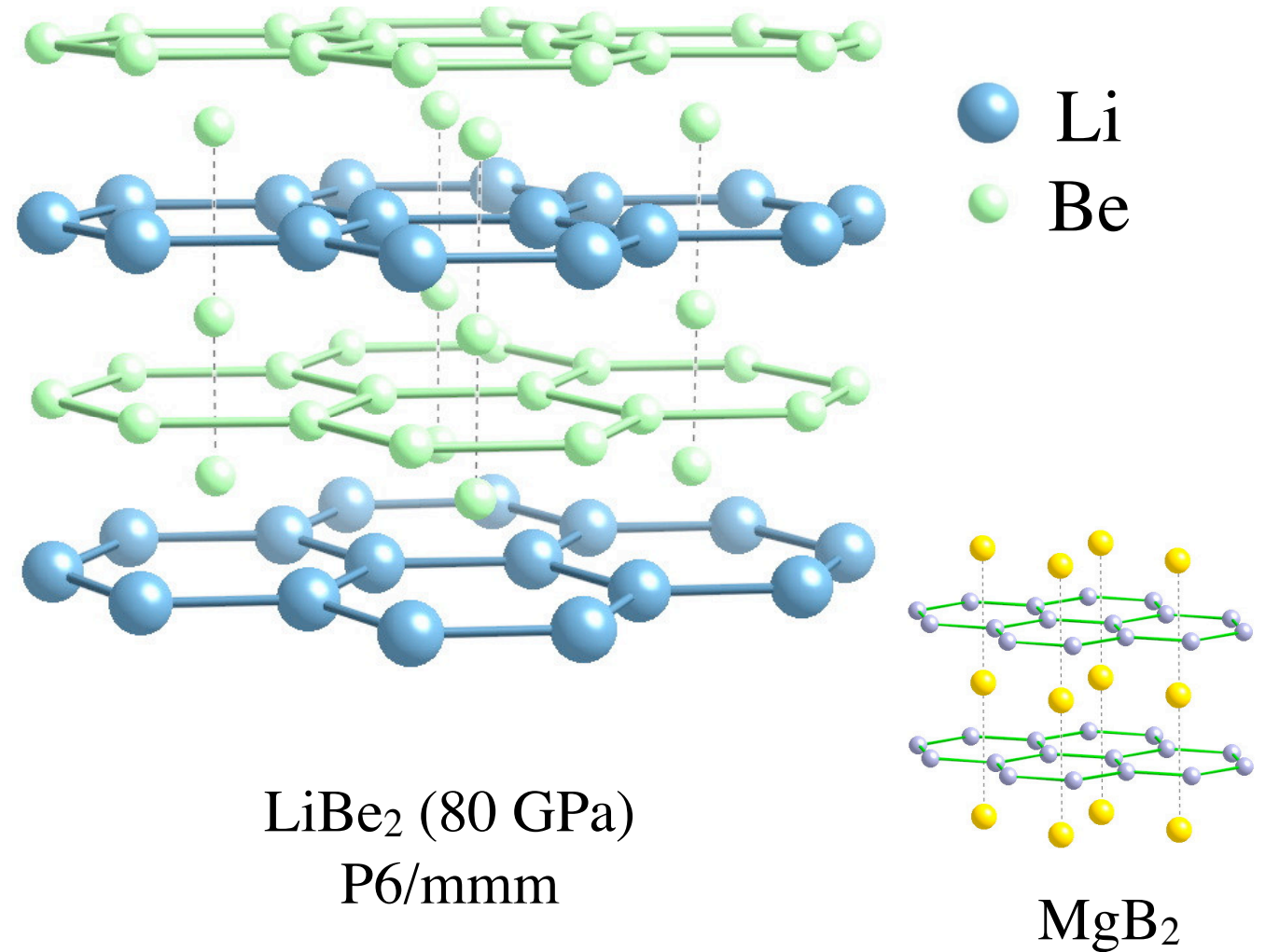
Stability ranges

Most stable $LiBe_2$ phase

$LiBe_2$ (80 GPa)
P6/mmm

MgB$_2$

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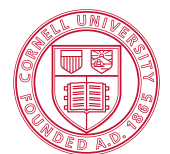**Electronic Structure Workshop**
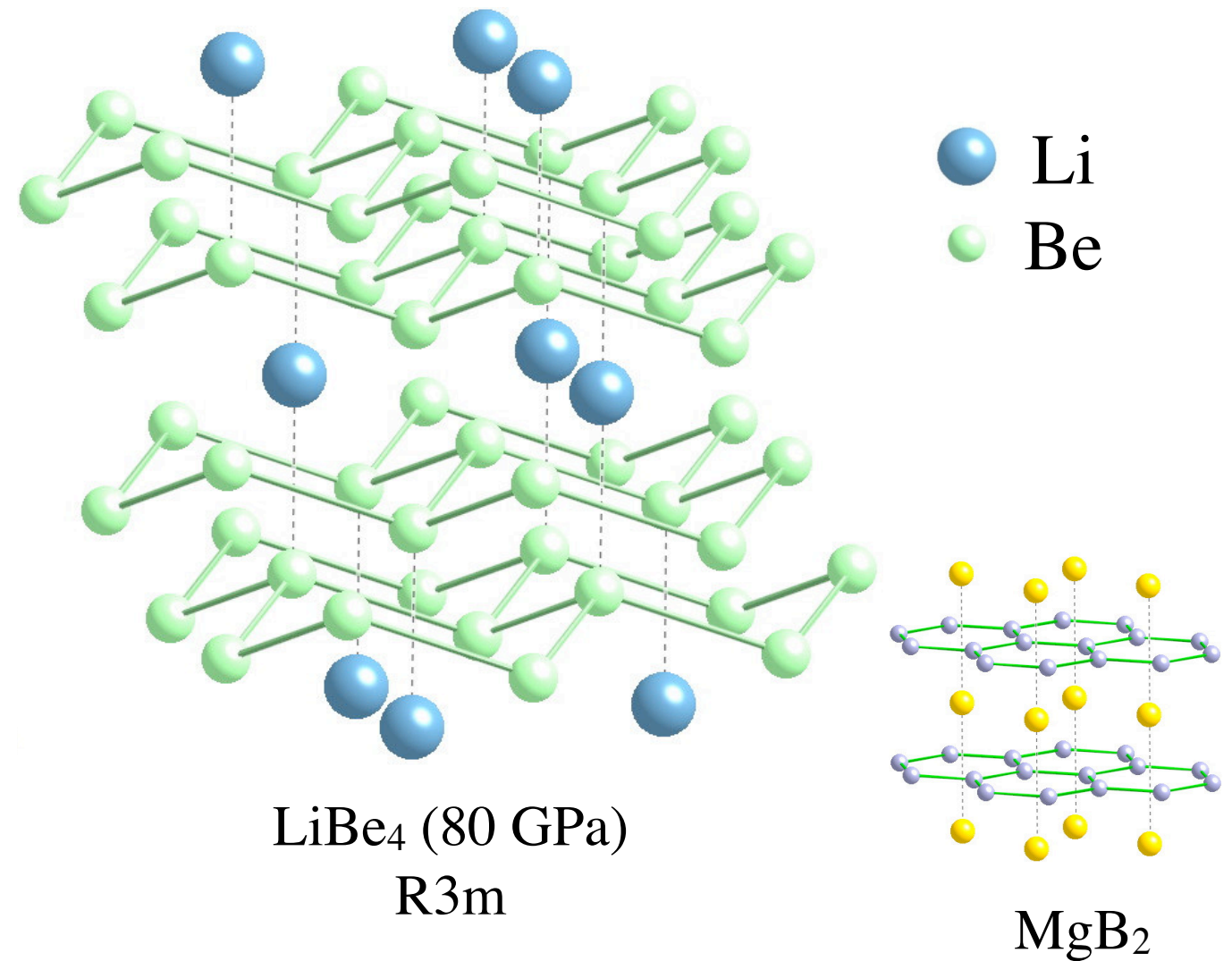June, 2008 • Urbana-Champaign, Illinois

Li-Be Phasediagram under Pressure
