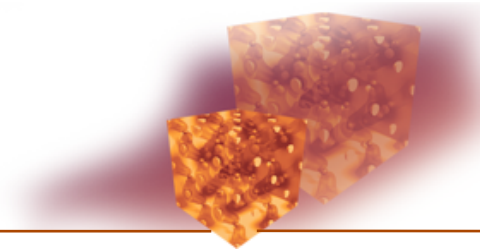
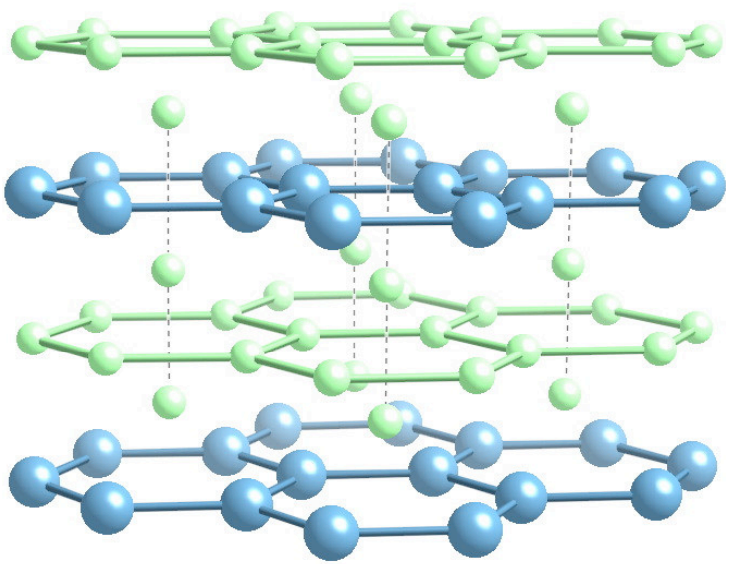
2007 International Workshop
Quantum Monte Carlo in the Appuan Alps
July 21 –28, 2007 • The Towler Institute, Vallico Sotto, Tuscany
http://www.vallico.net/tti/tti.html



Emergent 2d behaviour in a 3d electronic environment: Dense Be-Li alloys

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

- Do Be and Li form alloys?
- What is their electronic structure?
- Can they have higher superconducting temperatures than pure Be and Li?



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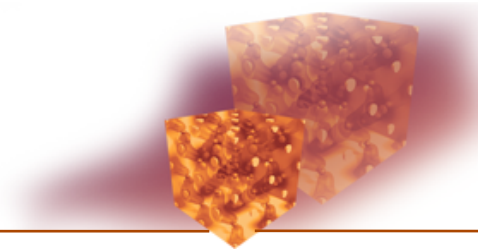
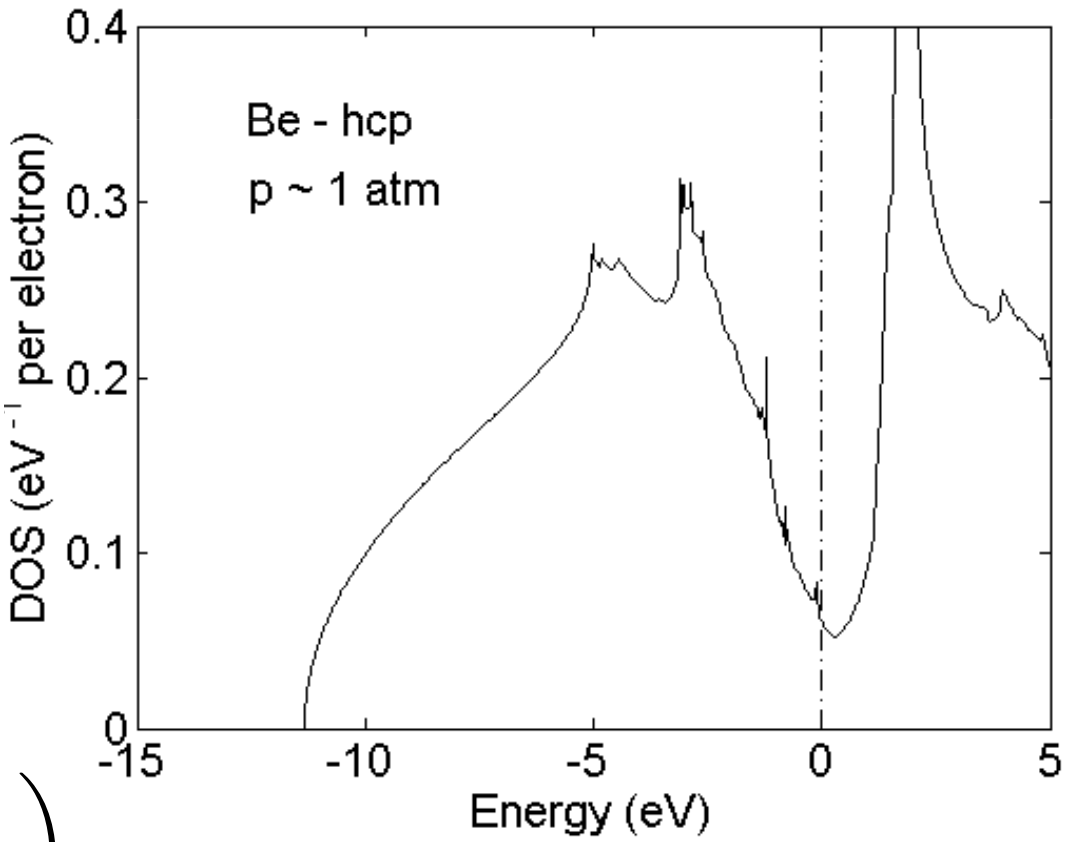
The Beryllium Story



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

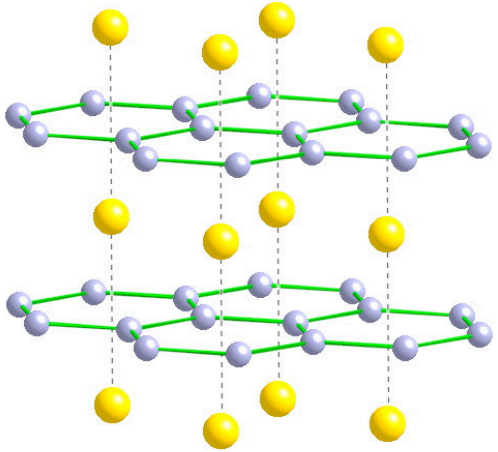
- BCS formula

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

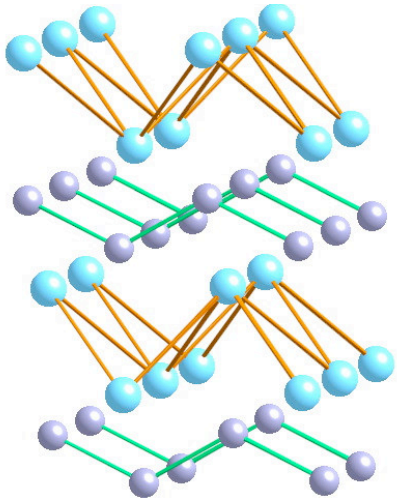
- If $g_0 V$ **increases** $\quad g_0' \cdot V' = \alpha \cdot g_0 \cdot V \qquad T_c' = T_c \cdot \dfrac{(2.3 \cdot 10^{-5})^{1/\alpha}}{2.3 \cdot 10^{-5}}$
- Alloying with light elements: Light, metallic, electropositive

Structural Prediction

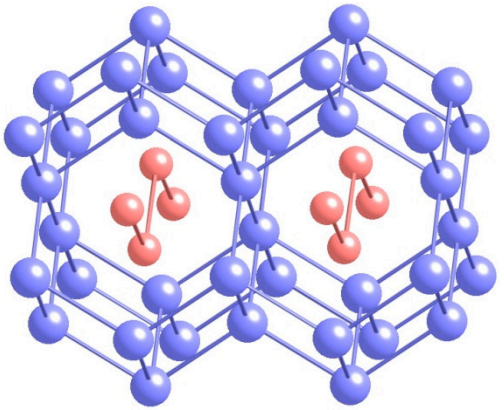
- Do we understand the structures of intermetallic compounds?
- Can we predict the structure of compounds given the stoichiometry?



