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Highly Accurate Calculations of the Phase Diagram of Cold Lithium

Luke Shulenburger
Department 1641
Pulsed Power Sciences Center
Sandia National Laboratories

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Mail: lshulen@sandia.gov

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Many thanks to my **collaborators**

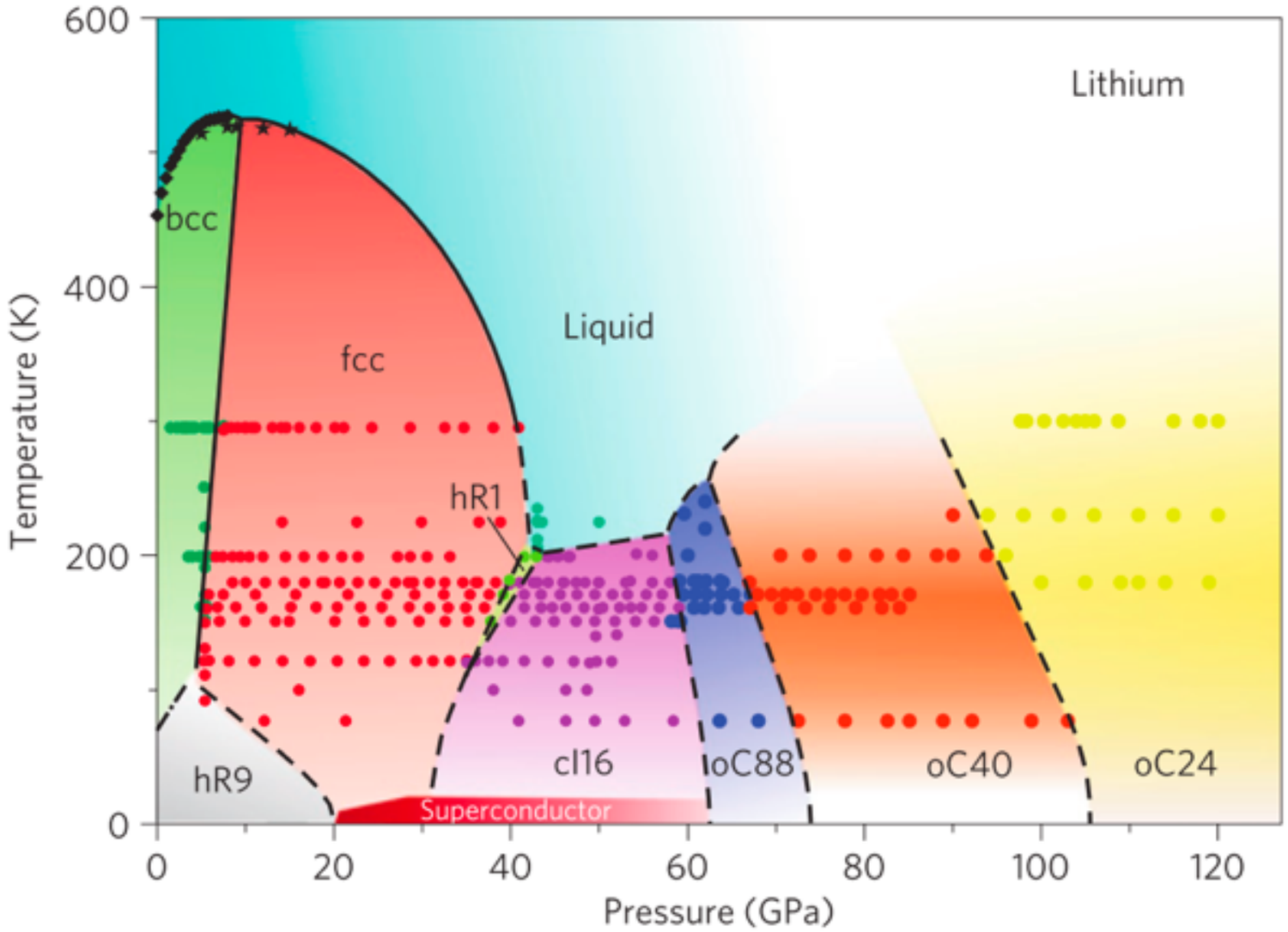
Andrew D. Baczewski
Michael P. Desjarlais
Christopher T. Seagle

Who are at **Sandia National Laboratories**

Motivation

Elemental Li has a surprisingly rich phase diagram

- 8 observed solid phases
- Electride phase (oC40)
- Metal-semiconductor-metal transition
- Smallest difference between T_c and melting



Guillaume, et. al., Nat. Phys., **7** (2011)

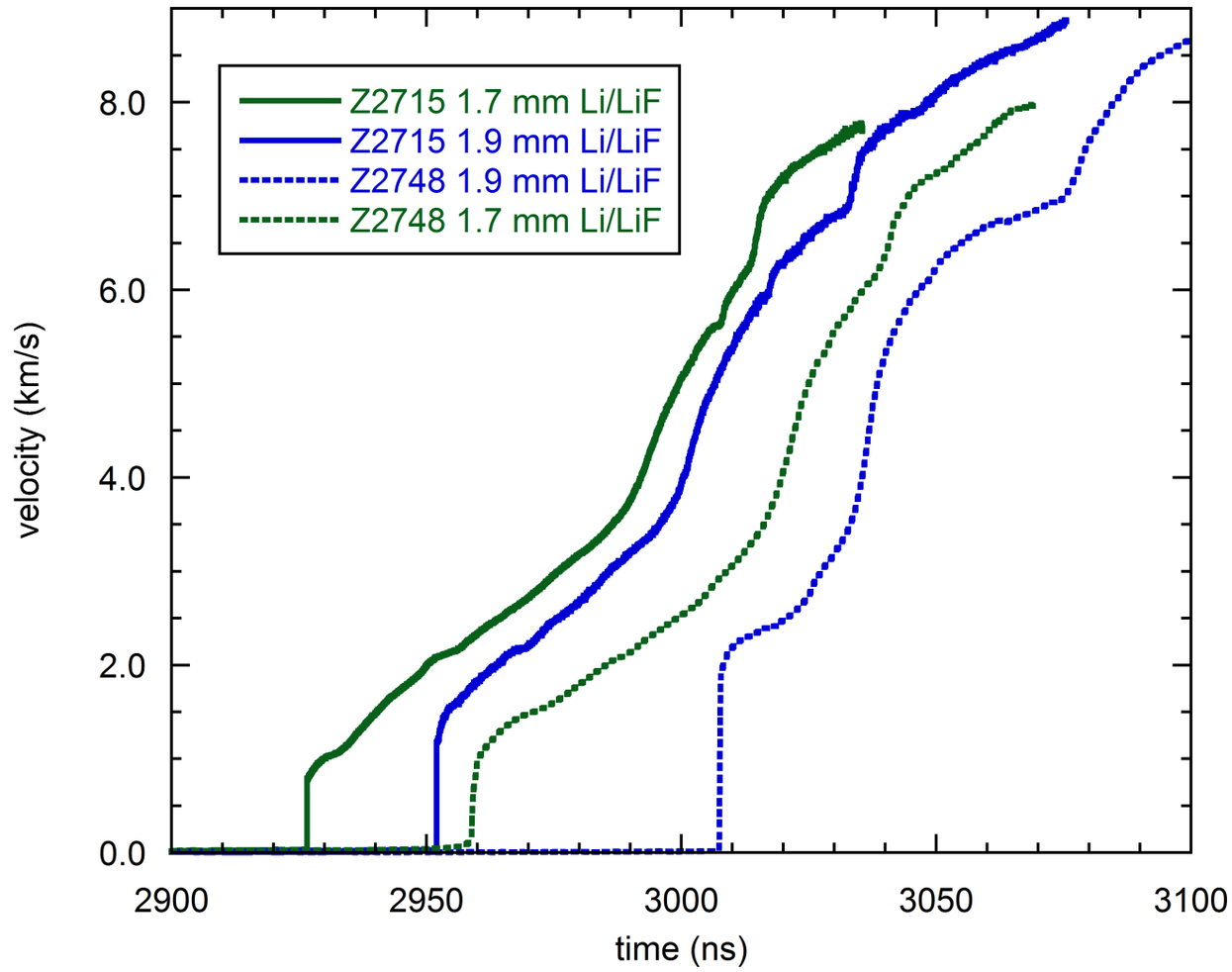
Motivation (cont.)