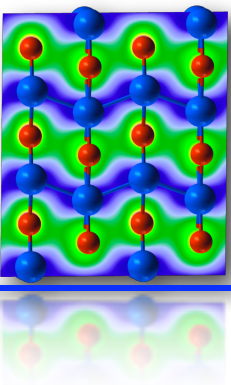
Stability ranges

Most stable LiBe$_4$ phase

- Li
- Be

LiBe$_4$ (80 GPa)
R3m

MgB$_2$

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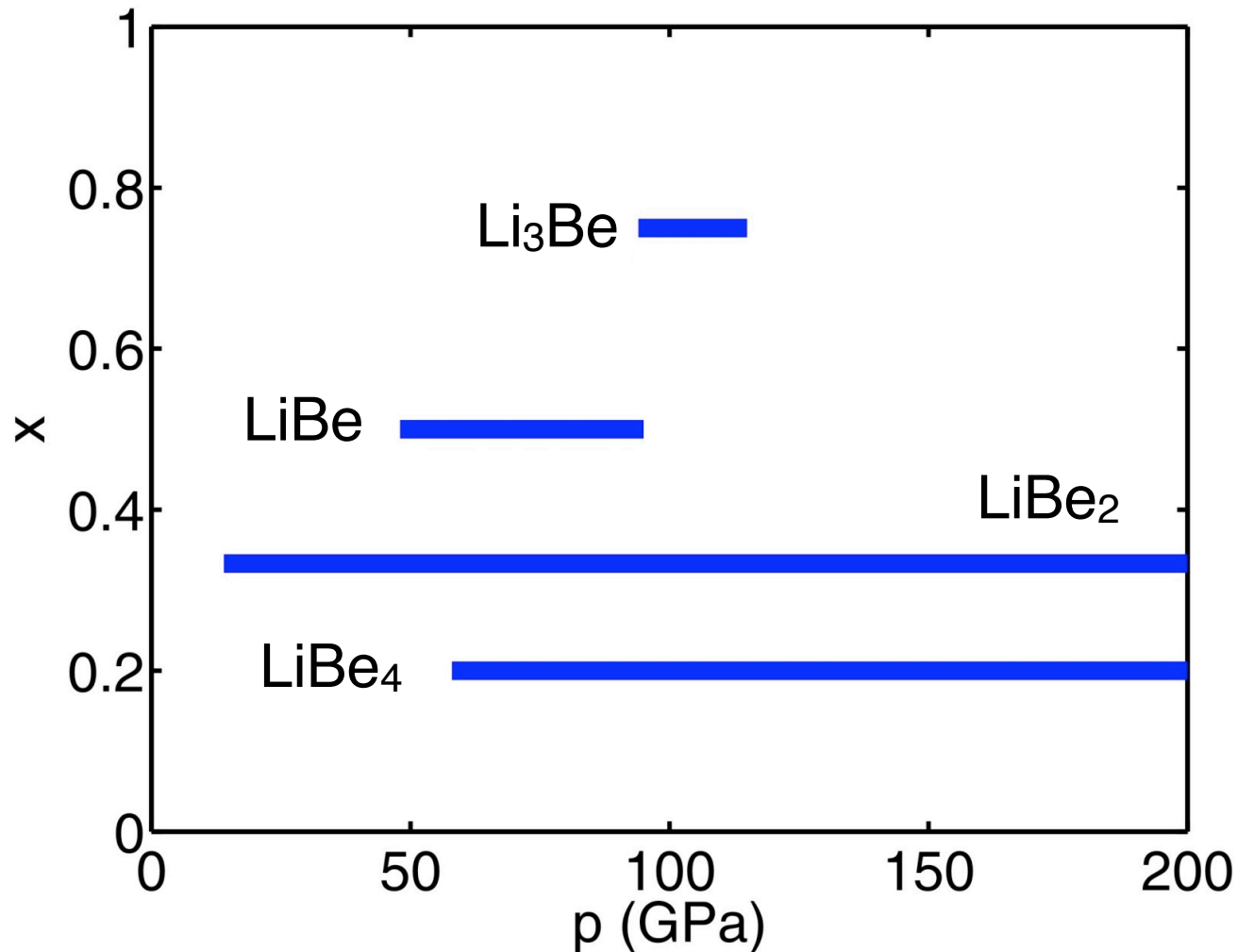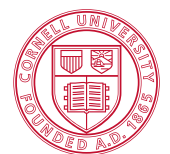**Electronic Structure Workshop**
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Li-Be Phasediagram under Pressure