MgB_2



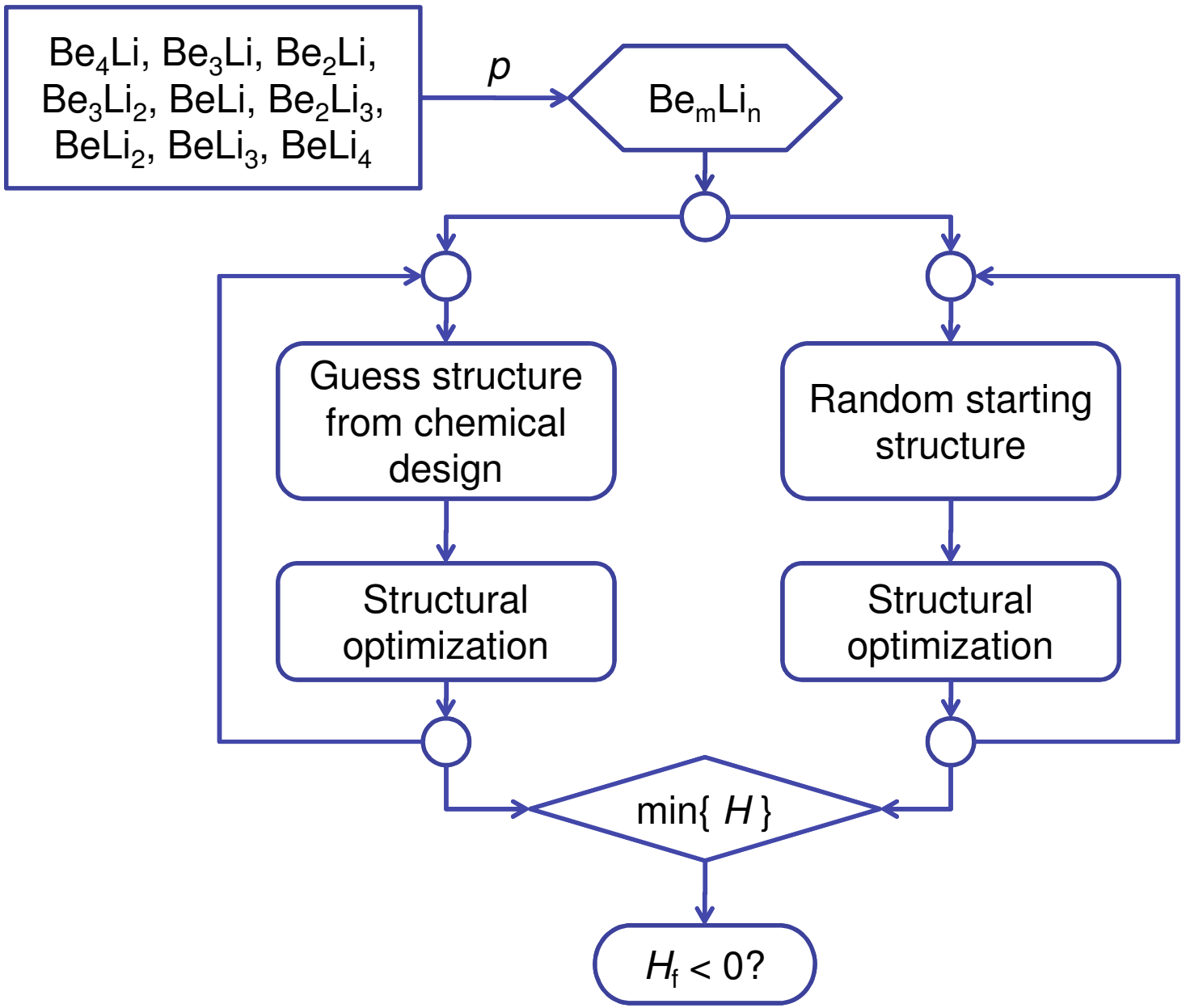
CrB



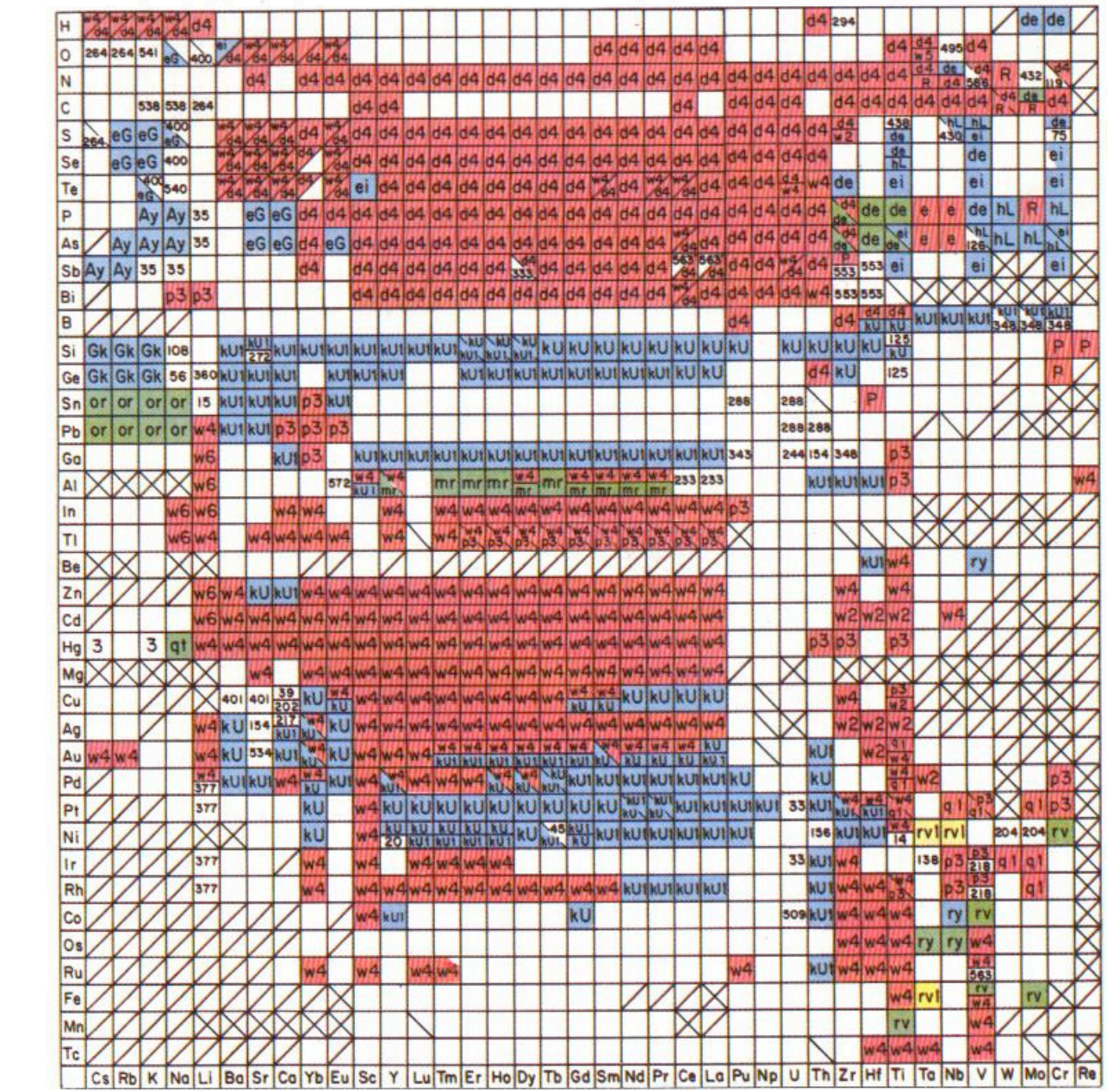
$GaLi_2$

- Now, what about MgB_4 or $Cr_{0.08}B_{3.10}$?
- Or prediction of high pressure phases?

Structural Search Algorithm

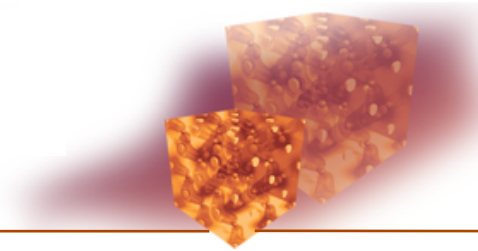


Structure Maps



- Pettifor structure map of ordered A–B alloys

Computational Detail



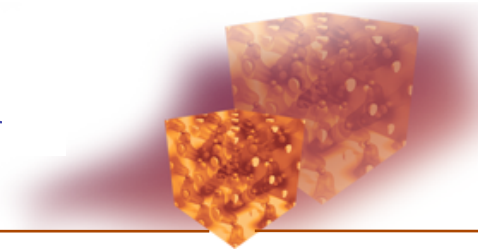
Density functional theory

- 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 %

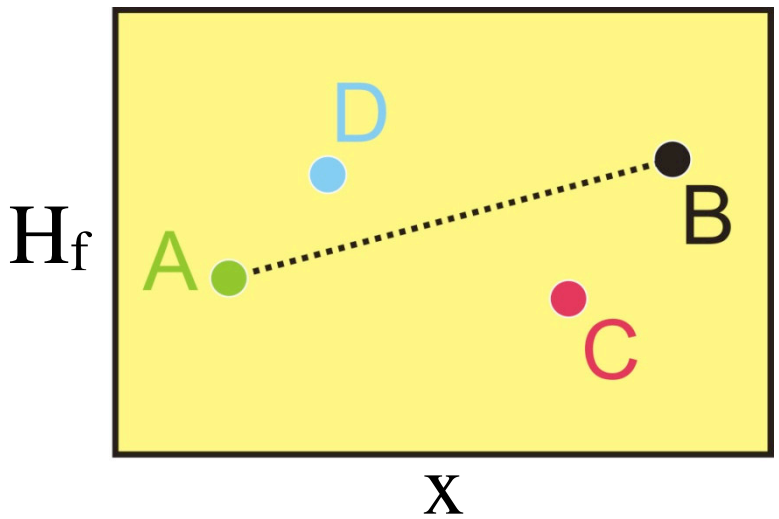
Enthalpy of Formation & Phase Diagram



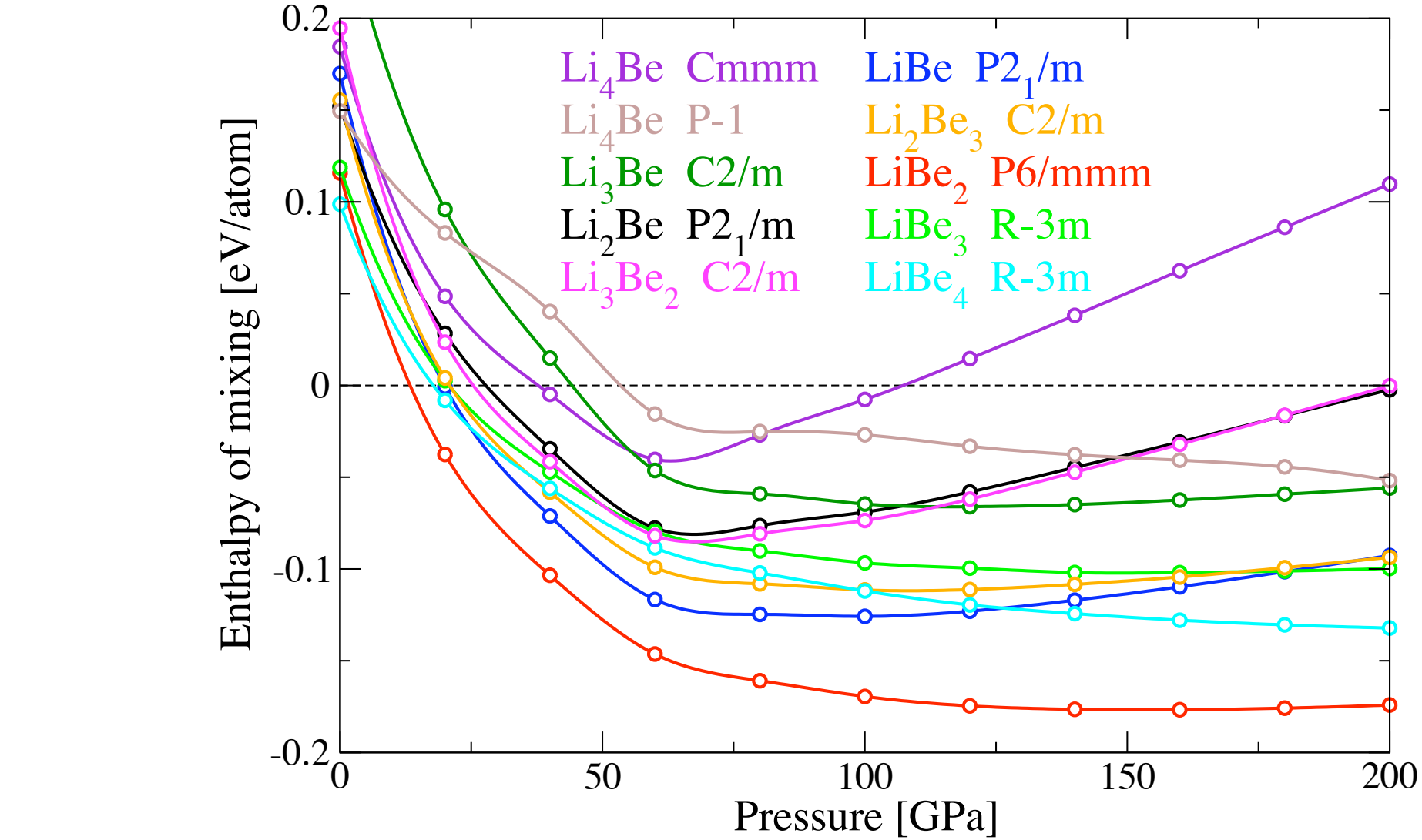
- Enthalpy of formation per atom from enthalpies at same pressure

$$H_f(\mathrm{Be}_{1-x}\mathrm{Li}_x) = H(\mathrm{Be}_{1-x}\mathrm{Li}_x) - (1-x)\cdot H(\mathrm{Be}) - x\cdot H(\mathrm{Li})$$