Recent dynamic compression experiments suggest passage through several phase transitions

- Two experiments performed with similar results

- VISAR measures Li/LiF interface velocity

- Traces show several interesting features



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Recent shock experiments suggest passage through several phase transitions

- Two experiments performed with similar results

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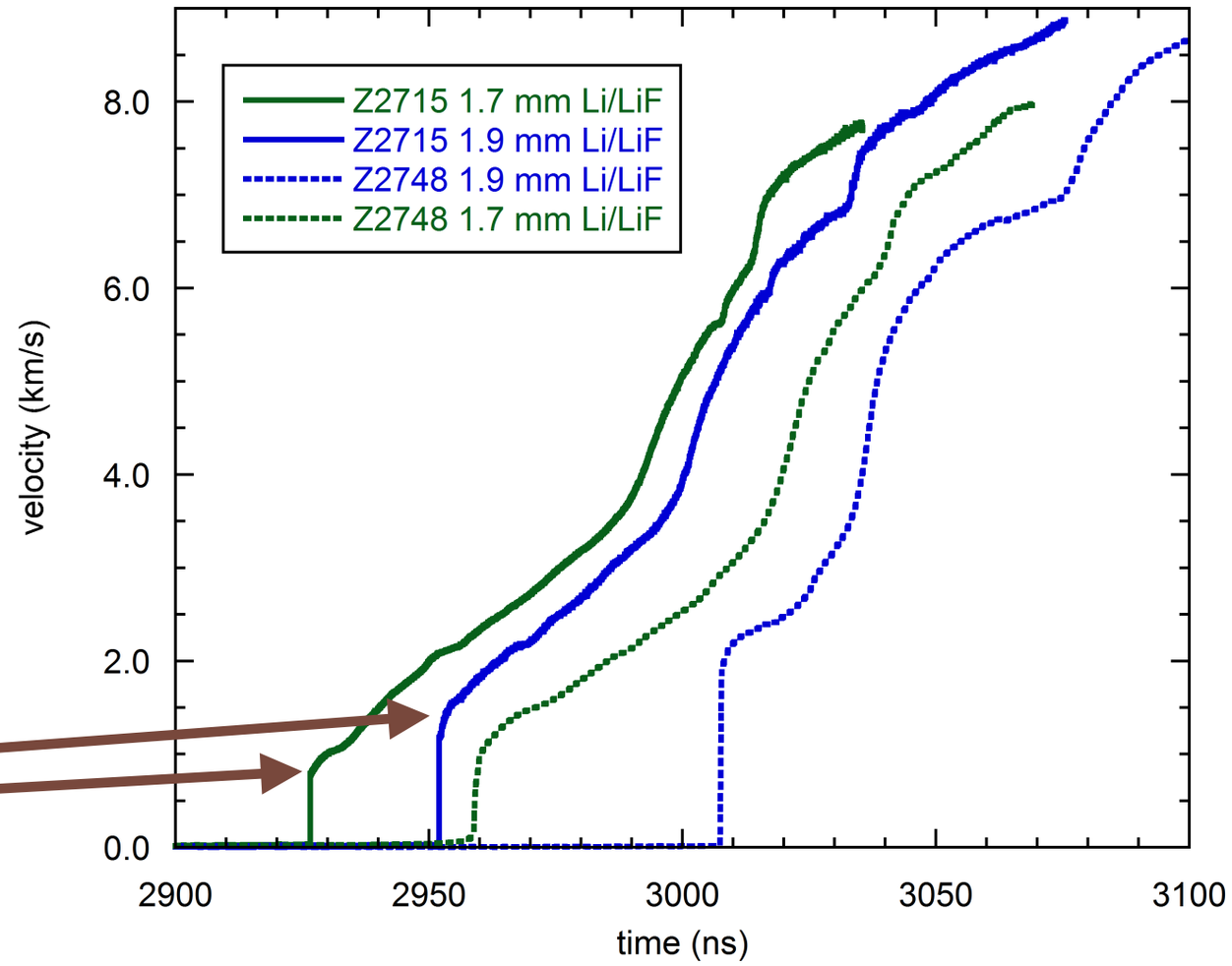
  - **Initial shock**
  - First softening
  - Late time softening
  - Reverberation



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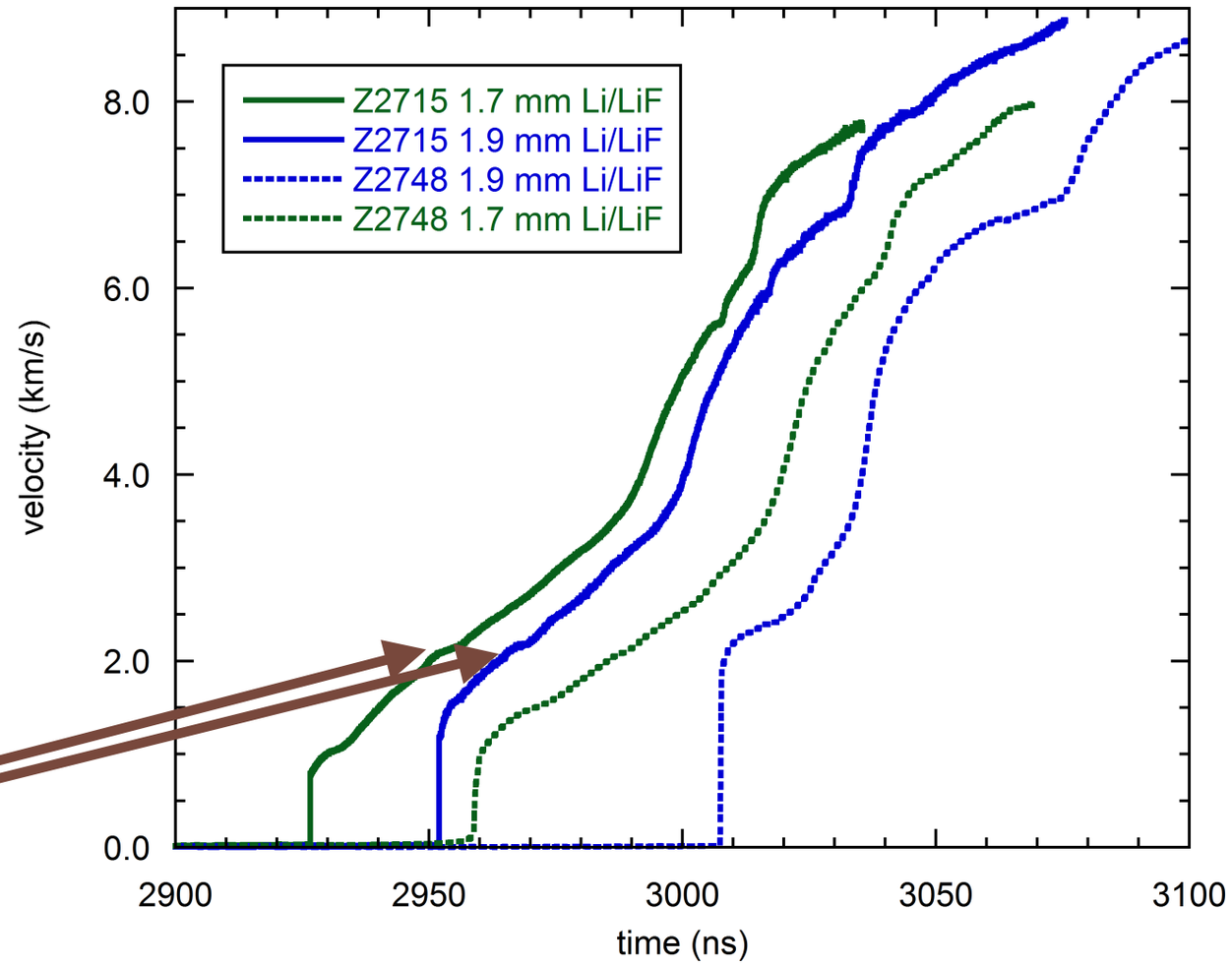