Stability ranges
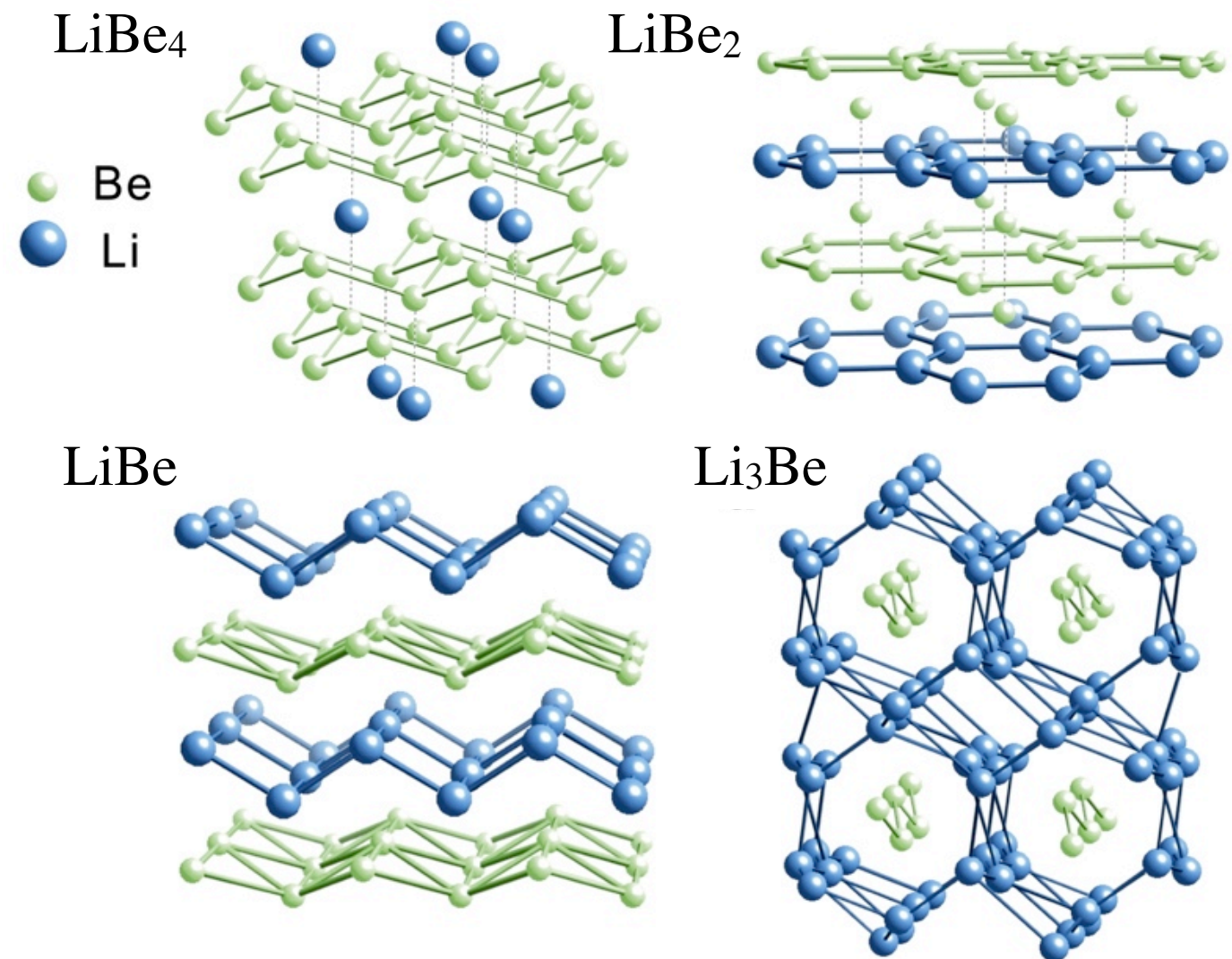
Four novel Li-Be phases become stable under pressure