- Also known as enthalpy of mixing
- Phase diagram from tie lines of formation enthalpies

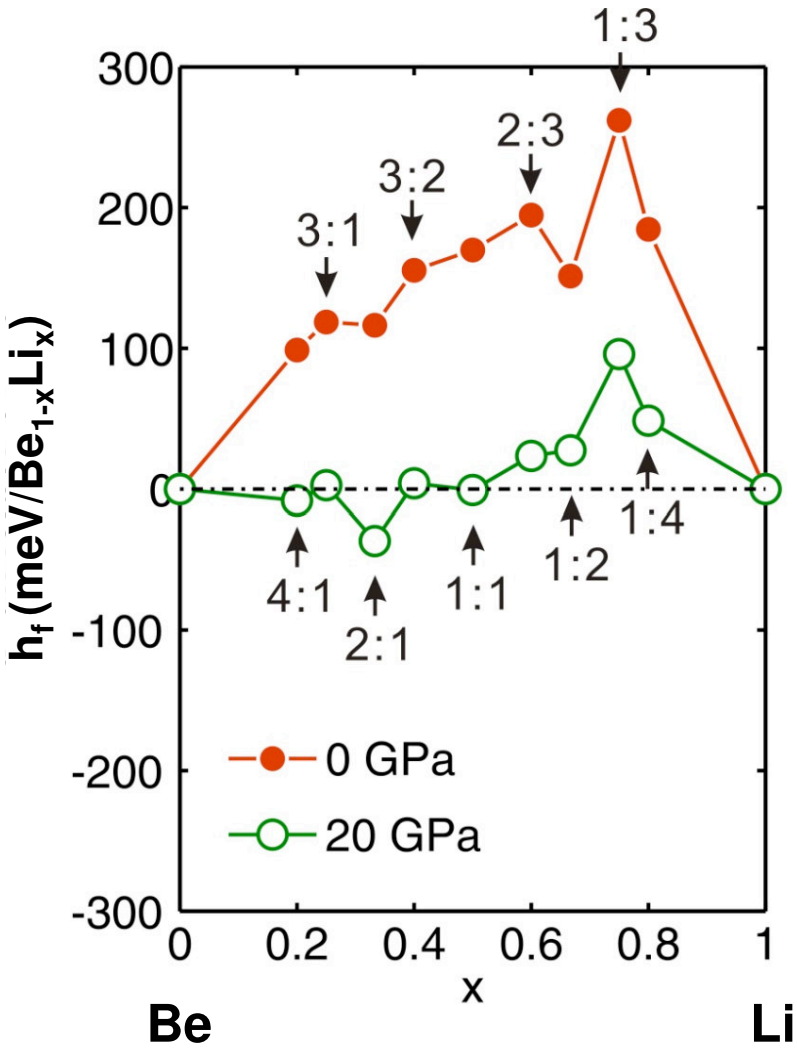


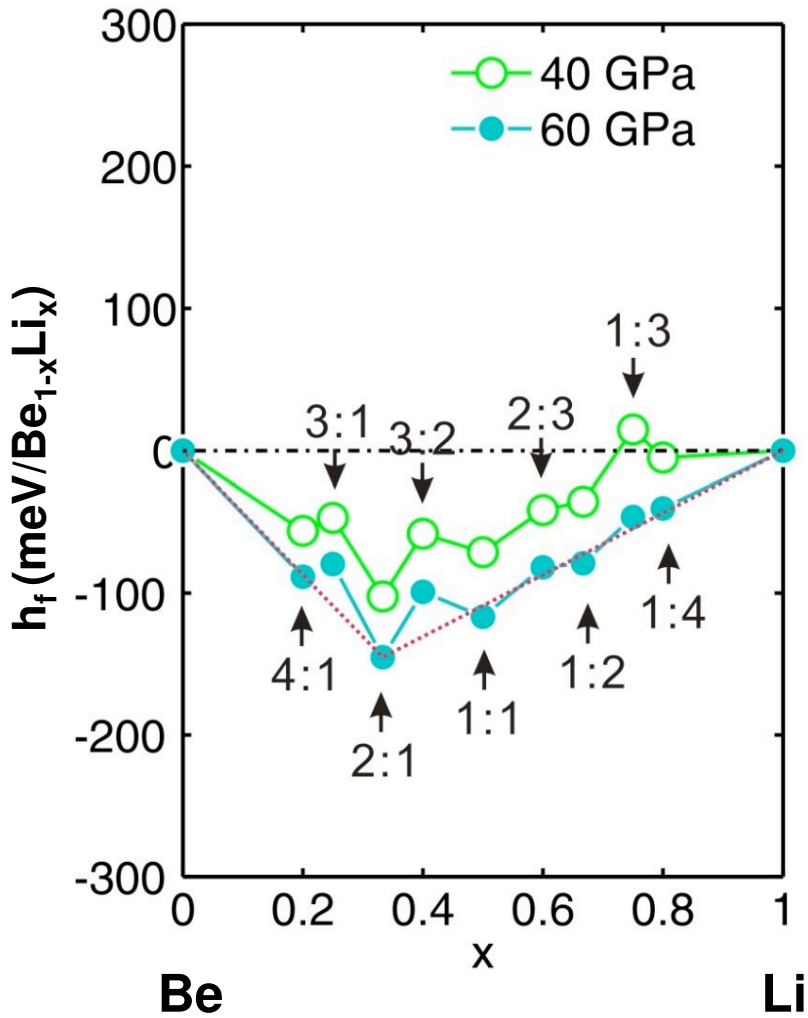
Results for Enthalpy of Formation



Stability increases with pressure dramatically at low pressures

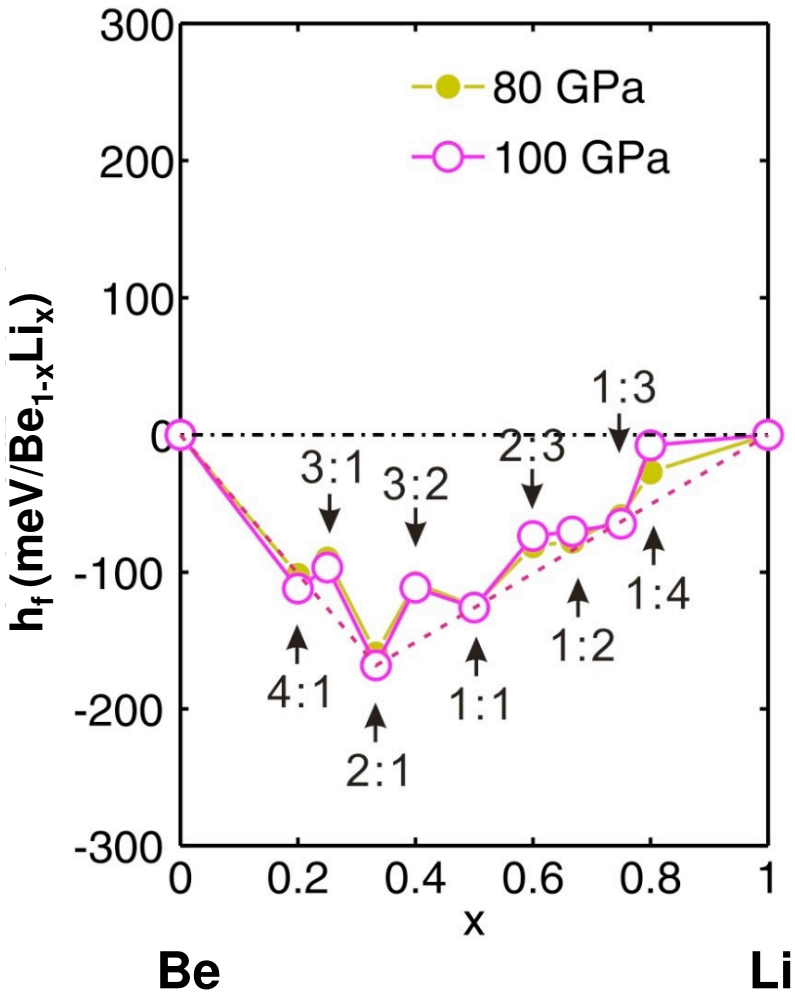
Low Pressure Phase Stability

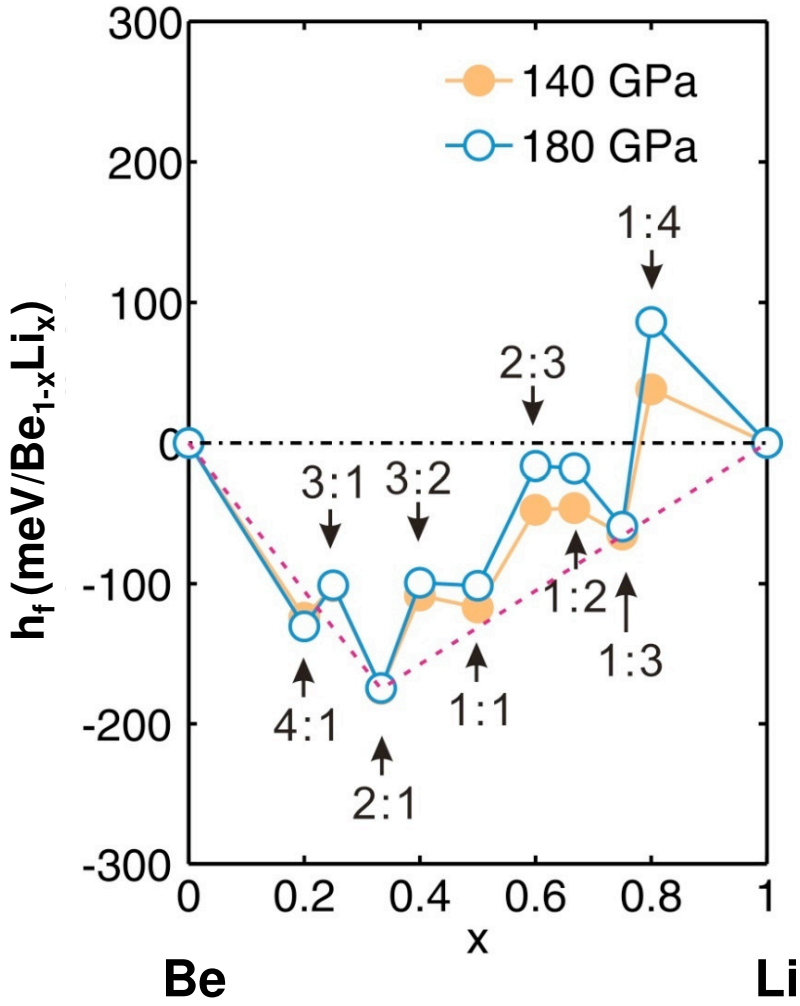




Be_2Li stable above 20 GPa and BeLi above 40 GPa

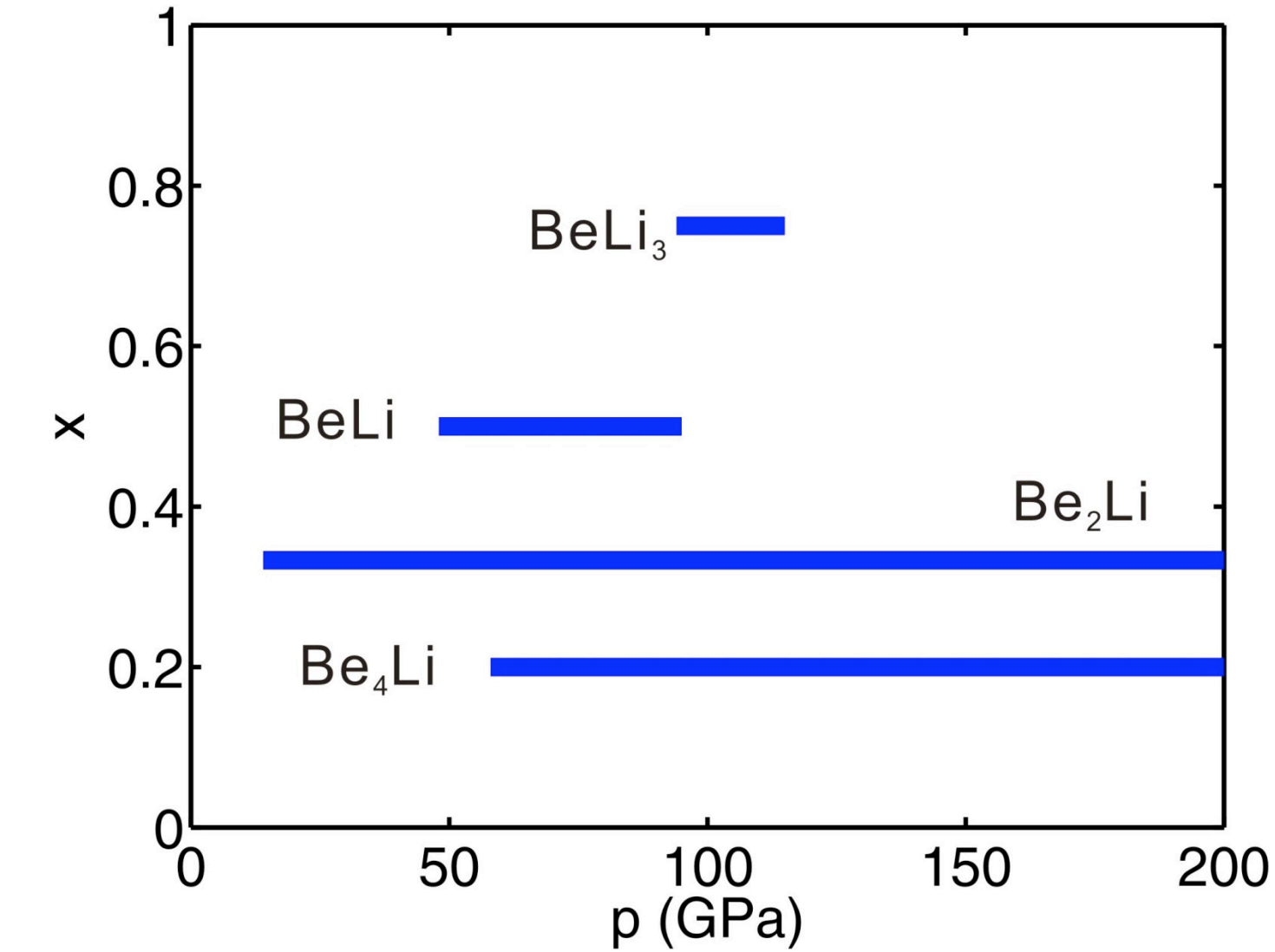