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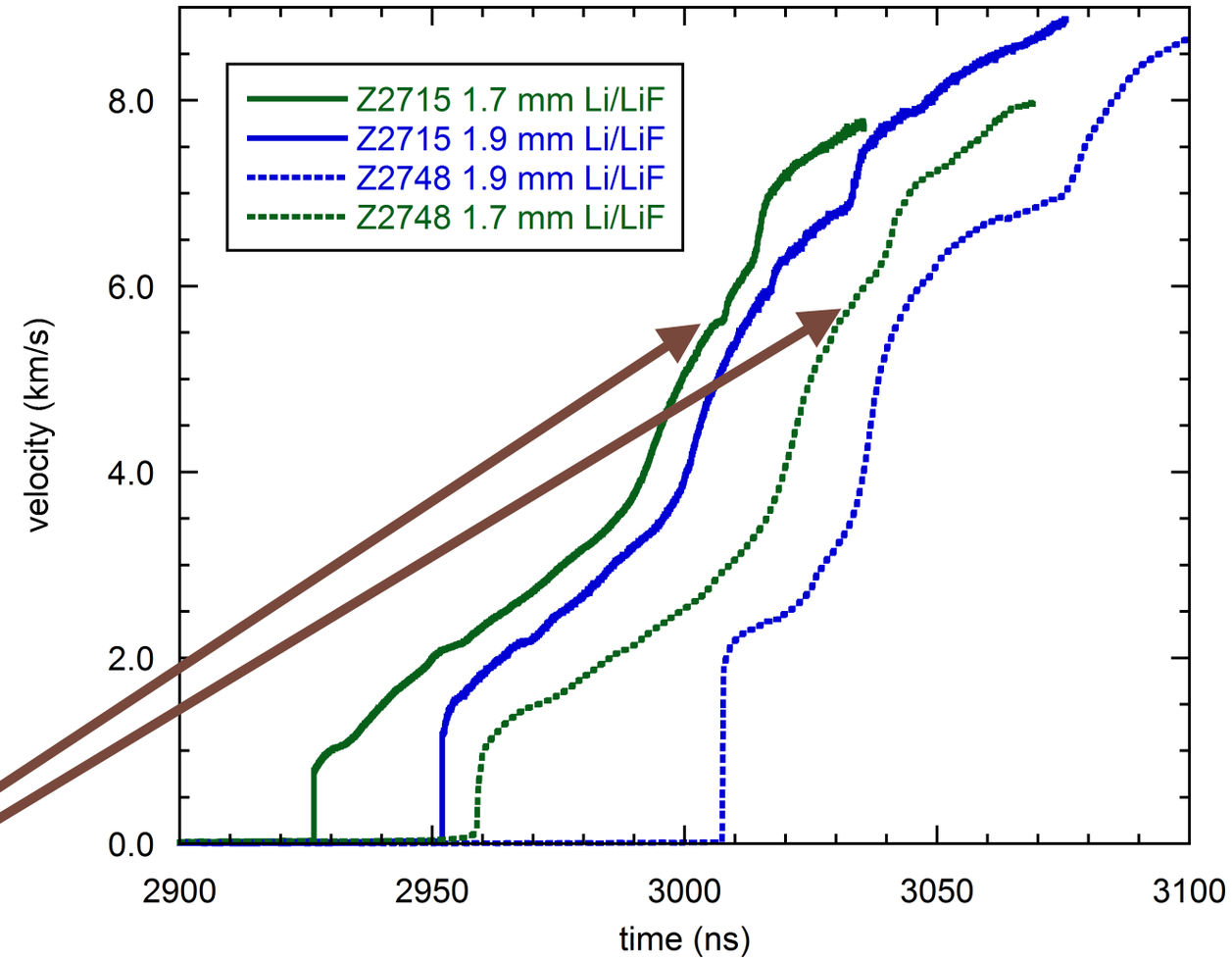