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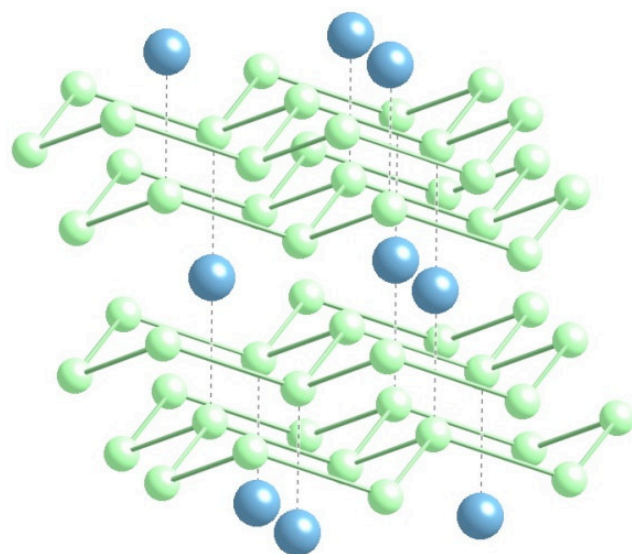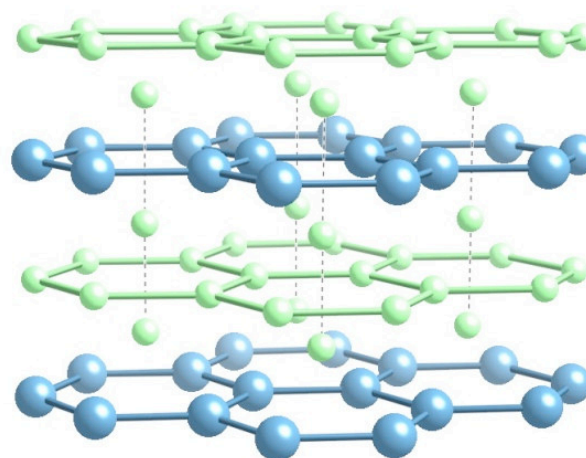
Electronic Structure of Li-Be phases
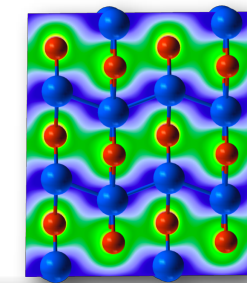
- Beryllium's DOS at the Fermi level is nearly constant over entire pressure range: $g(\varepsilon_F) = 0.04$ eV^{-1} per valence electron
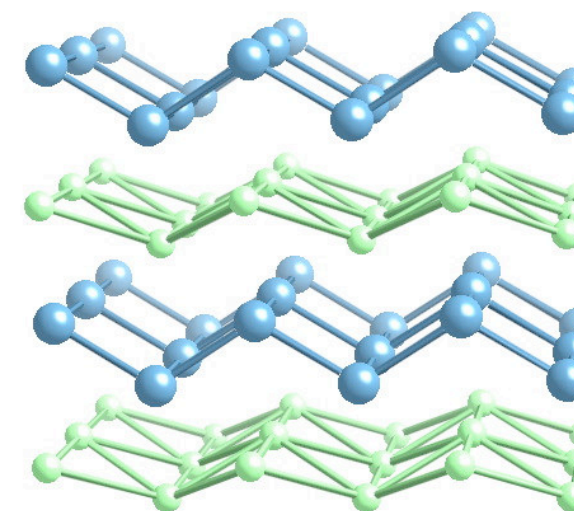
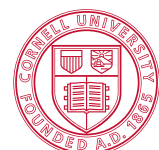| 80 GPa	LiBe$_4$ R-3m	LiBe$_2$ P6/mmm	LiBe P2$_1$/m
$g(\varepsilon_F)$ in eV^{-1} per valence electron)	0.06	0.06	0.12

LiBe$_4$ LiBe$_2$ LiBe

For a comparable e-ph coupling T_c would be about 32 K

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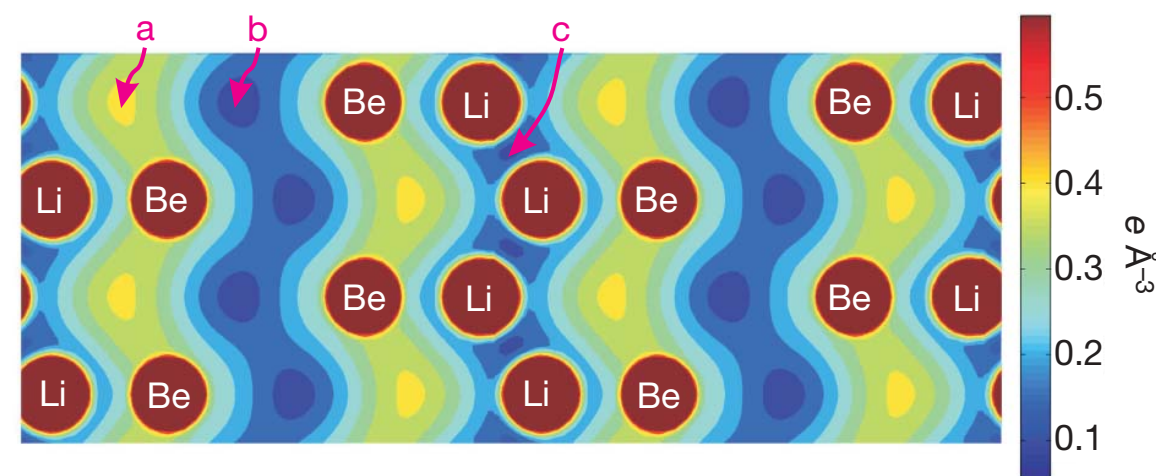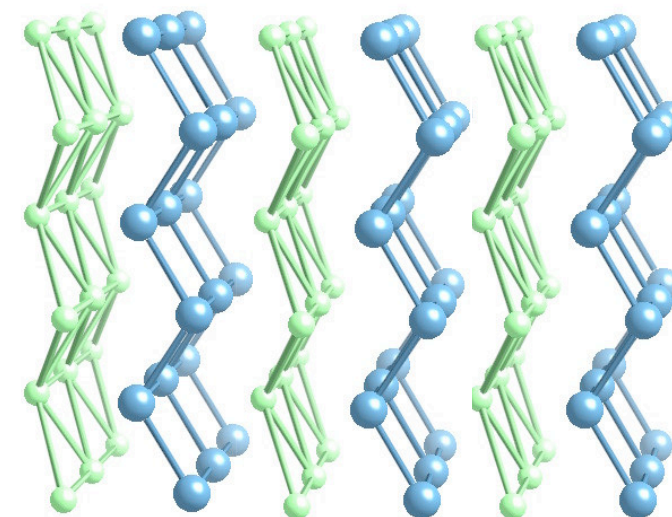rhennig@cornell.edu