High Pressure Phase Stability





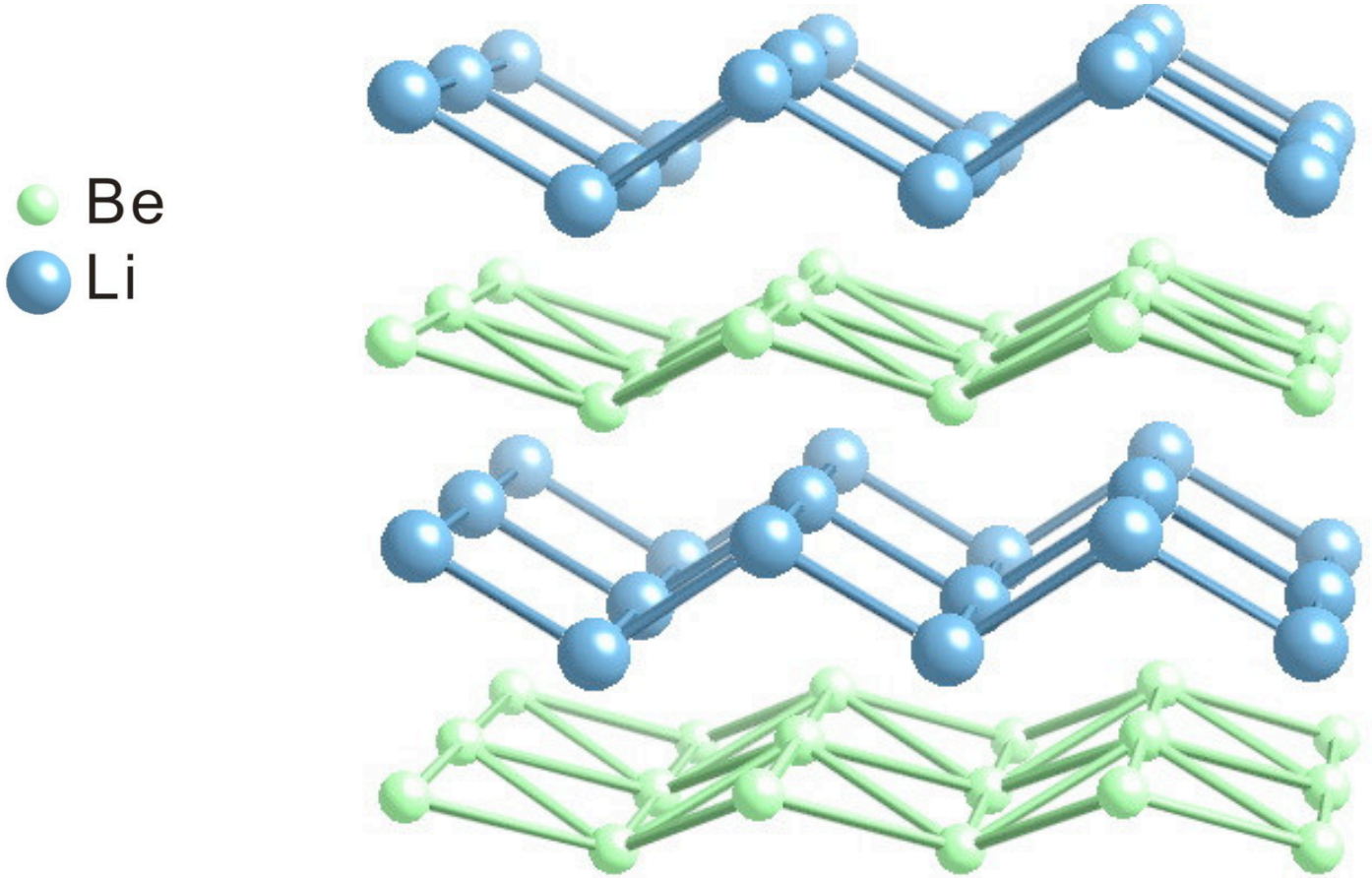
Be_4Li stable above 80 GPa and $BeLi_3$ almost stable at 140 GPa

Phase Diagram of LiBe under Pressure

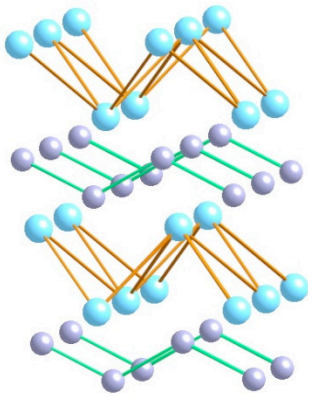


Four novel BeLi phases become stable under pressure

The Stable BeLi phase ($P2_1/m$)

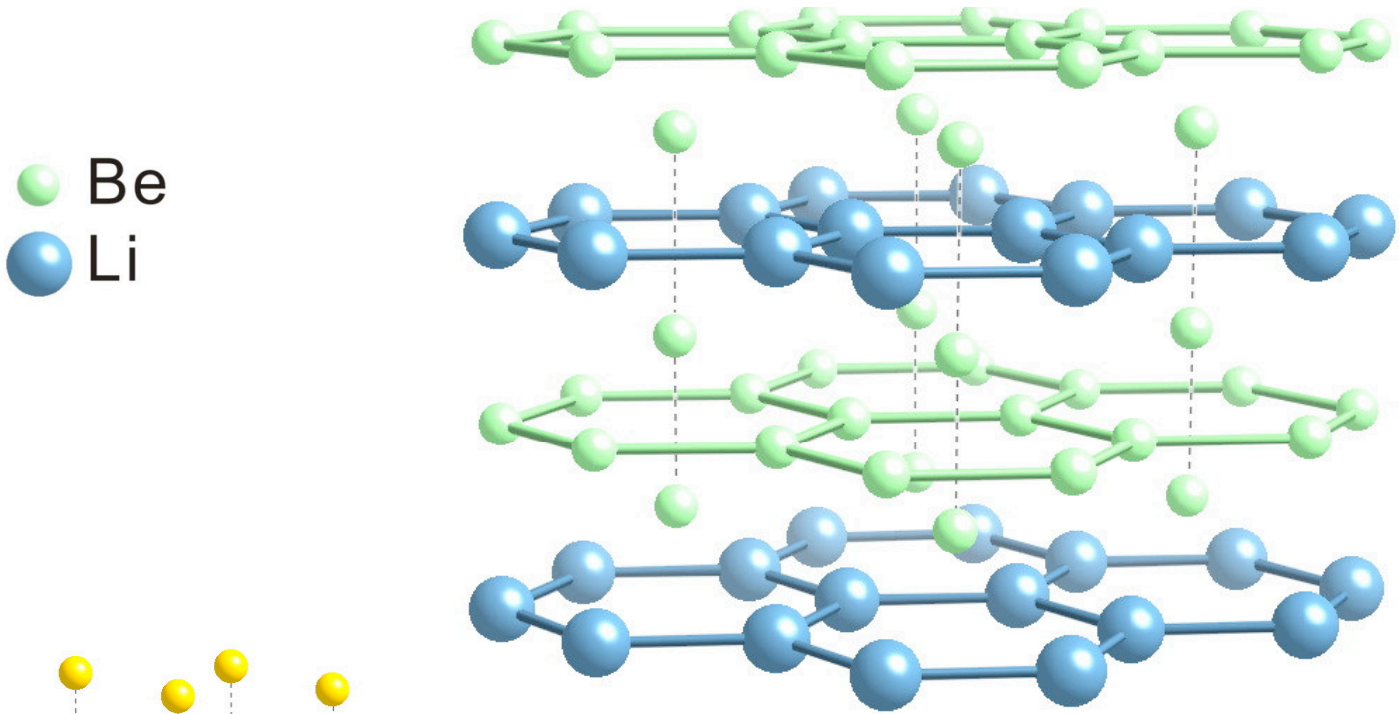


BeLi (82 GPa)
$P2_1/m$

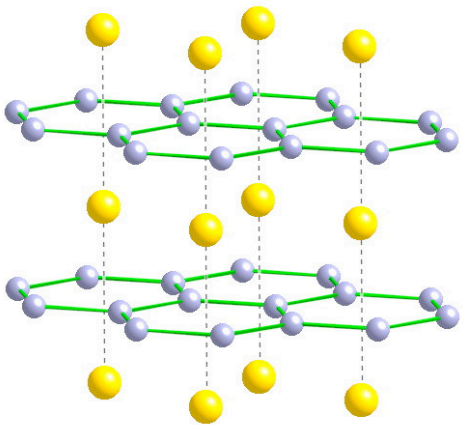


CrB

The Stable Be_2Li phase (P6/mmm)