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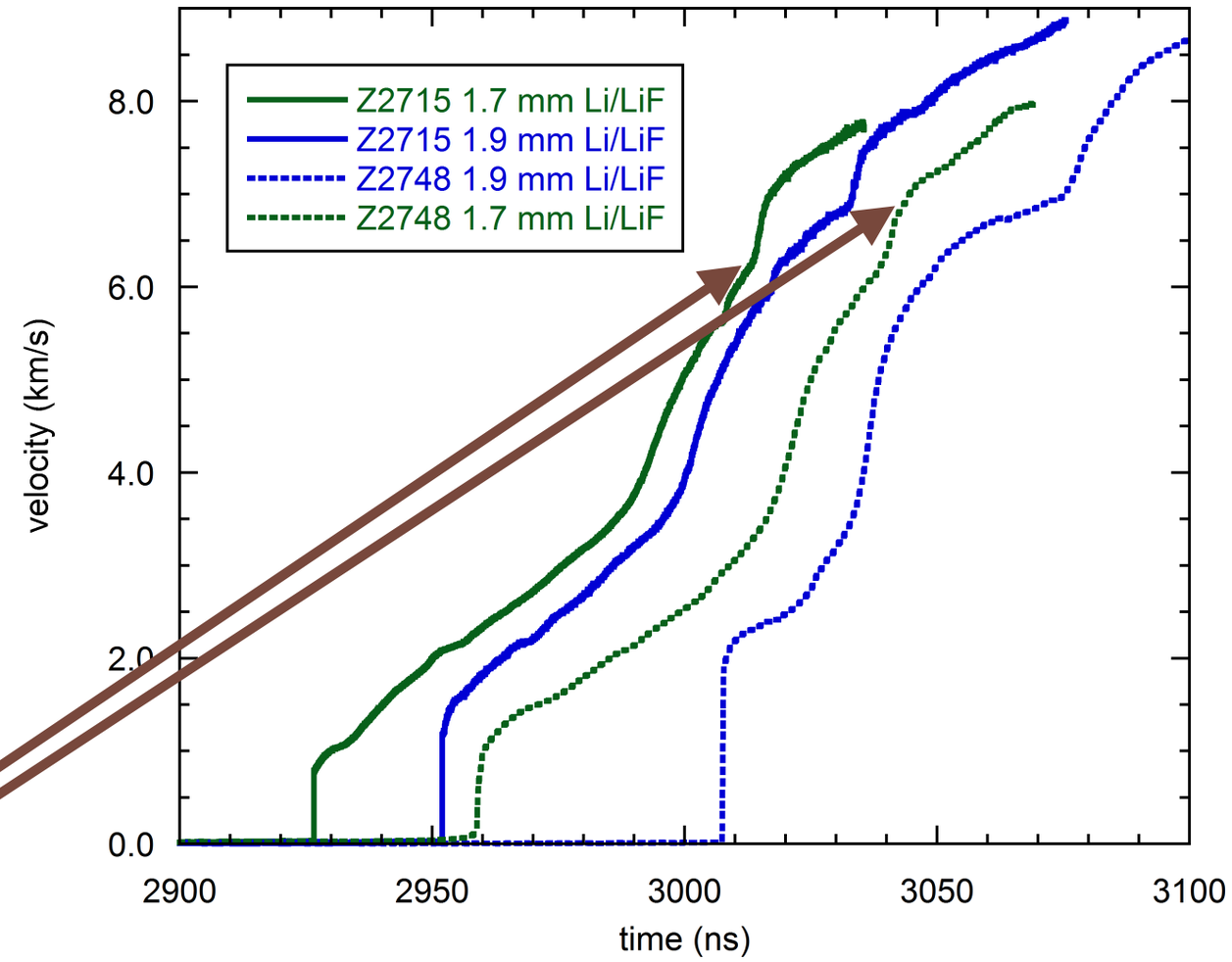


Theoretical Challenges

We would like an **equation of state** for Li to help rationalize these experiments

Today we will only consider **structural phase transitions** but the melt line is of deep interest

DFT is a popular approach, but it relies upon a choice of exchange-correlation functional

LDA/GGA do remarkably well for low pressure Li…

…but at high pressure we know of 2 issues:

1. **Electride phase** - semi-local DFT should not describe this well
2. **Re-entrant behavior** - gap opens and closes in pressure

Why QMC?

Using methodology in Shulenburger and Mattsson, PRB **88** (2013)
We are developing an equation of state for Li using quantum Monte Carlo (QMC)

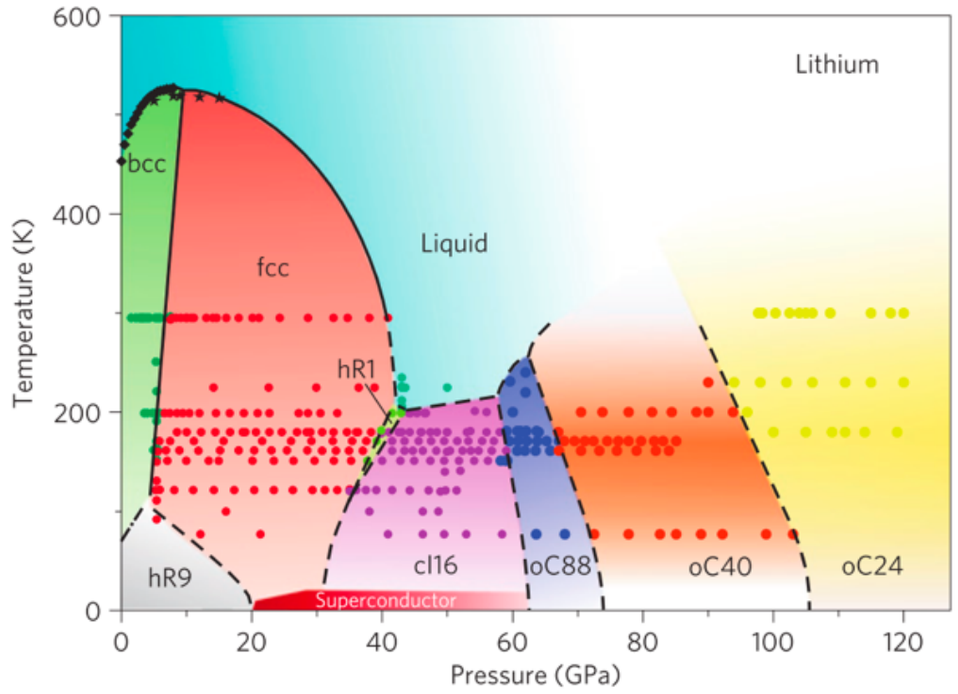
- Shulenburger, Mattsson, and Desjarlais, arXiv:1501.03850
  - **Pseudopotential error** largest in Be transition pressures
  - We can afford to study Li with **all 3 electrons**

- Rasch and Mitas, PRB, **92** (2015)
  - Fixed-node DMC gets **96-99% of correlation energy in Li**
  - Only solid phase considered was bcc (STP stable)

Methodology

Phases studied:

- bcc, fcc - volume uniquely determined
- hR9 - fixed c/a = 7.31 (expt.)
- cI16, oC40, Pbca, Aba2-24
  - “relaxed” with DFT - GGA
  - DFT energies sensitive at level of microHa/atom (inside DMC error bar)



Guillaume, et. al., Nat. Phys., **7** (2011)

- Quasi-harmonic treatment of thermal degrees of freedom
- Nuclear quantum effects effect melt weakly (Feng et al. J. Chem Phys **142**, 064506 (2015))

- All QMC calculations done with O(200) Li atoms
- Finite size extrapolation appears to be largest approximation

Computing Phase Transitions

- Phase transition pressures are calculated from total energies with statistical error
- Forces fit of auxiliary equation of state to provide pressure (vinet)
- Requires calculations far from transition to constrain equation of state

