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# **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?





# **The Beryllium Story**

#### **Elemental beryllium**

- Highest Debye temperature of all metallic elements:  $\Theta_{\rm D} = 1100 \text{ K}$
- Superconducting transition temperature of only  $T_c = 26 \text{ mK}$
- Because Be is barely a metal

#### Improve T<sub>c</sub> by alloying

• BCS formula  $T_{\rm c} = 1.13 \cdot \theta_D \exp\left(-\frac{1}{g_0 \cdot V}\right)$ 

• If  $g_0 V$  increases  $g'_0 \cdot V' = \alpha \cdot g_0 \cdot V$   $T'_c = T_c \cdot \frac{(2.3 \cdot 10^{-5})^{1/\alpha}}{2.3 \cdot 10^{-5}}$ 

• 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?



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

### **Structural Search Algorithm**



### **Structure Maps**

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• 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:

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

## **Enthalpy of Formation & Phase Diagram**

• Enthalpy of formation per atom from enthalpies at same pressure

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

- 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<sub>2</sub>Li stable above 20 GPa and BeLi above 40 GPa

### **High Pressure Phase Stability**



Be<sub>4</sub>Li stable above 80 GPa and BeLi<sub>3</sub> almost stable at 140 GPa

### Phase Diagram of LiBe under Pressure





#### The Stable BeLi phase (P2<sub>1</sub>/m)





CrB

### The Stable Be<sub>2</sub>Li phase (P6/mmm)



### The Stable BeLi<sub>3</sub> phase (C2/m)





### The Stable Be<sub>4</sub>Li phase (R-3m)



## **Stabilization of Be-Li alloys**

#### **Simulated x-ray diffraction pattern**

- Cluster of diffraction peaks near 2  $k_{\rm F}$
- 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:  $g(\varepsilon_F) = 0.04 \text{ eV}^{-1}$  per valence electron

<b>80 GPa</b>	Be4Li R-3m	Be2Li P6/mmm	BeLi P2 <sub>1</sub> /m				
g(ε <sub>F</sub> ) in eV <sup>-1</sup> per valence electron	0.06	0.06	0.12				
Be <sub>4</sub> Li	Be	<sub>2</sub> Li	BeLi				

For a comparable e-ph coupling, T<sub>c</sub> would be about 32 K

### **Electronic Structure of BeLi (P21/m)**



#### **Electronic Structure of BeLi (P21/m)**



Simple model Hamiltonian can be solved exactly

#### **Electronic Structure of BeLi (P21/m)**



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

### **Electron Density of BeLi (P21/m)**



#### **Electron density shows layered structure**

## **Electron Density of metastable Be<sub>2</sub>Li (Pmcm)**



**Electron density shows layered structure** 

#### **Electron Density of stable Be<sub>2</sub>Li (P6/mmm)**



# **Origin of Charge Disproportionation**



Overlapping core makes internuclear region less accessible to valence electrons





#### 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<sub>c</sub> 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