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Two-dimensional Electronic Gas in LiBe
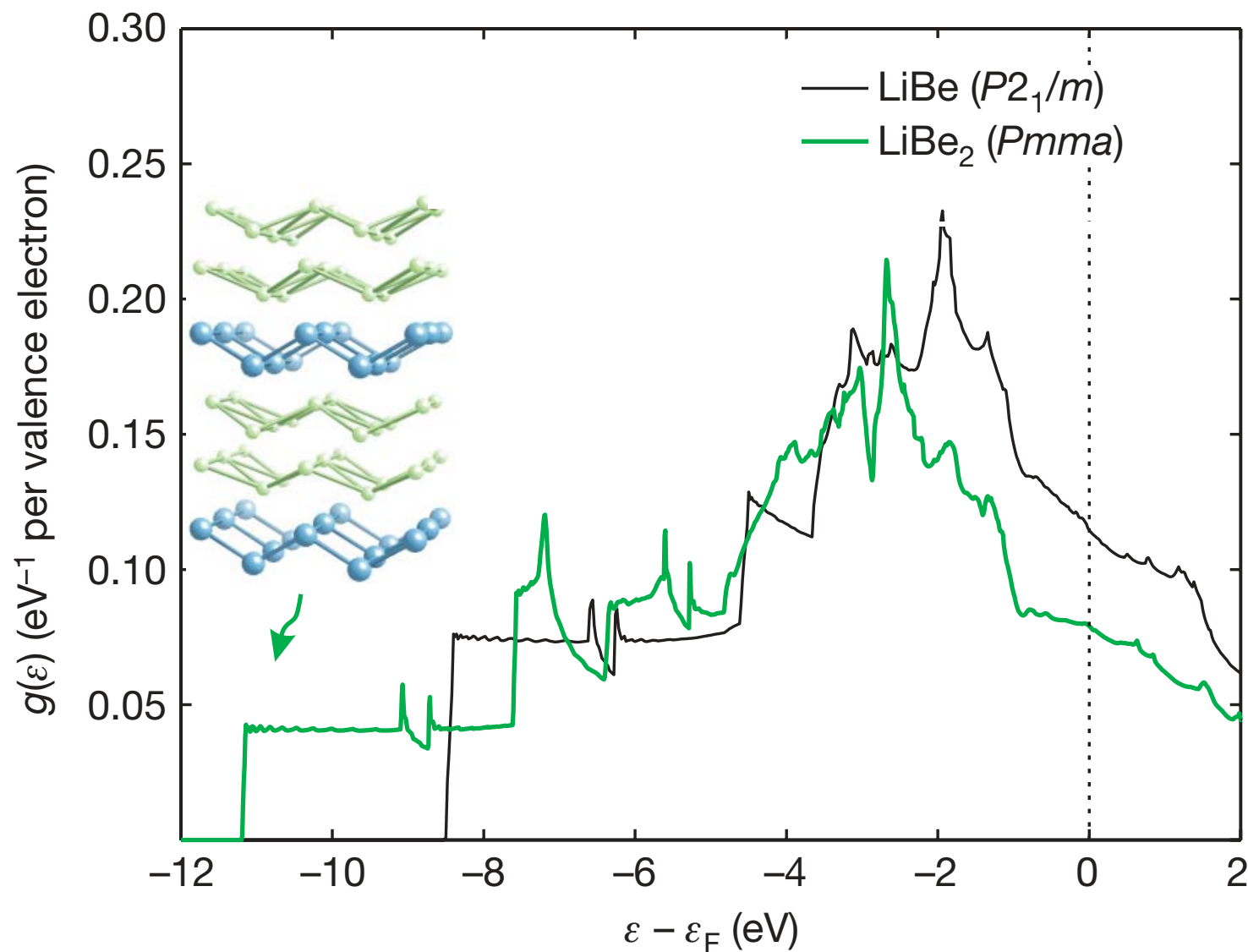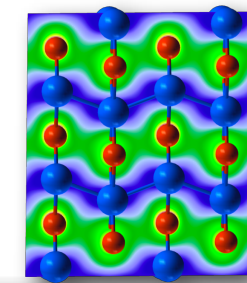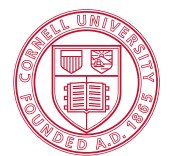