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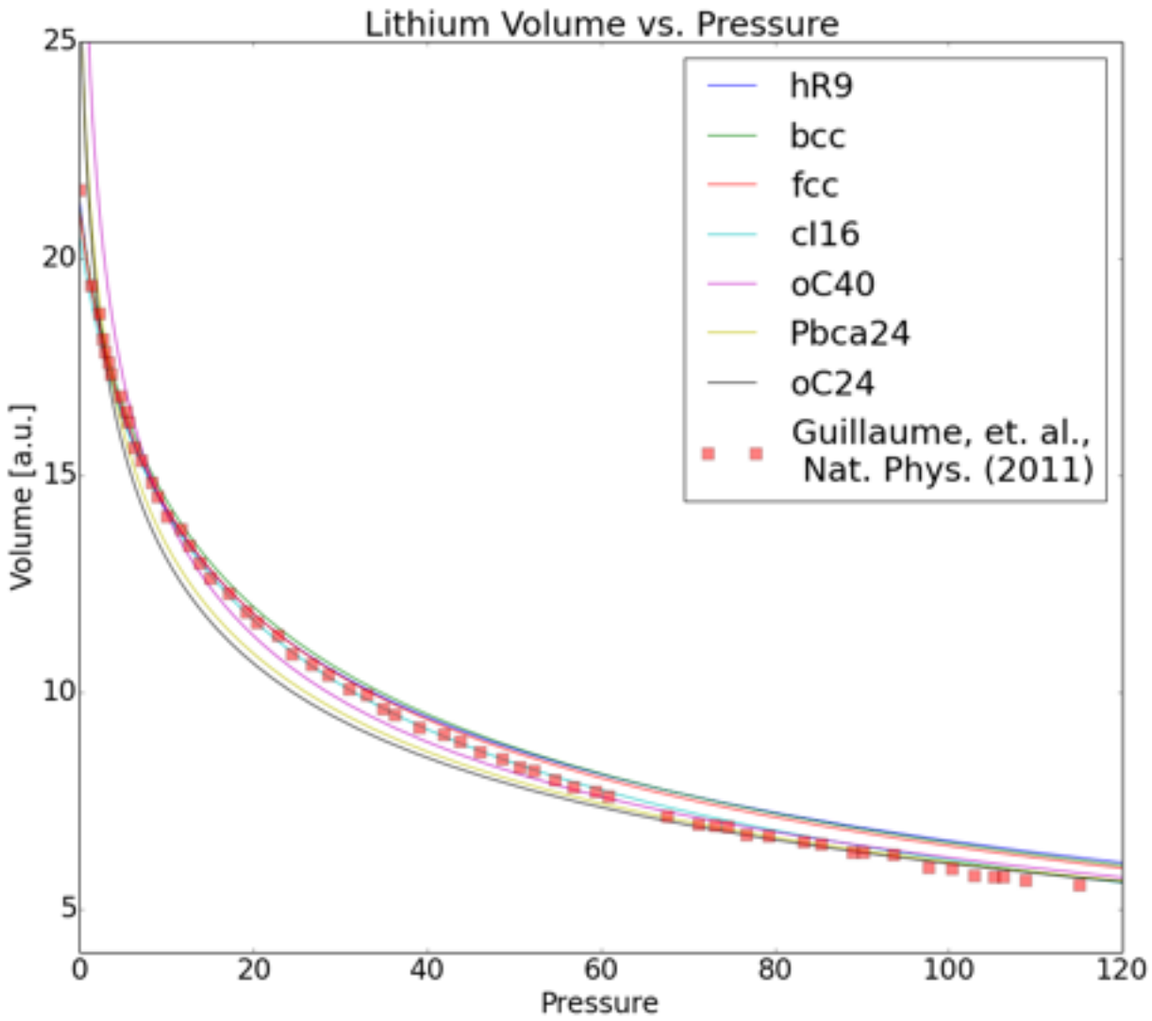
Vinet fit of energy vs. volume curve gives pressure



Comparison made against DAC experiment

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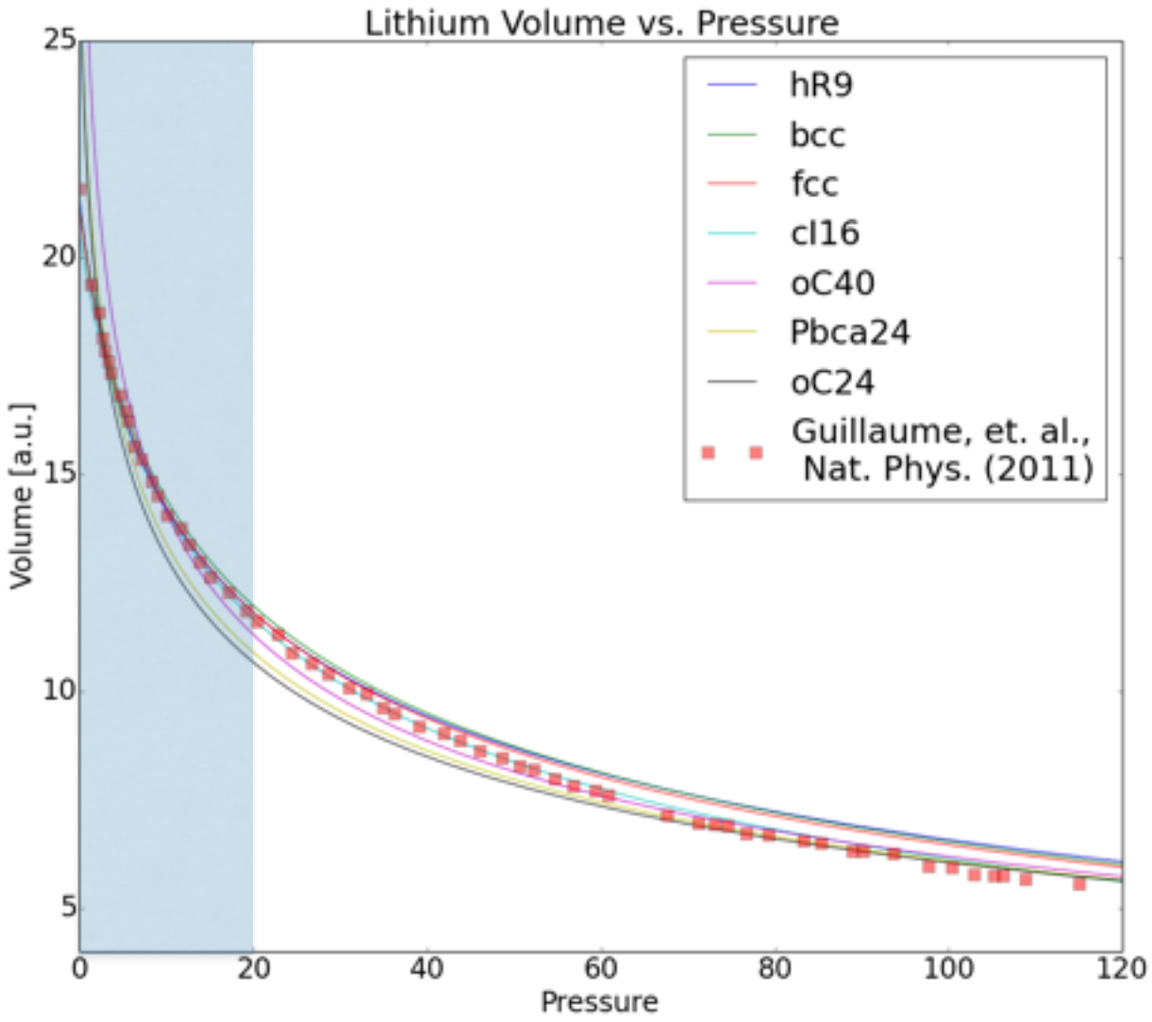
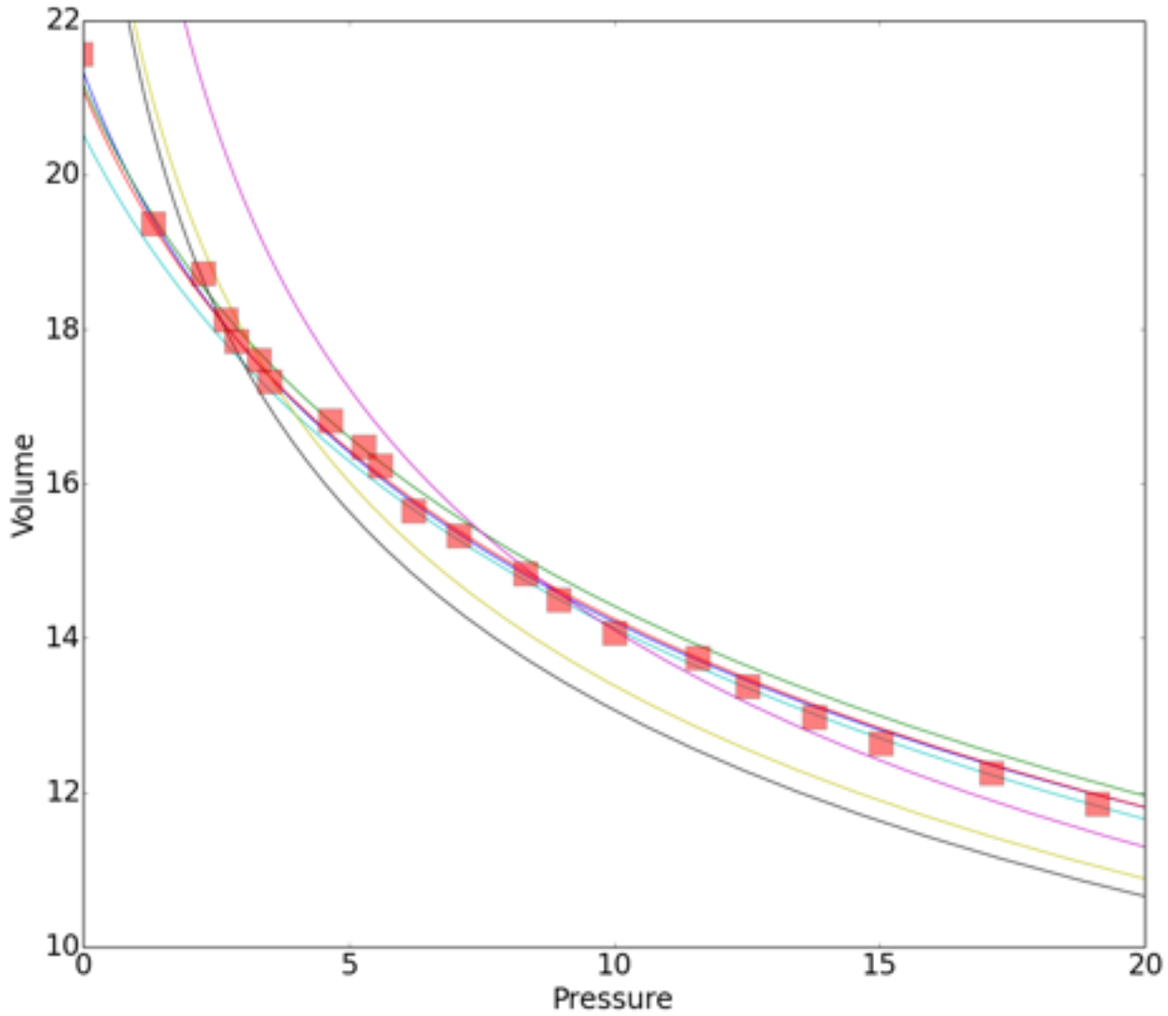
Vinet fit of energy vs. volume curve gives pressure





