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Title:	DFT Calculations for the Uranium EOS
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DFT Calculations for the Uranium EOS

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We present results of density functional theory calculations on the Uranium equation of state. We examine the influence of approximations for the exchange-correlation functional and spin-orbit interaction, as well as numerical methods such as pseudopotentials. We compare calculated properties, such as static lattice energies and electronic specific heats, to their empirically derived counterparts.

DFT Calculations for the Uranium EOS

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Overview

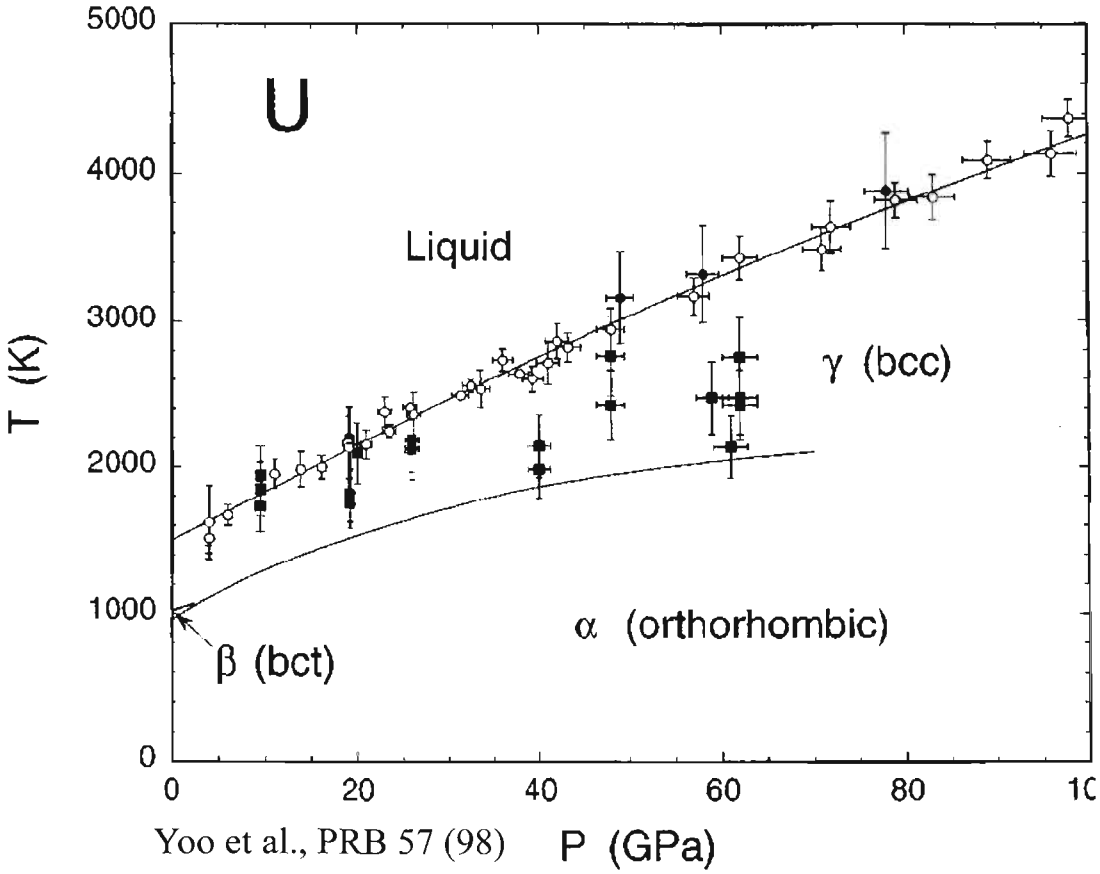
Uranium is an *easy* actinide: 5f electrons itinerant at ambient conditions.

We want to test usefulness of standard EOS models:

- Additivity of electronic, ion thermal free energies
- Quasi-harmonic approximation