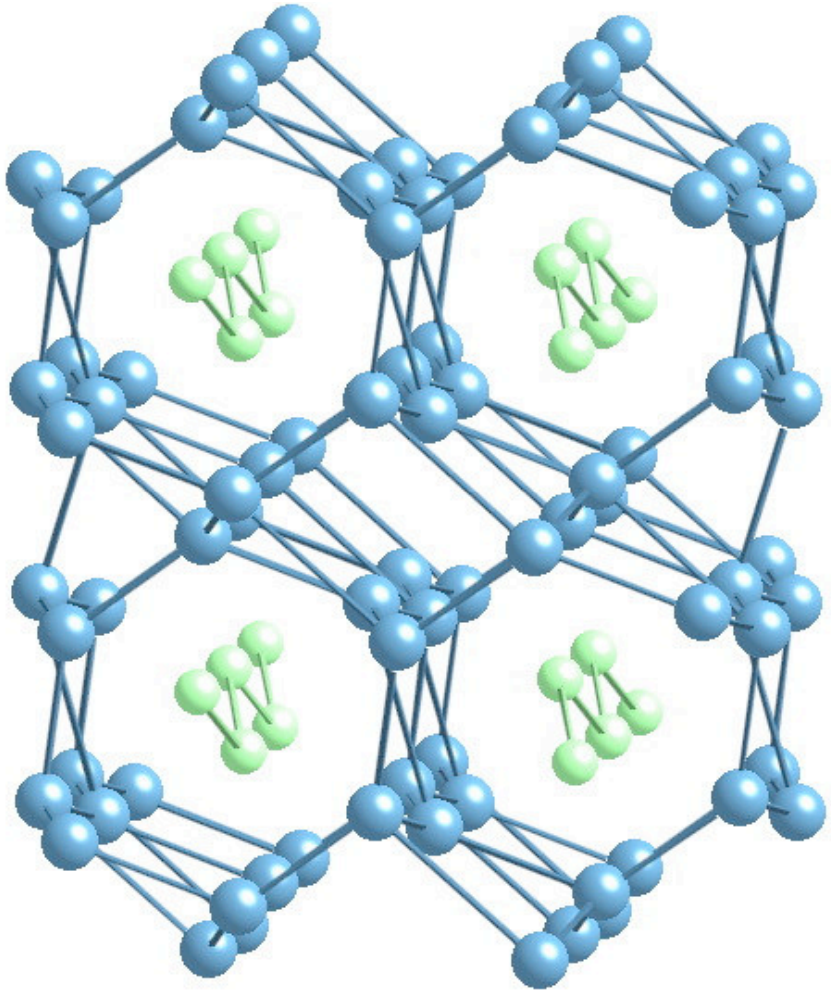


Be_2Li (80 GPa)
P6/mmm

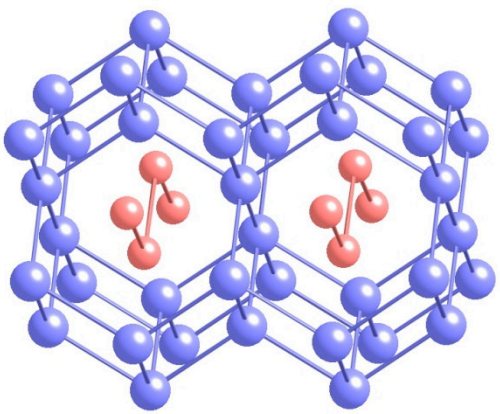


MgB_2

The Stable $BeLi_3$ phase (C2/m)

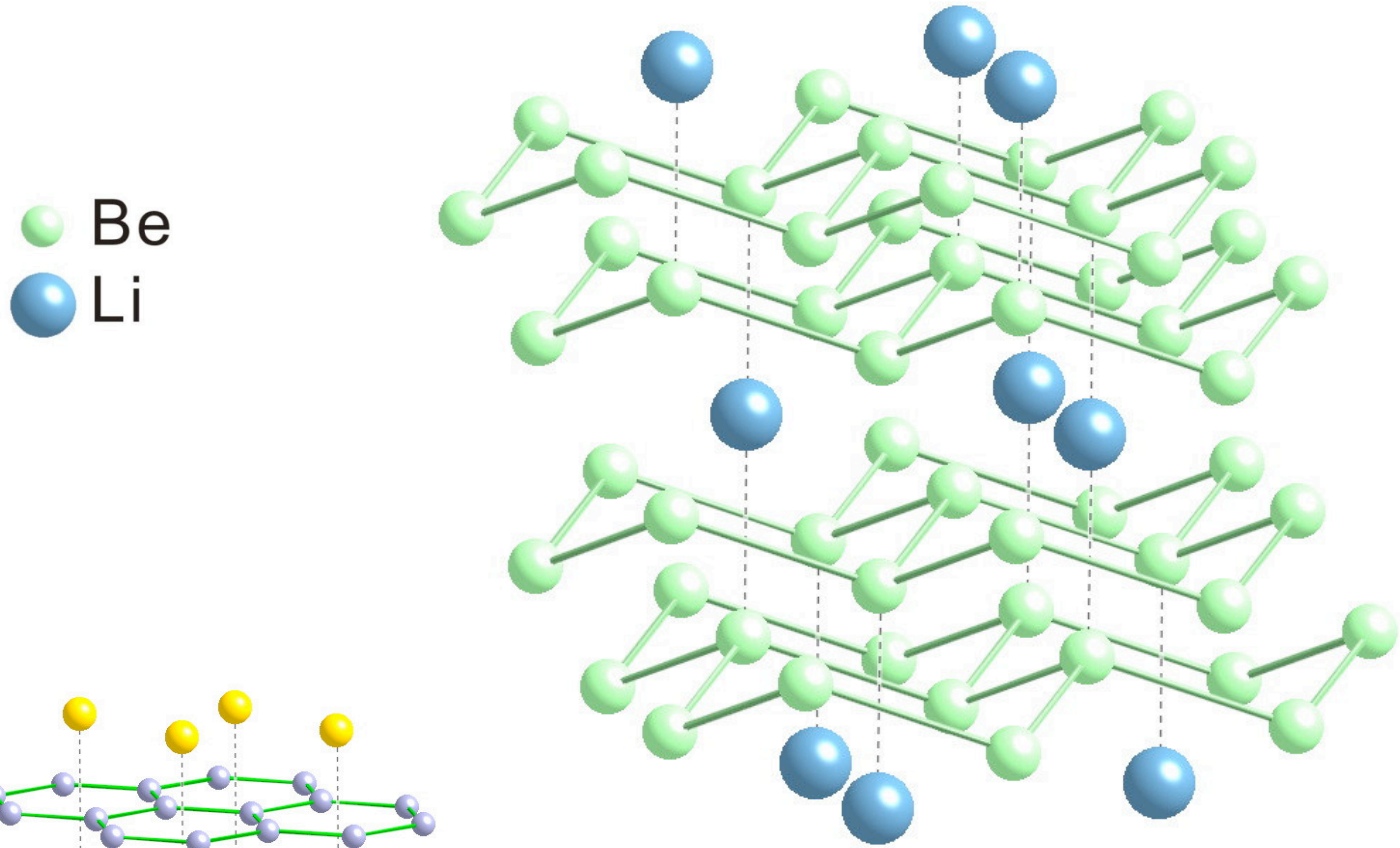


BeLi3 (80 GPa)
C2/m

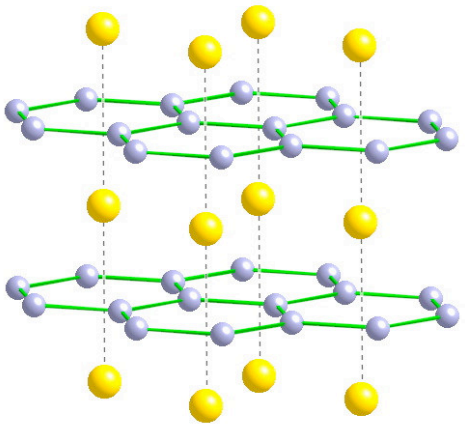


$GaLi_2$

The Stable Be_4Li phase (R-3m)



Be_4Li (80 GPa)
R3m

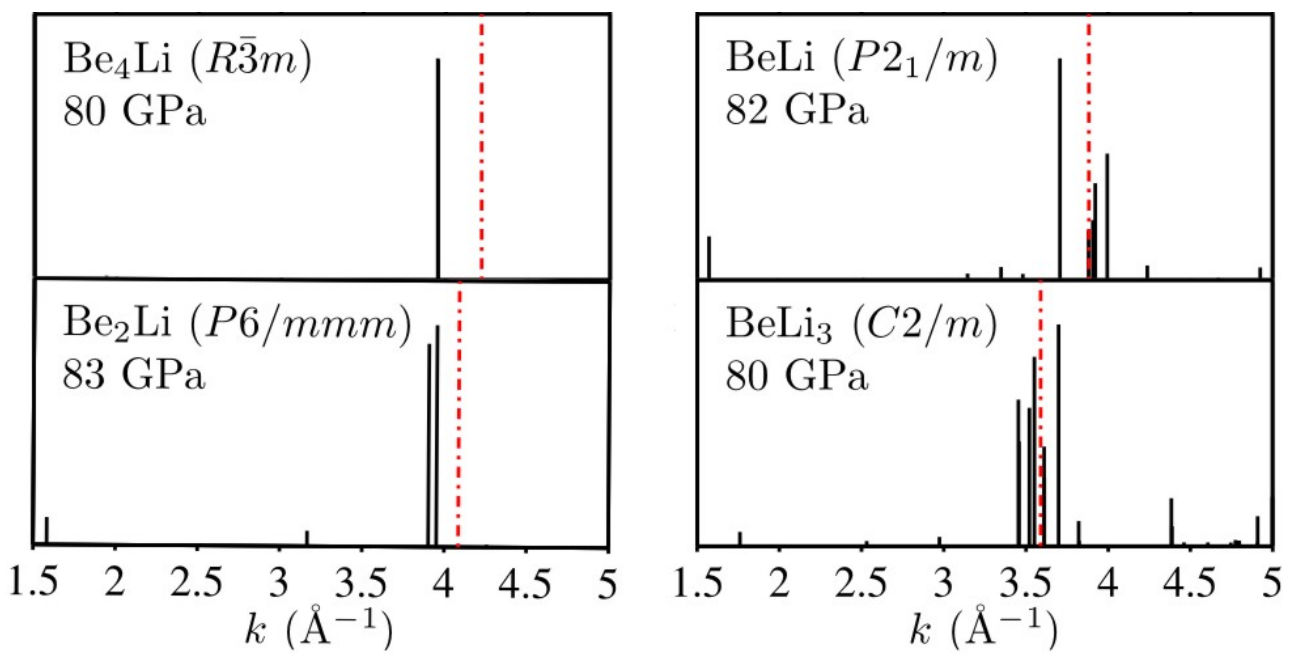


MgB_2

Stabilization of Be-Li alloys

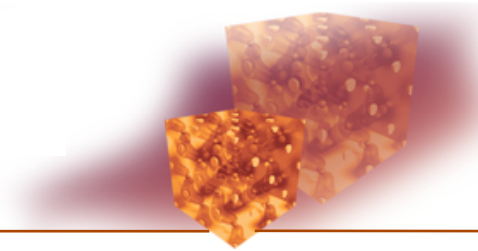
Simulated x-ray diffraction pattern

- Cluster of diffraction peaks near 2 k_F
- Strong interaction between Brillouin zone and initially free-electron Fermi surface ⇒ Pseudogap in density of states