Electron density shows a two-dimensional, layered structure

Electronic Structure of Li-Be phases

LiBe

$P2_1/m$

🔵 Li

🟢 Be
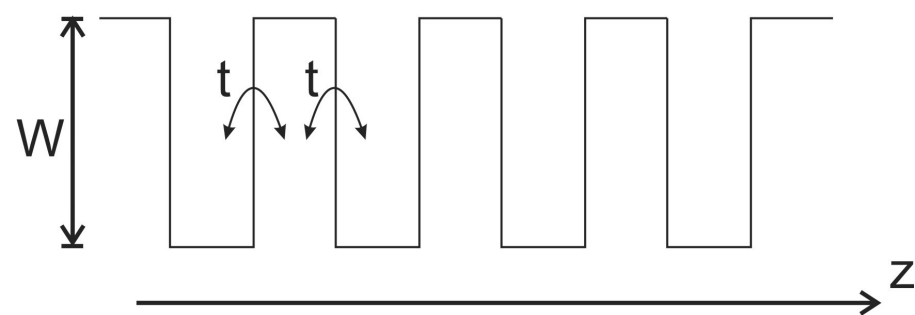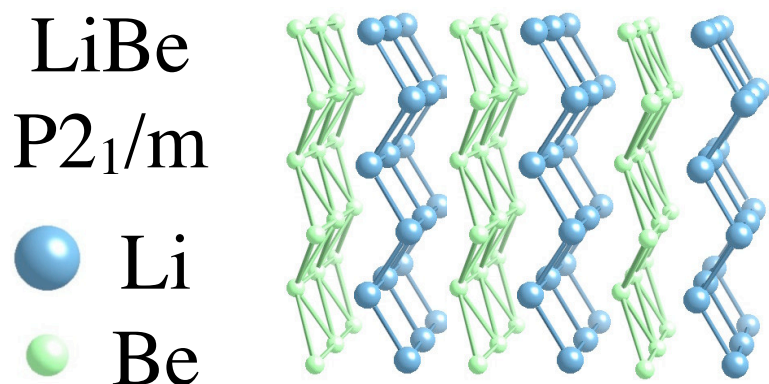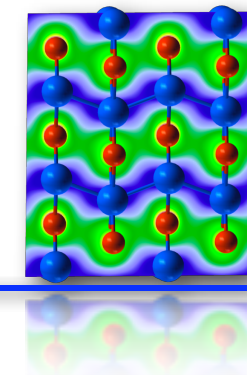
Analytically solvable model

$$\mathcal{H}_{xy} = \sum_{\mathbf{k}} \frac{\hbar^2 k^2}{2m^*} c_k^\dagger c_k$$

$$\mathcal{H}_z = W \sum_i n_{2i} - t \sum_i \left(c_i^\dagger c_{i+1} + h.c. \right)$$

$2t^2/W$

- In the limit $W \gg t$ it yields the shown DOS

BeLi - "CrB" structure

0.25

27 GPa, r_s = 2.05

75 GPa, r_s = 1.89

Electronic Structure of Li-Be phases

- Extract W from step-shape of density of states: $2t^2/W = 0.05$ eV

- Assuming a typical value of $t = 1...2$ eV yields a value of **$W > 20$eV**

  ‣ Observe *large effective electronegativity difference* between Li and Be
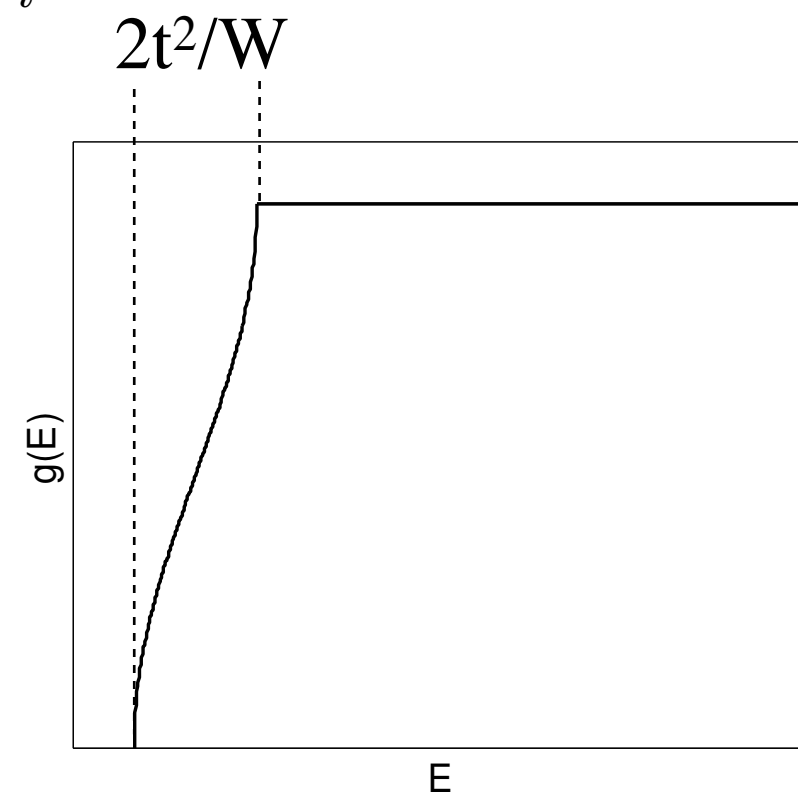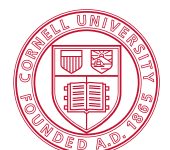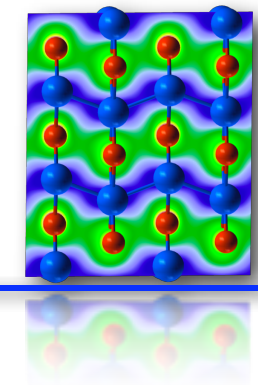
  ‣ However, first ionization potential is only 4 eV higher in Li than in Be

  ‣ Insufficient to produce narrow step at bottom of valence band

What is the origin of the large potential difference between Li and Be layers?