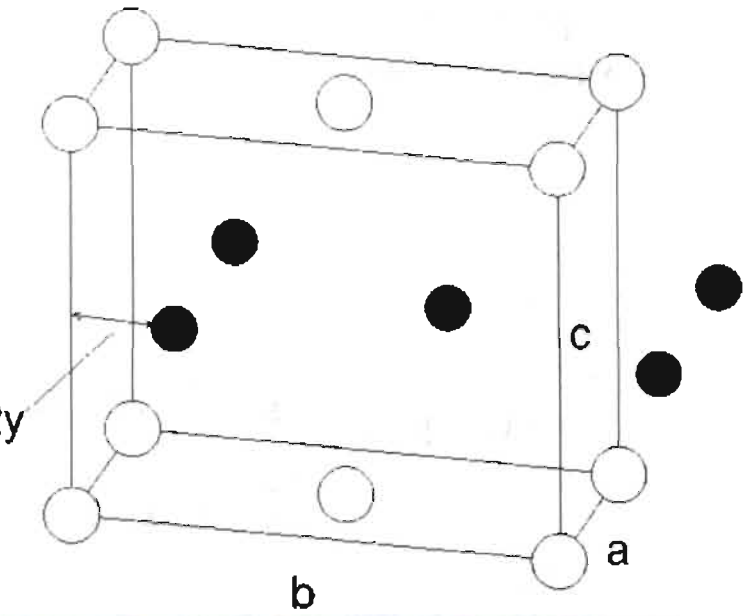
Also test applicability of DFT to calculate inputs to these.

U phases



Yoo et al., PRB 57 (98)

We will consider ambient α structure and high T bcc.



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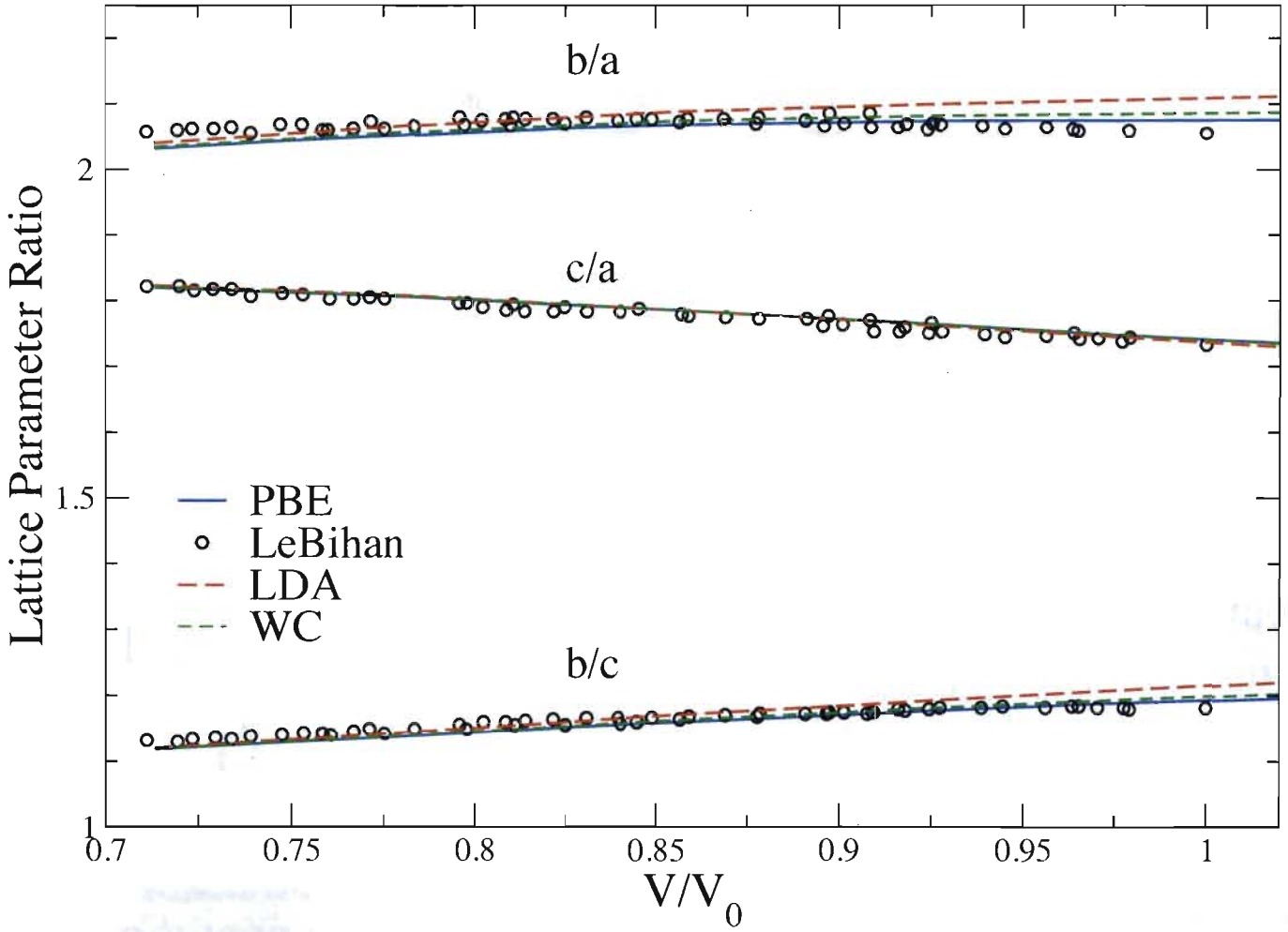
Lattice parameters under compression



Calculations use the PAW method in plane wave code *abinit.*

Data from Le Bihan et al., PRB 67 (2003).