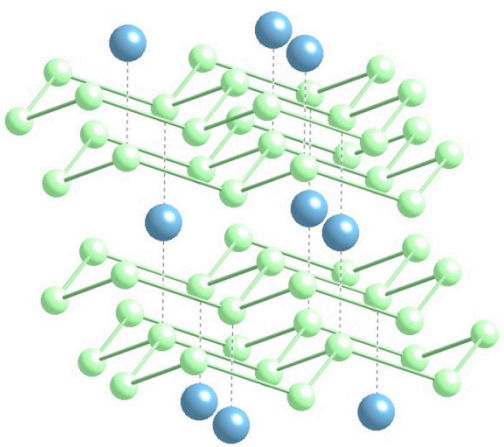
Potential stabilization by Hume-Rothery mechanism

Fermi Density of States

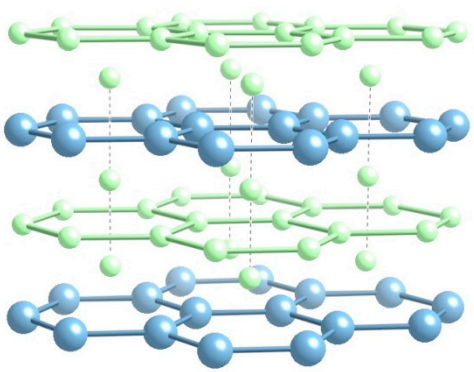


- Beryllium's DOS at the Fermi level is nearly constant over entire pressure range: $g(\varepsilon_F) = 0.04$ eV^{-1} per valence electron

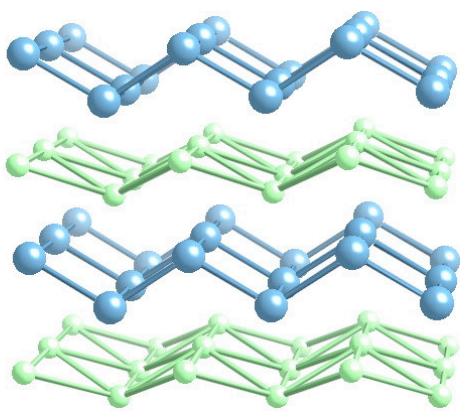
80 GPa	Be_4Li R-3m	Be_2Li P6/mmm	BeLi $P2_1/m$
$g(\varepsilon_F)$ in eV^{-1} per valence electron	0.06	0.06	0.12



Be_4Li



Be_2Li

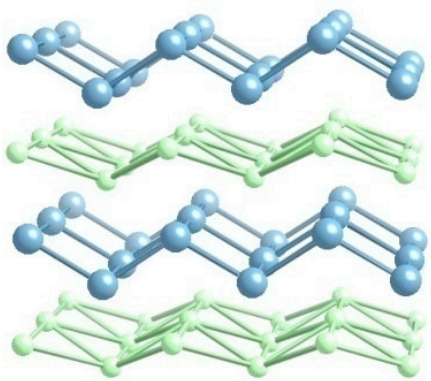


BeLi

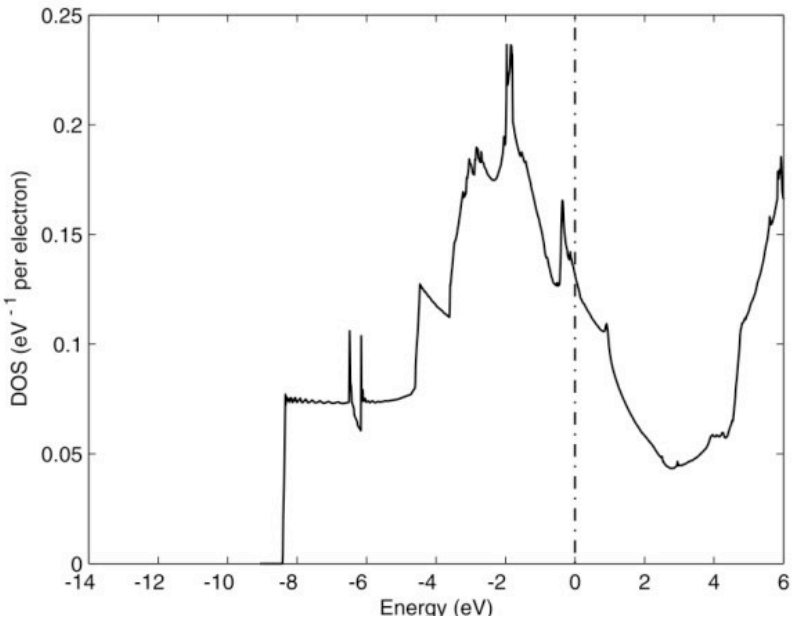
For a comparable e-ph coupling, T_c would be about 32 K

Electronic Structure of BeLi ($P2_1/m$)

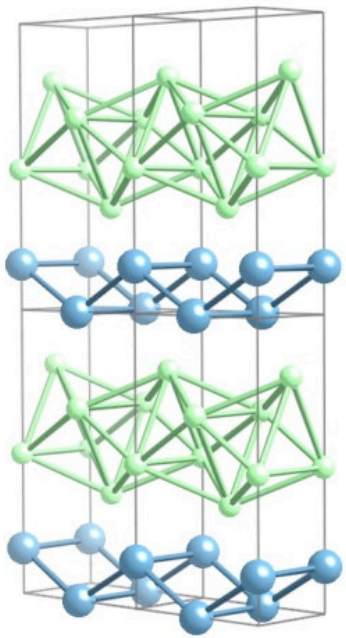
BeLi
$P2_1/m$

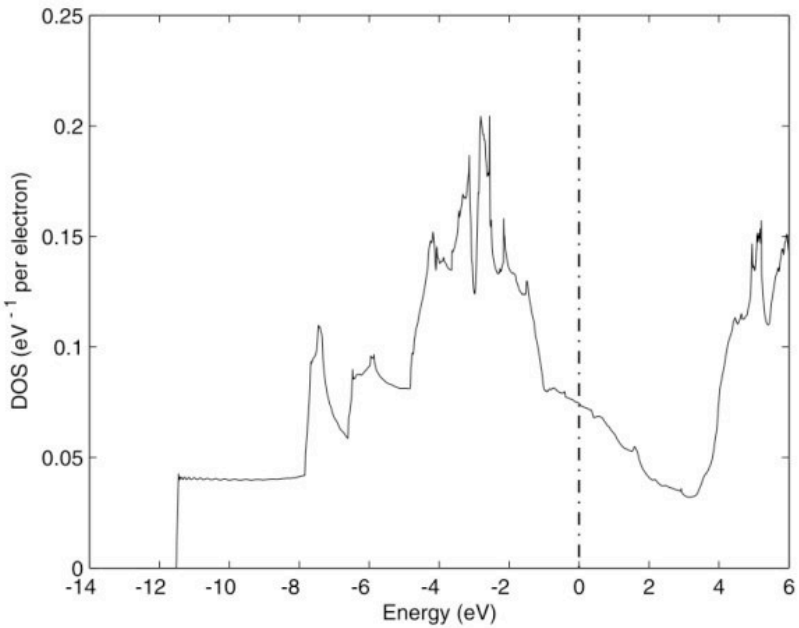


Be
Li

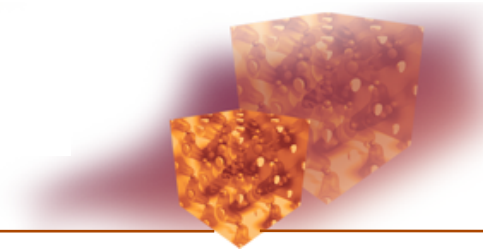


Be_2Li
Pmcm

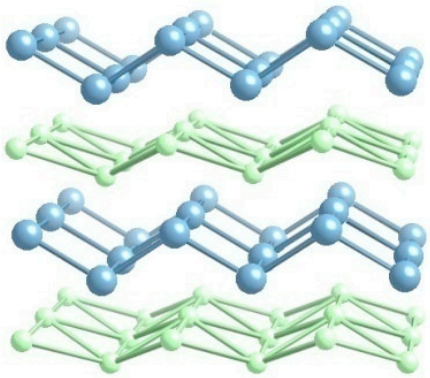




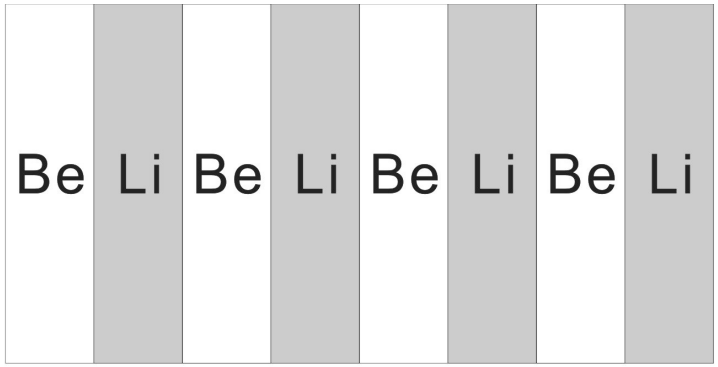
Electronic Structure of BeLi ($P2_1/m$)