Low pressures - consistent with hR9, bcc, and fcc curves

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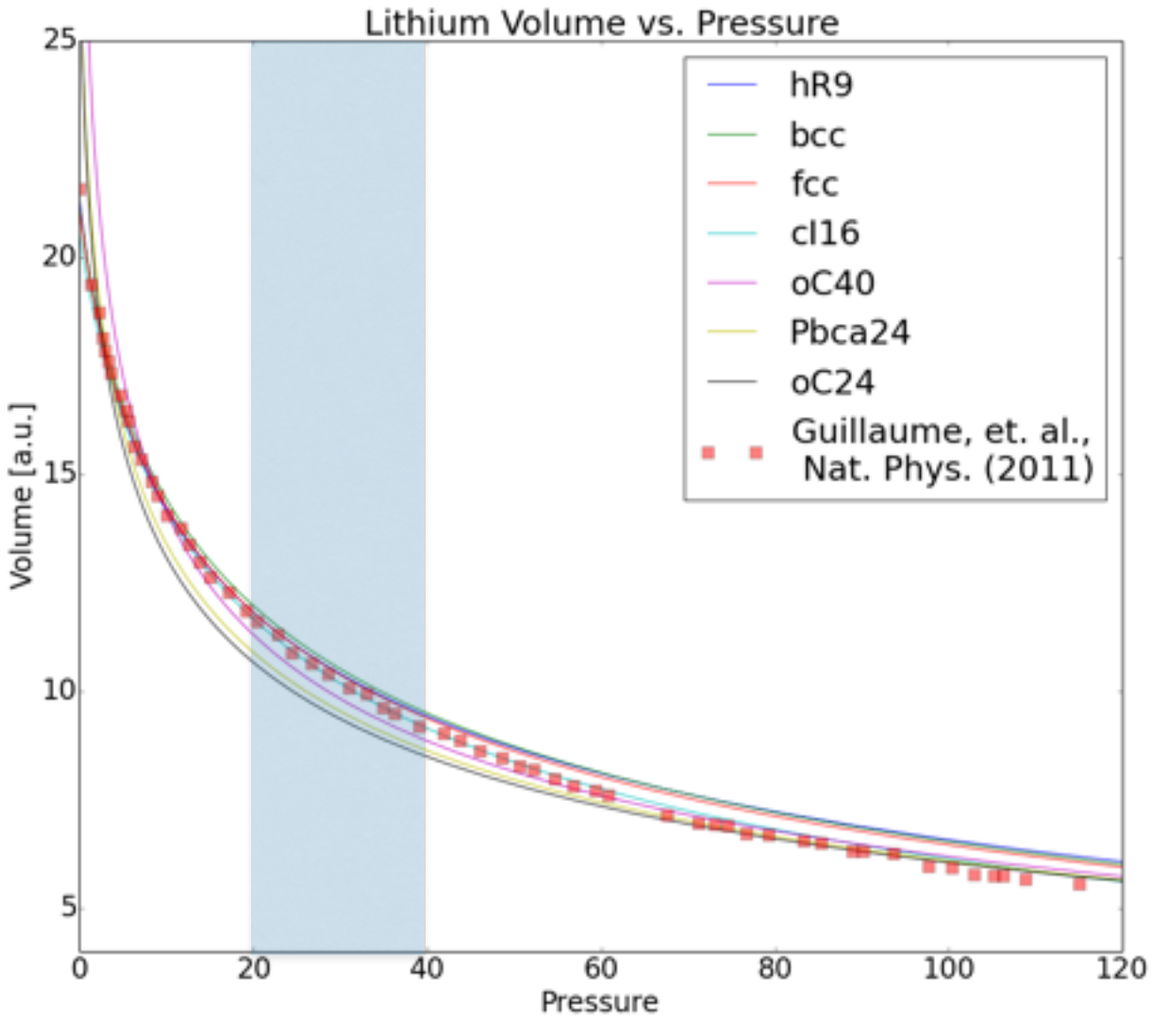