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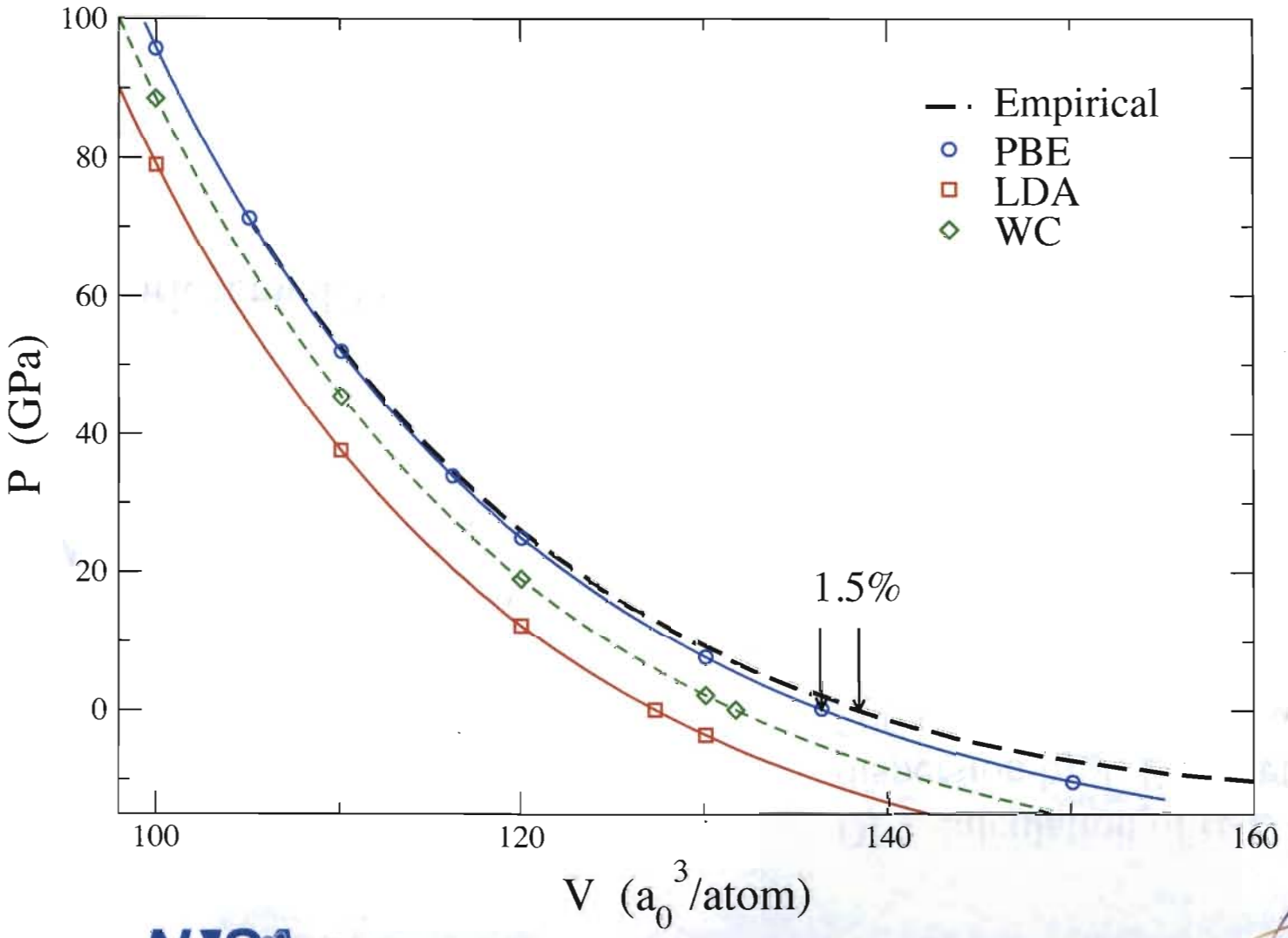
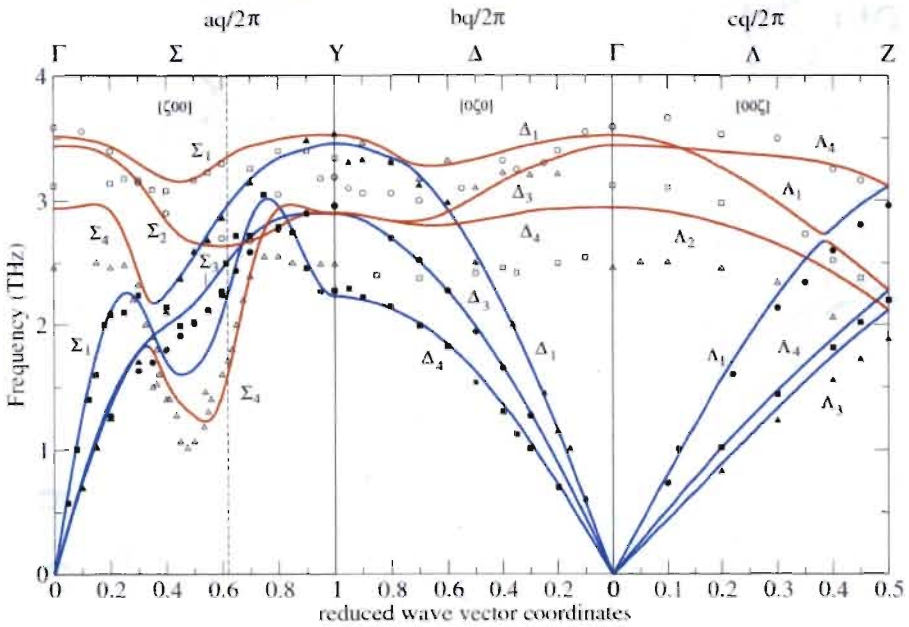
Cold pressure – empirical vs. DFT