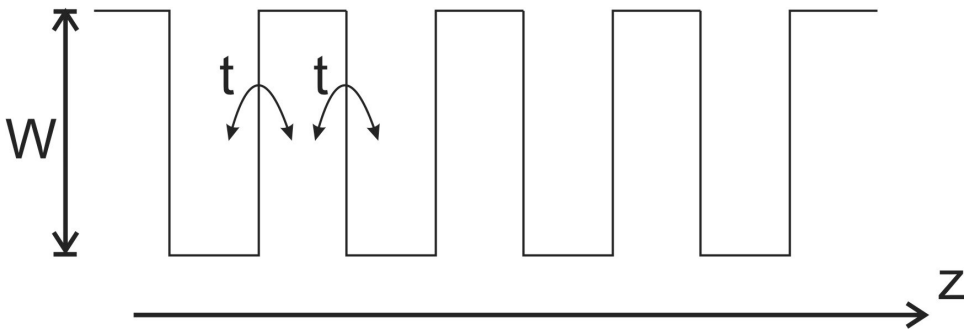


BeLi
$P2_1/m$



Be
Li



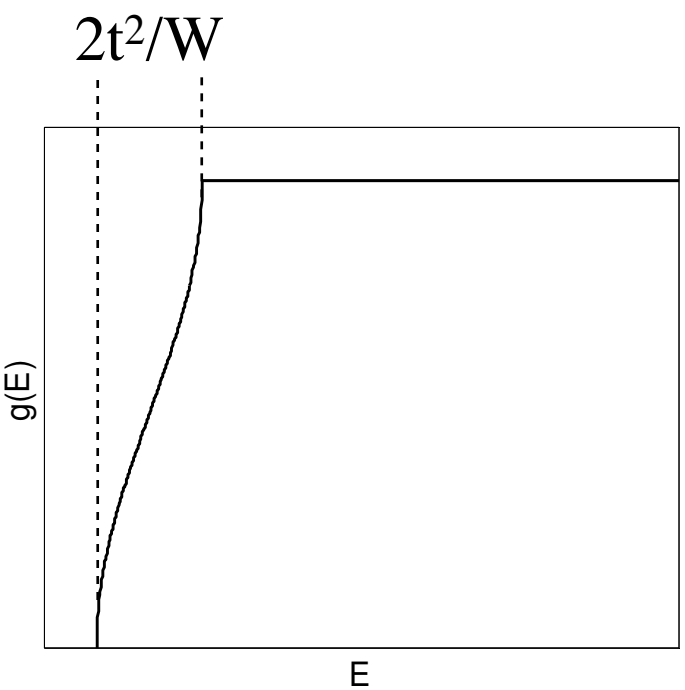


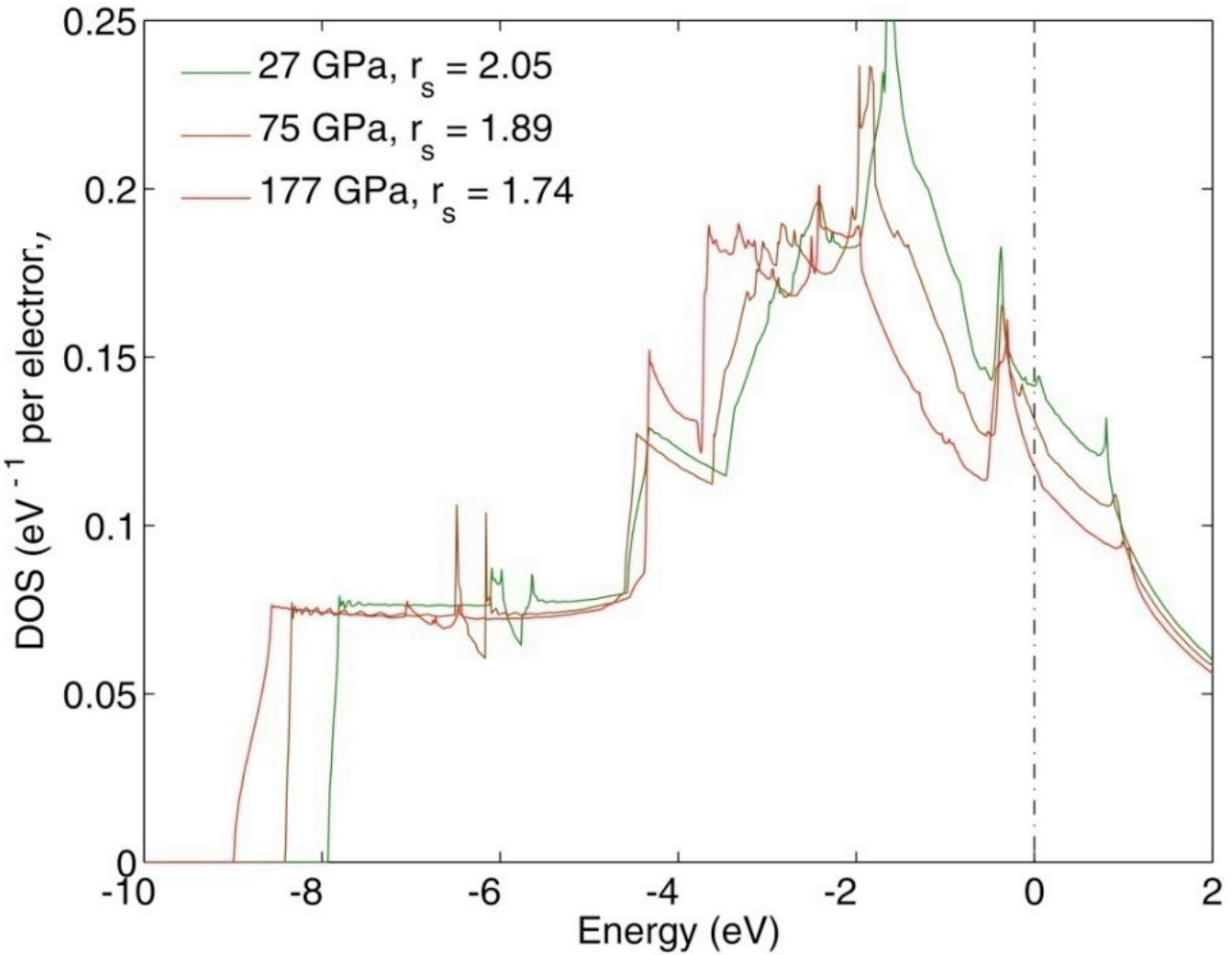
$$\mathcal{H}_{xy} = \sum_{\mathbf{k}} \frac{\hbar^2 k^2}{2m} c_k^\dagger c_k$$

$$\mathcal{H}_z = \epsilon_0 \sum_i n_i + W \sum_i n_{2i+1} - t \sum_i \left(c_i^\dagger c_{i+1} + h.c. \right)$$

Simple model Hamiltonian can be solved exactly

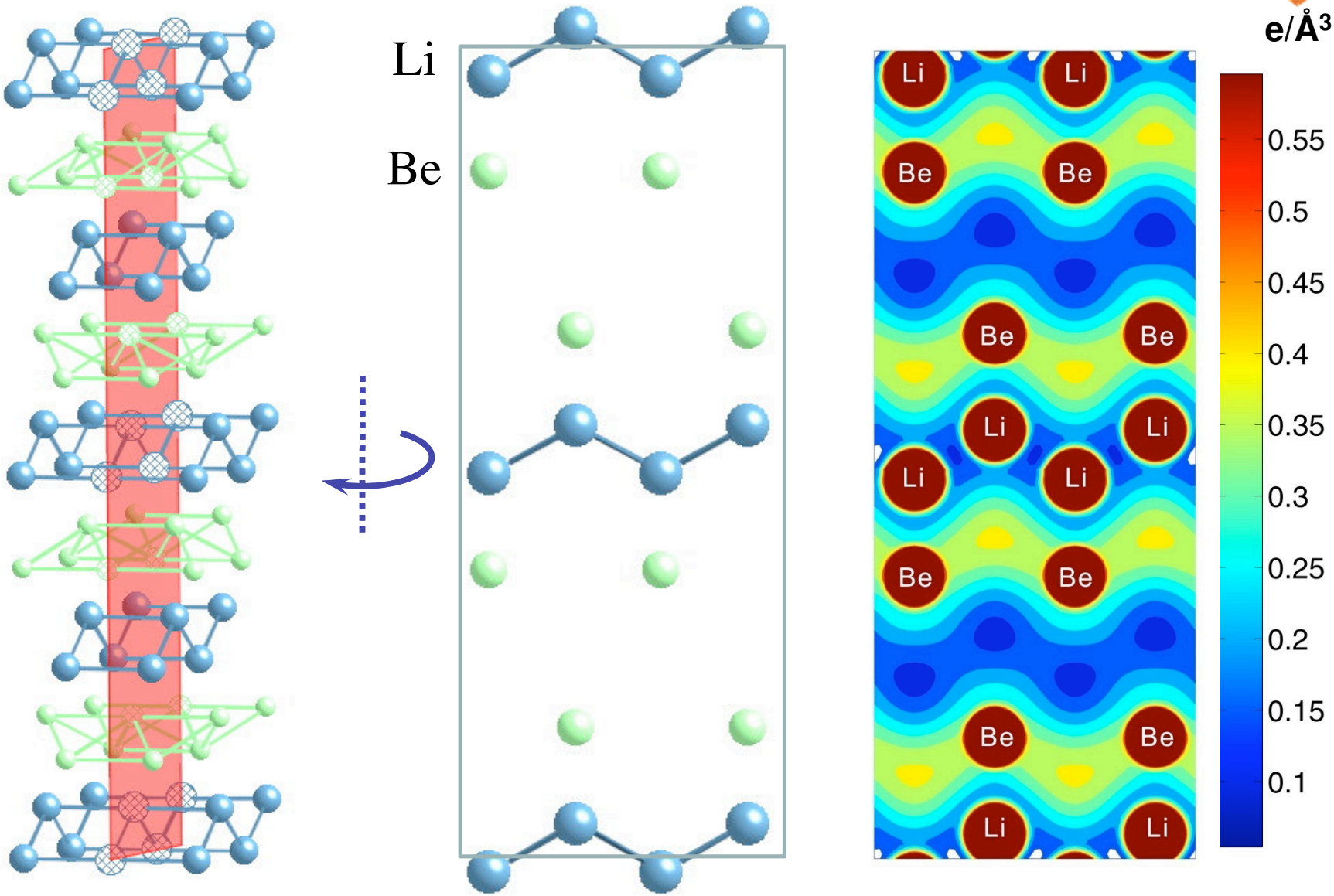
Electronic Structure of BeLi ($P2_1/m$)





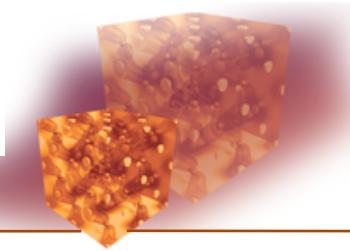
The electronic density of states from model Hamiltonian matches the calculated one.