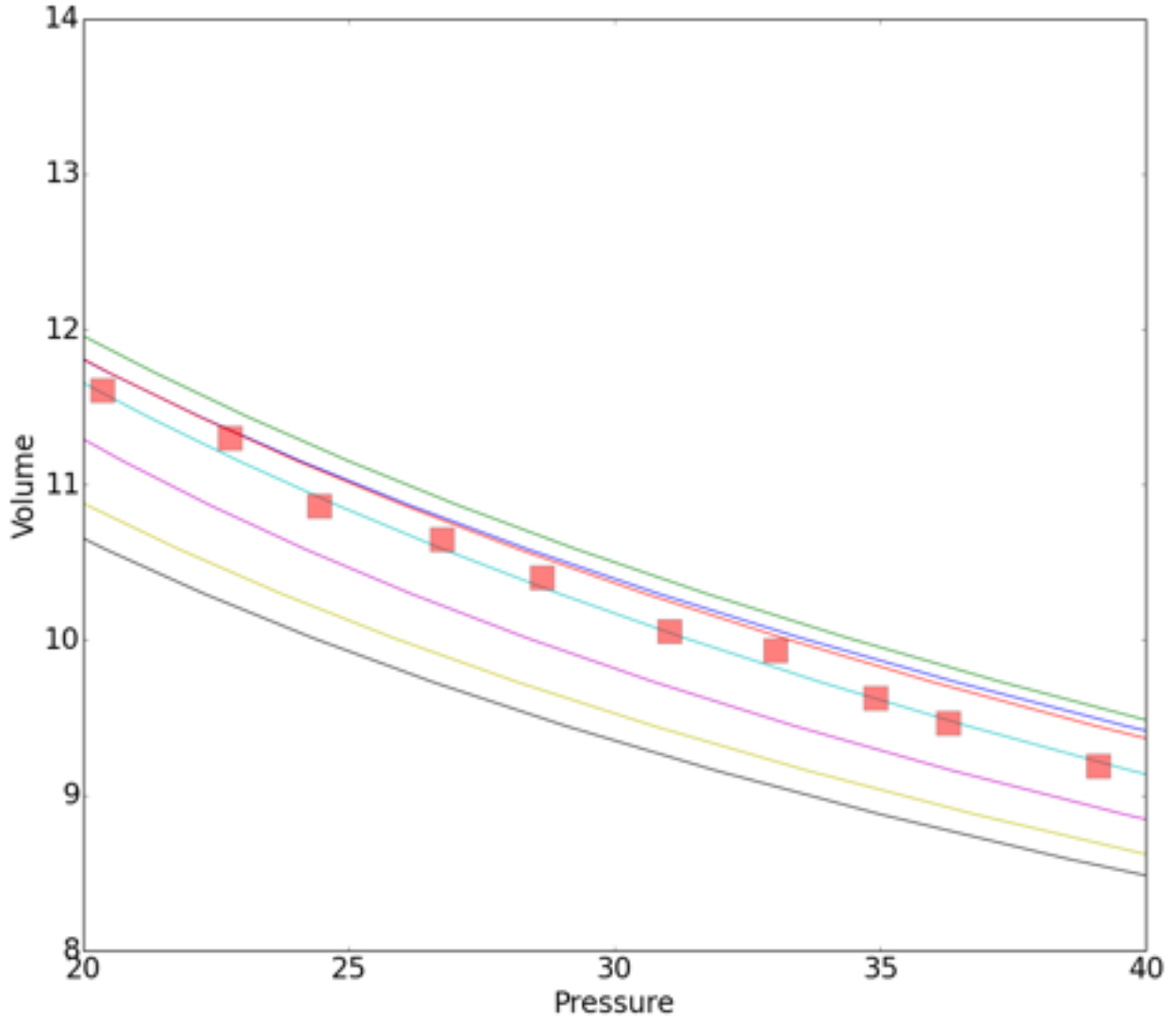

Intermediate pressures - crossover to cI16

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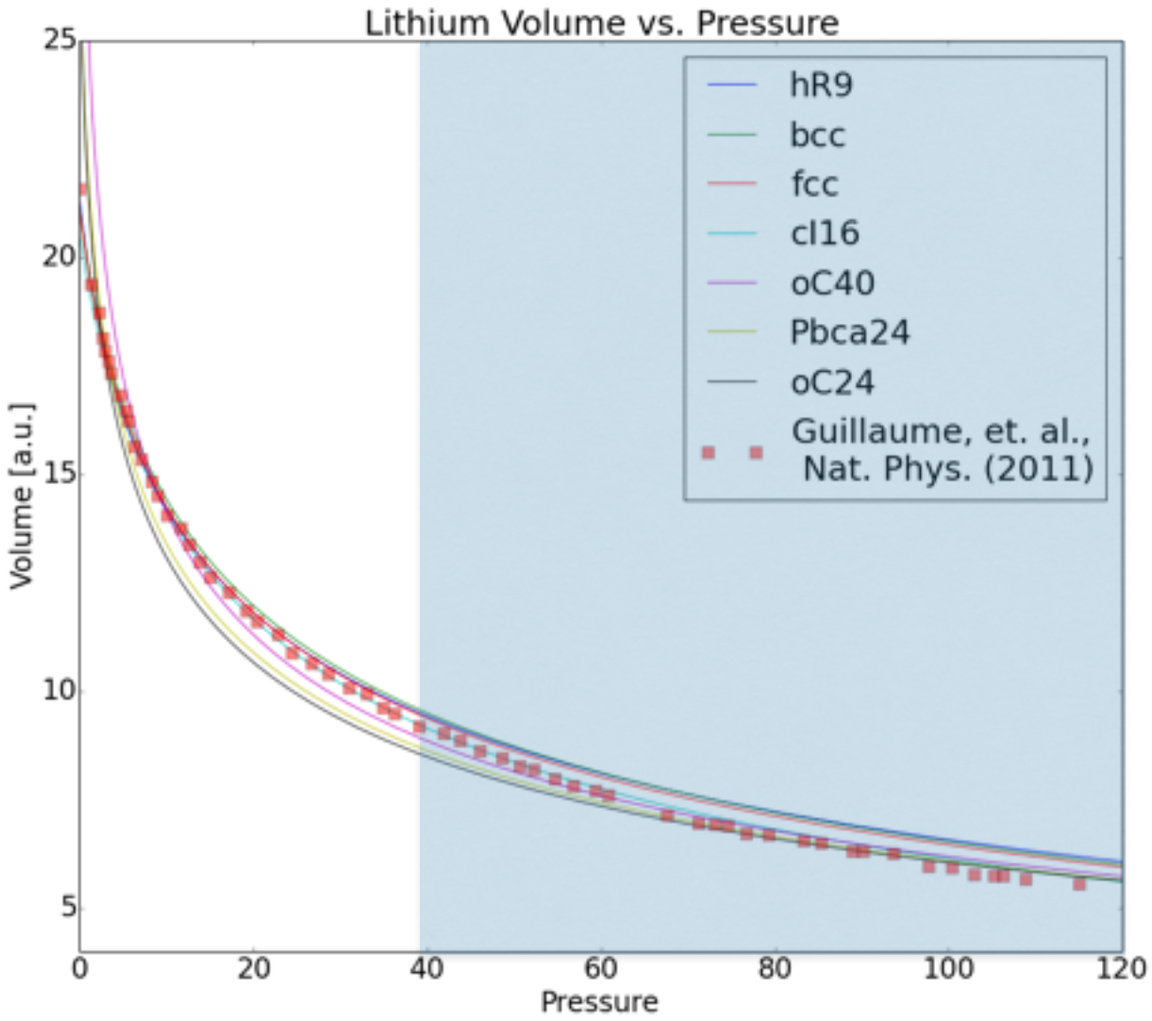
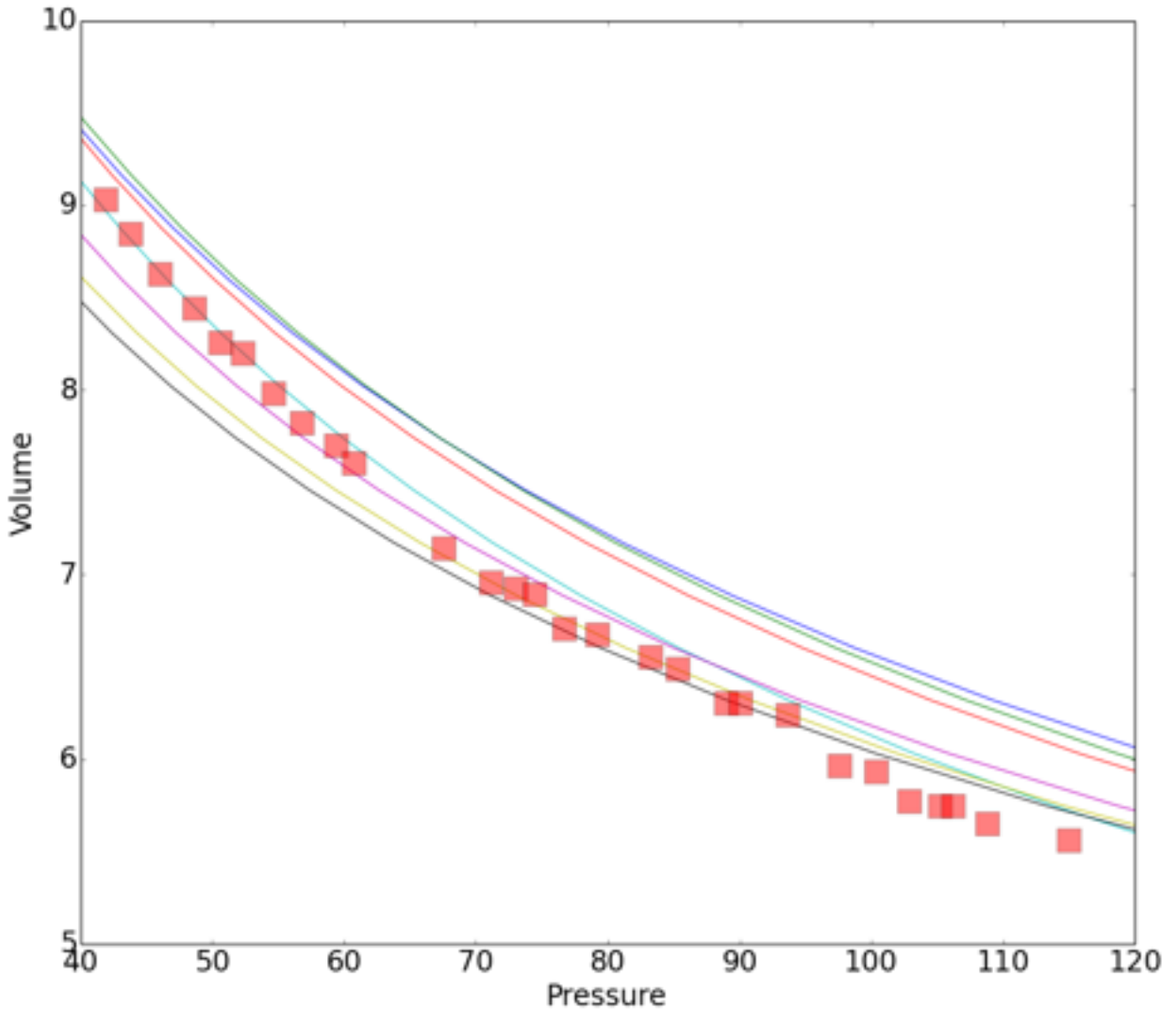
Vinet fit of energy vs. volume curve gives pressure



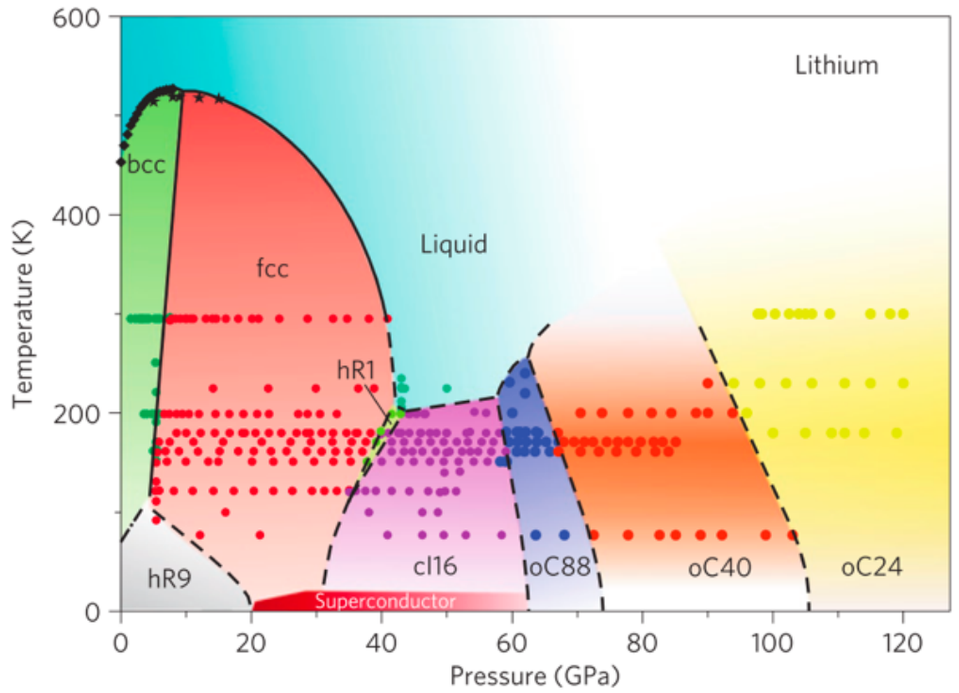


High pressures - crossover to low symmetry phases

Summary/Outlook

Preliminary results for phase transition pressures:

- bcc to fcc - **8.6 GPa**
- fcc to cI16 - **30.2 GPa**
- cI16 to oC40 - **66.5 GPa**



- Understand the role of temperature
- Incorporate more phases

- Examine sensitivities to finite size correction schemes
- Impact of implicit reliance on DFT:
  - Generation of geometries
  - Quasi-harmonic contributions

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