S. D. Crockett, session S6 9:15 Thursday, empirical EOS

Static lattice contribution to to P(V).

Phonons and thermodynamics of α-U

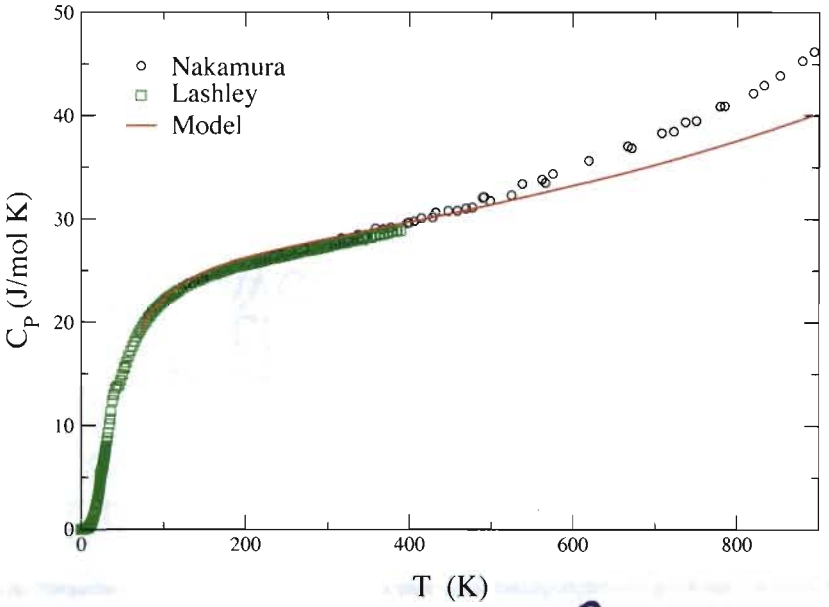


DFT calculation of α-U phonon dispersion by J. Bouchet, PRB 77 2008, generally agrees well with experiment.