Electron Density of BeLi ($P2_1/m$)

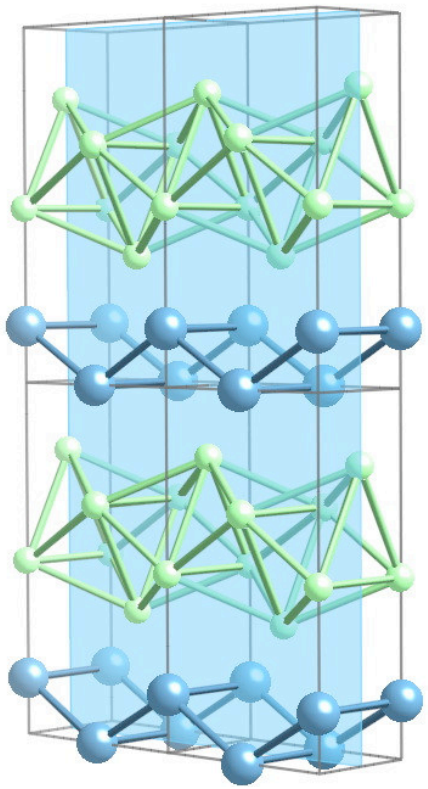


Electron density shows layered structure

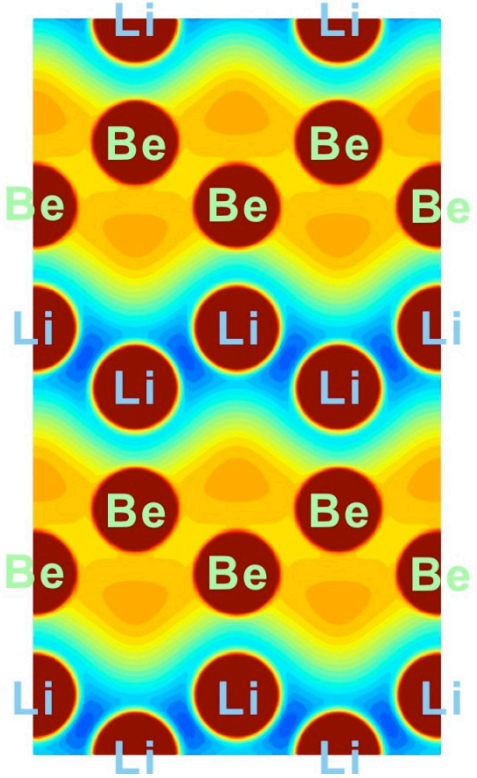
Electron Density of metastable Be_2Li (Pmcm)



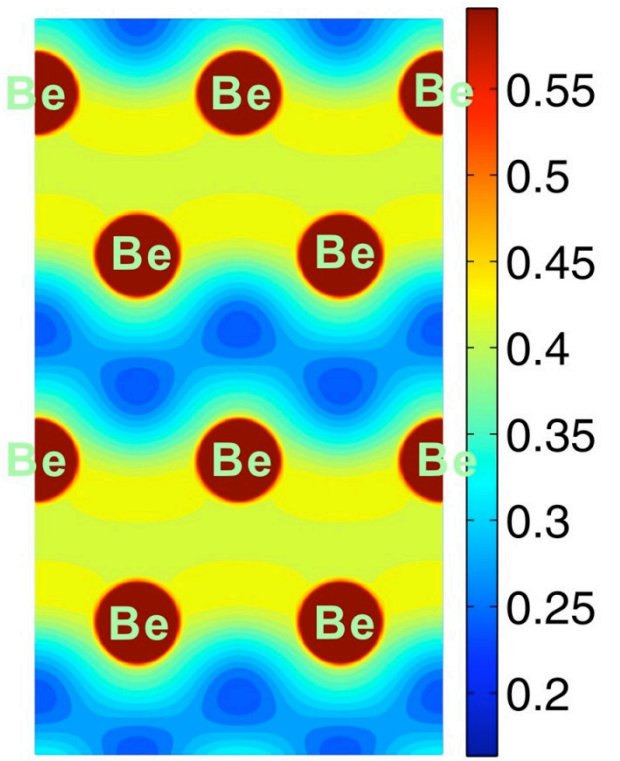
Be_2Li
Pmcm



Front face of the cells

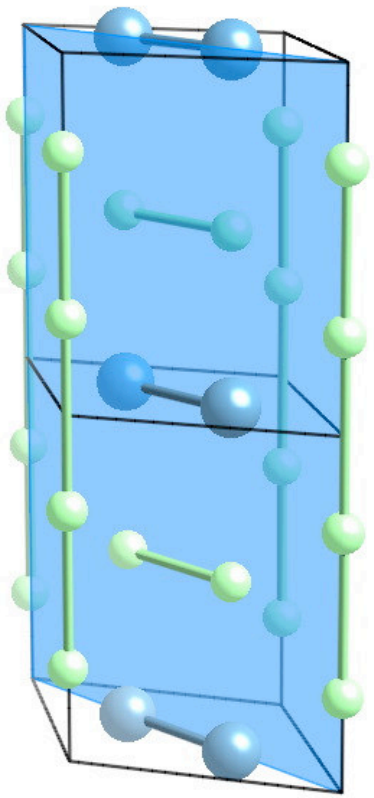


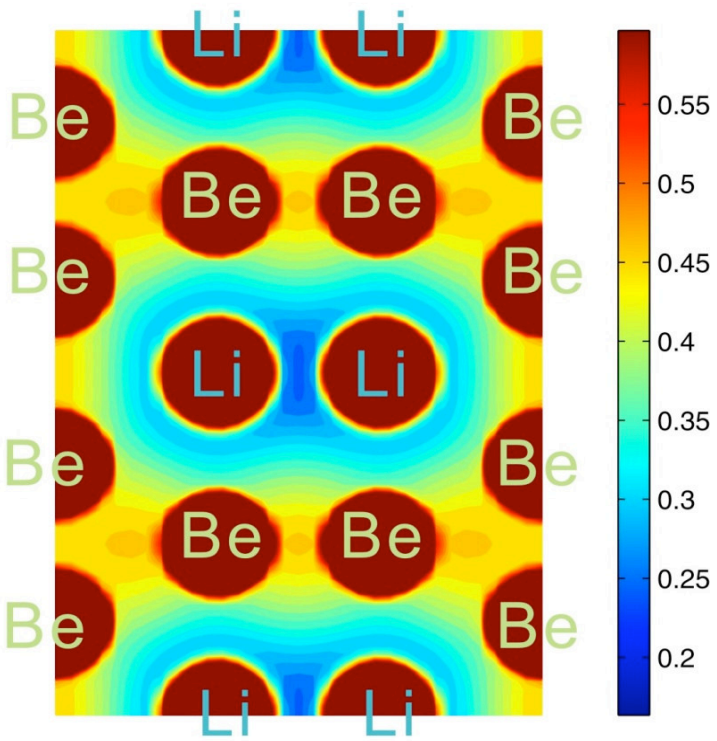
"Blue" cross-section

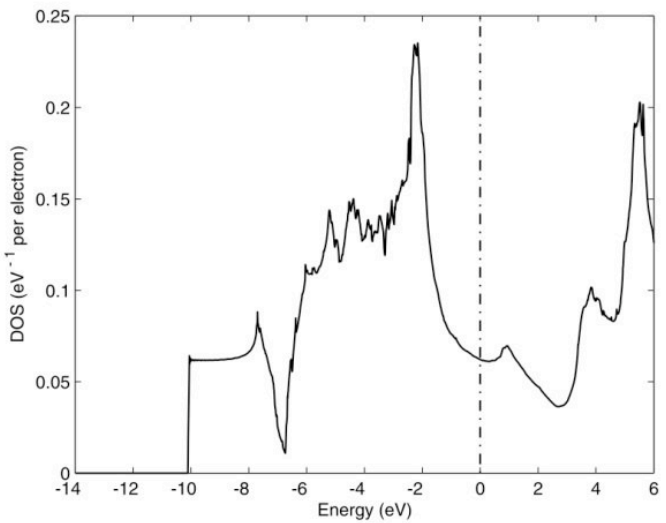


Electron density shows layered structure

Electron Density of stable Be_2Li (P6/mmm)





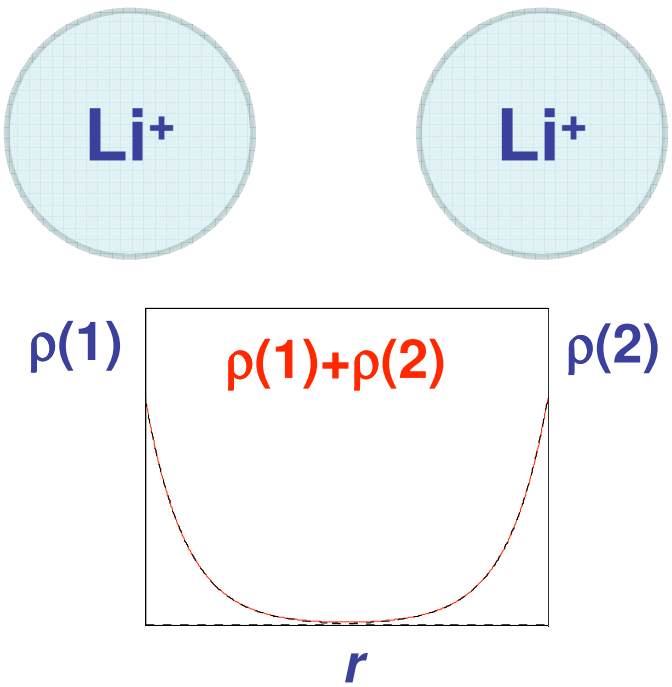


Origin of Charge Disproportionation

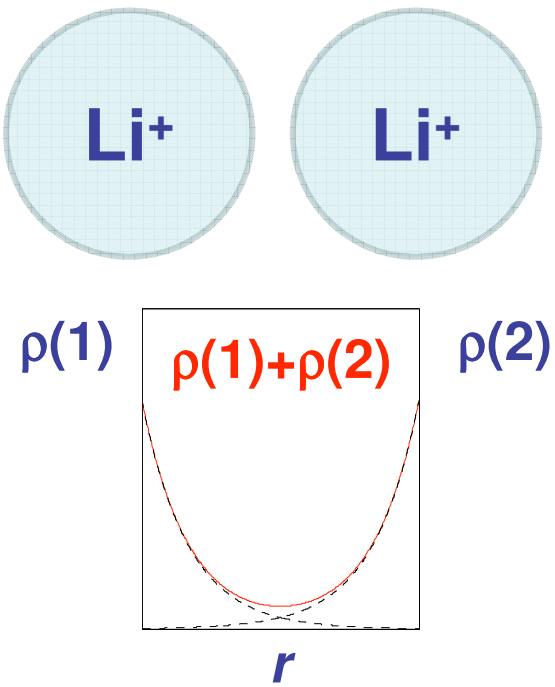
- Large difference in core size of Be and Li

	Li	Be
Z	3	4
Ionic Radius (Å)	0.76	0.27

Low density



High density



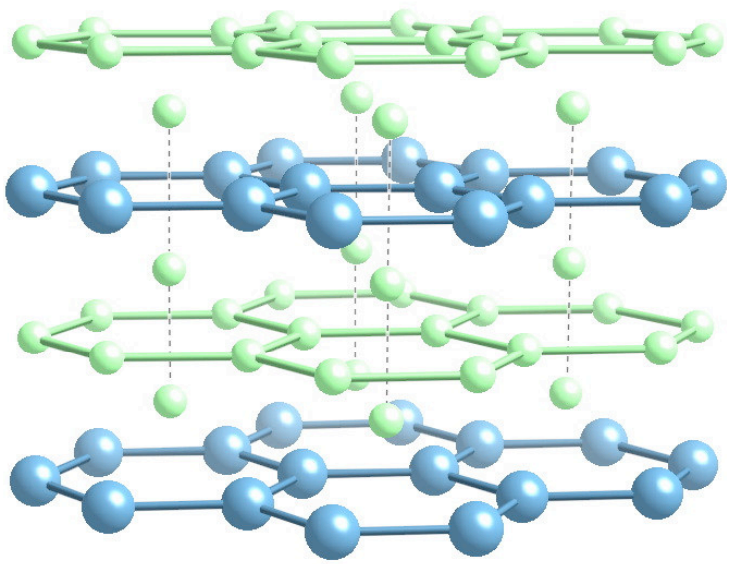
Overlapping core makes internuclear region less accessible to valence electrons

Emergent quasi-2d behaviour in a

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

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