- Electronegativity difference arises because potential energy difference between Li and Be layers increases as a result of **core overlap**

  ‣ At 80 GPa: d_{Li-Li} and $d_{Be-Be} = 1.9–2.0$ Å

  ‣ Ionic radii: $r_{Li+} = 0.76$ Å and $r_{Be2+} = 0.27$ Å

  ‣ Li core electrons show 1 eV dispersion

Substantial core overlap of the large Li ions pushes valence electrons into Be layers resulting in a quasi-2D electron gas.
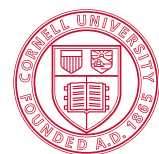
Formation of a Two-Dimensional Electron Gas
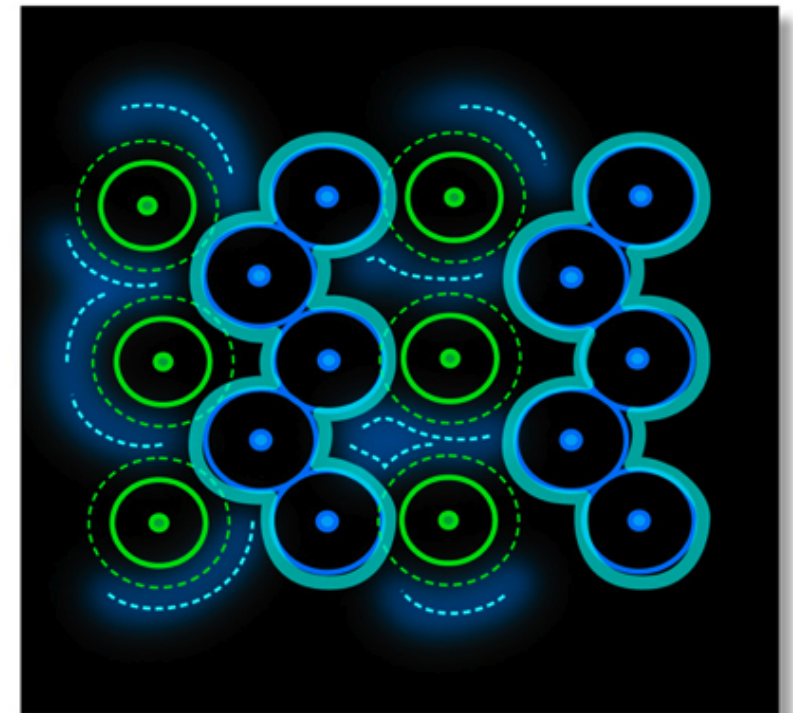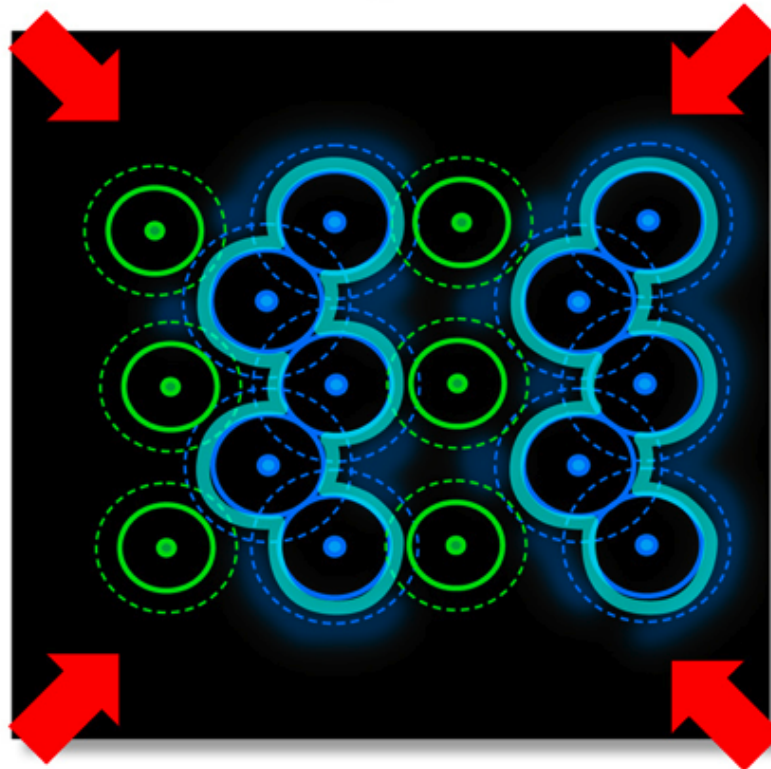# in a Dense Lithium-Beryllium Alloy
Richard G. Hennig, Ji Feng, Neil W. Ashcroft and Roald Hoffmann
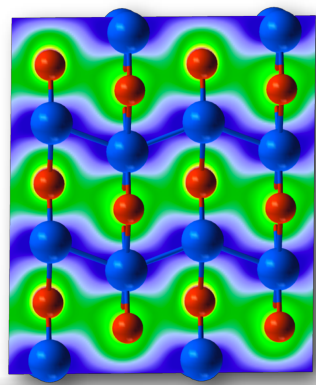
Li-Be alloy is unstable at ambient pressure.

Li-Be alloy is stabilized at high density & pressure. Li ionic cores start to overlap, forming "walls".

Li's outer electrons are forced to Be's layer, forming a 2D electron gas there
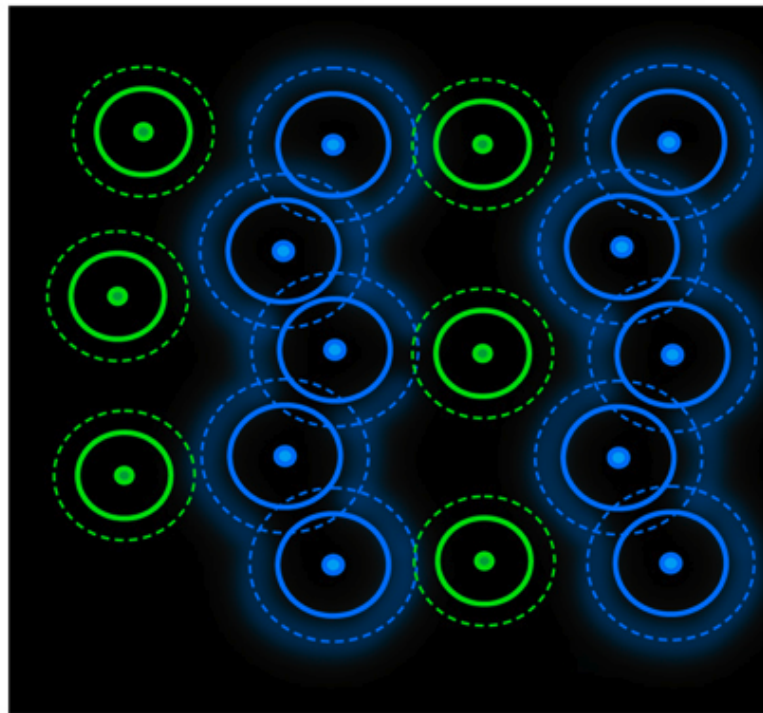
Element	Ionic core	Outer electrons
Li—Lithium 3rd element; elemental metal	Larger core than Be	1e
Be—Beryllium 4th element; elemental metal	Smaller core than Li	These are valence electrons that bounce about quite freely in the elemental metals 2e

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Nature 451, 445 (2008)

Formation of a Two-Dimensional Electron Gas in a Dense Lithium-Beryllium Alloy

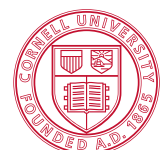**Richard G. Hennig, Ji Feng, Neil W. Ashcroft and Roald Hoffmann**
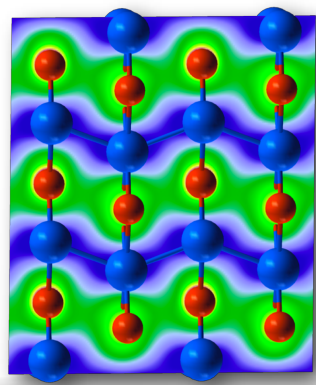
Do Li and Be form alloys?   What are their electronic structures? Can they have higher superconducting temperatures than pure Li and Be?

- Li and Be form intermetallic compounds under pressure

- Possible enhancement of T_c through increased density of states

- 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

(a)   (b)

Be
Li
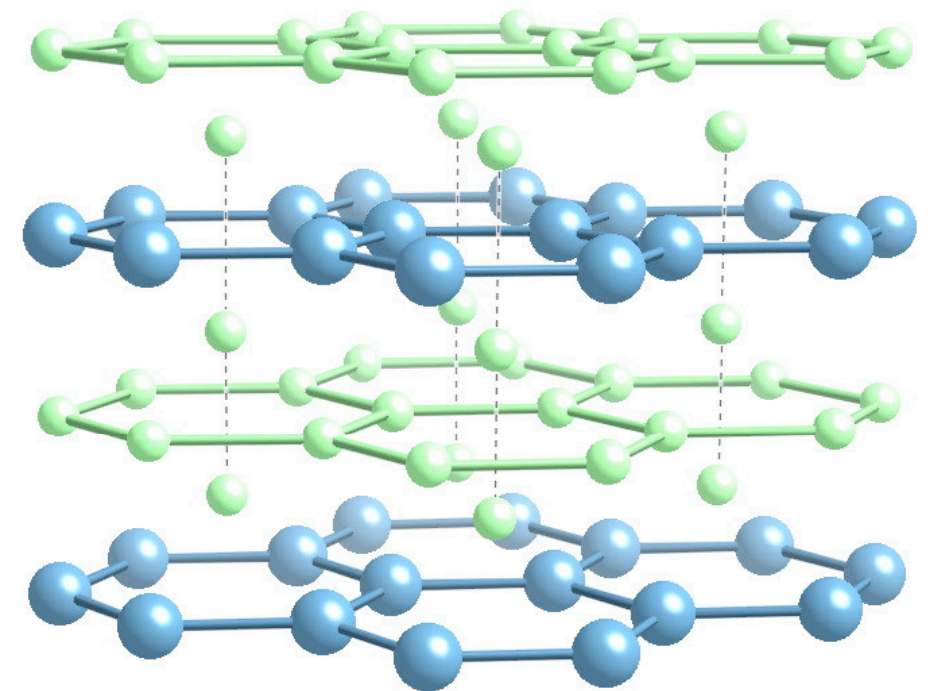
They used to be called the simple elements

Cornell University
College of Engineering
Materials Science and Engineering

rhennig@cornell.edu

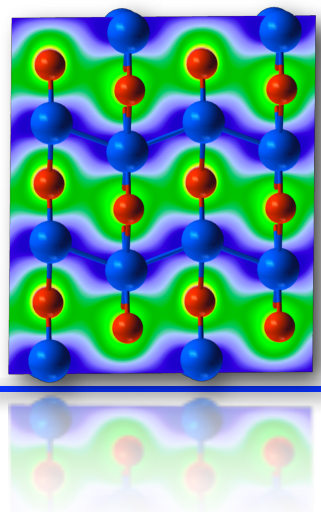# Two Open Postdoc Positions
Computational Materials Science – Cornell University

1. Modeling and design of strongly correlated transition metal oxides

- Joined between RGH (Materials Science and Engineering) and Craig Fennie (Applied and Engineering Physics)

- DFT, GW, and QMC computations to understand the physics and materials science of complex oxide bulk solids and nanostructures

- MRSEC program "Controlling ComplexElectronic Materials"

2. Quantum Monte Carlo Petascale Algorithms and Applications

- Joined between RGH (Materials Science and Engineering) and Cyrus Umrigar (Physics)

- DOE program "Quantum Monte Carlo Endstation for Petascale Computing"

If you are interested, talk to me or Cyrus or e-mail us.

Cornell University
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rhennig@cornell.edu