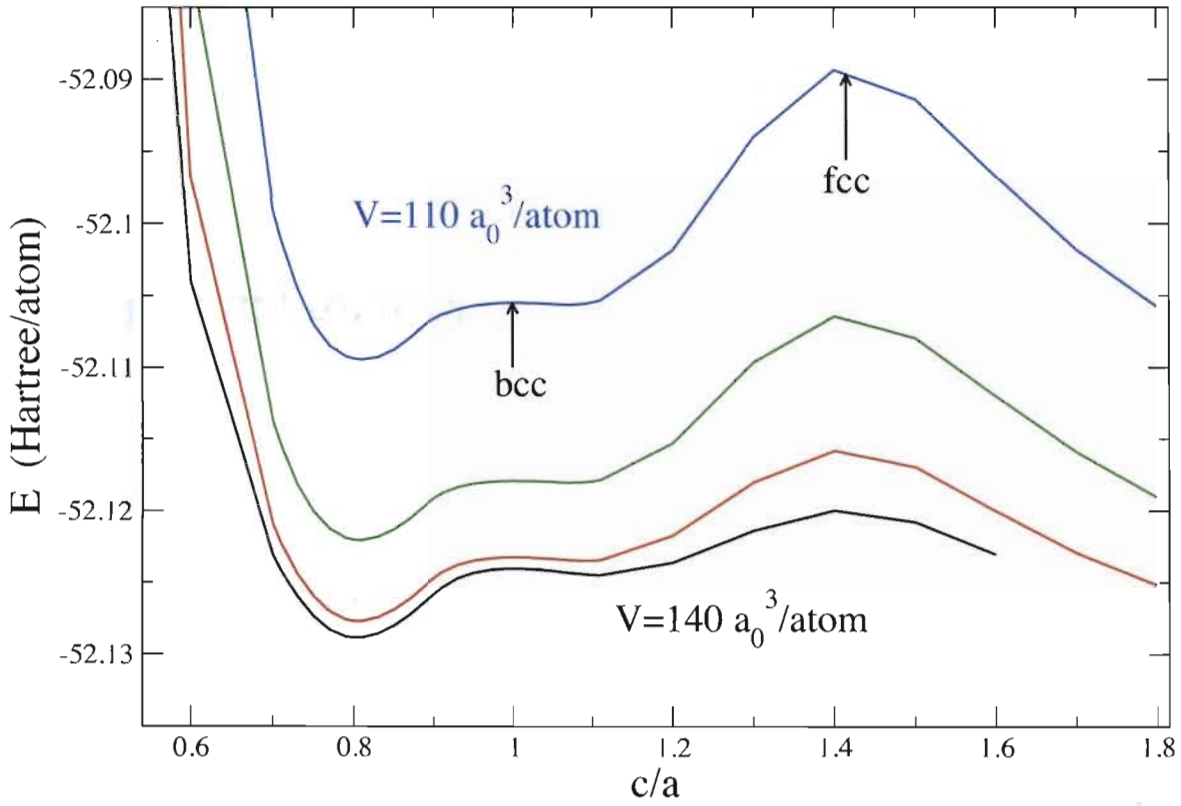
Gives effective Debye T, θ_2=168 K.

Empirical model based on specific heat, entropy.

Debye T, θ=173 K.



Elastic instability of bcc U



Bcc U is unstable wrt tetragonal distortion at the static lattice energy level. (Soderlind 98)

This instability persists under compression to at least 50 GPa.

Phonon instability of bcc U

The bcc structure is also unstable wrt phonon displacement corresponding to the H-point at the Brillouin zone boundary.

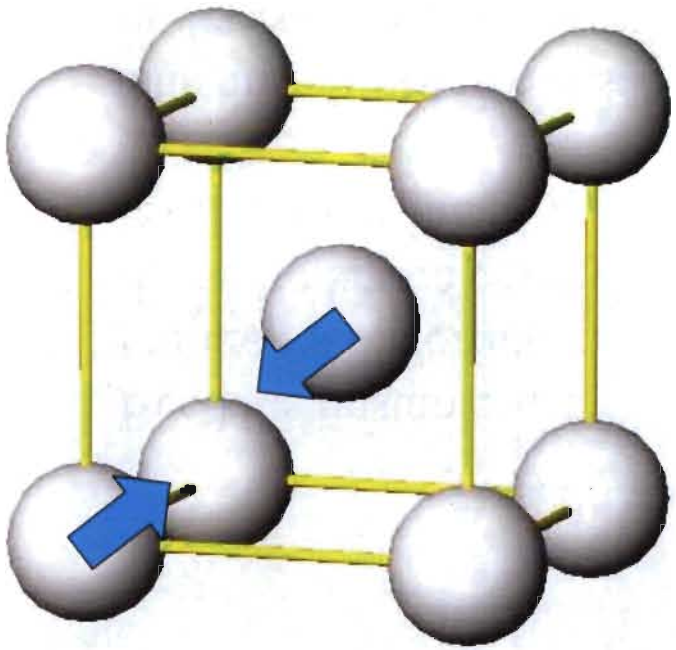
We examine the influence of electron-ion coupling by noting, for classical ion motion,

$$Z = \frac{1}{(2\pi\hbar)^{3N}} \int dP e^{-\beta T_n} \int dR \, \mathrm{Tr}\, e^{-\beta\left[V_{nn}(R)+\hat{V}_{ne}(R)+\hat{T}_e+\hat{V}_{ee}\right]}$$

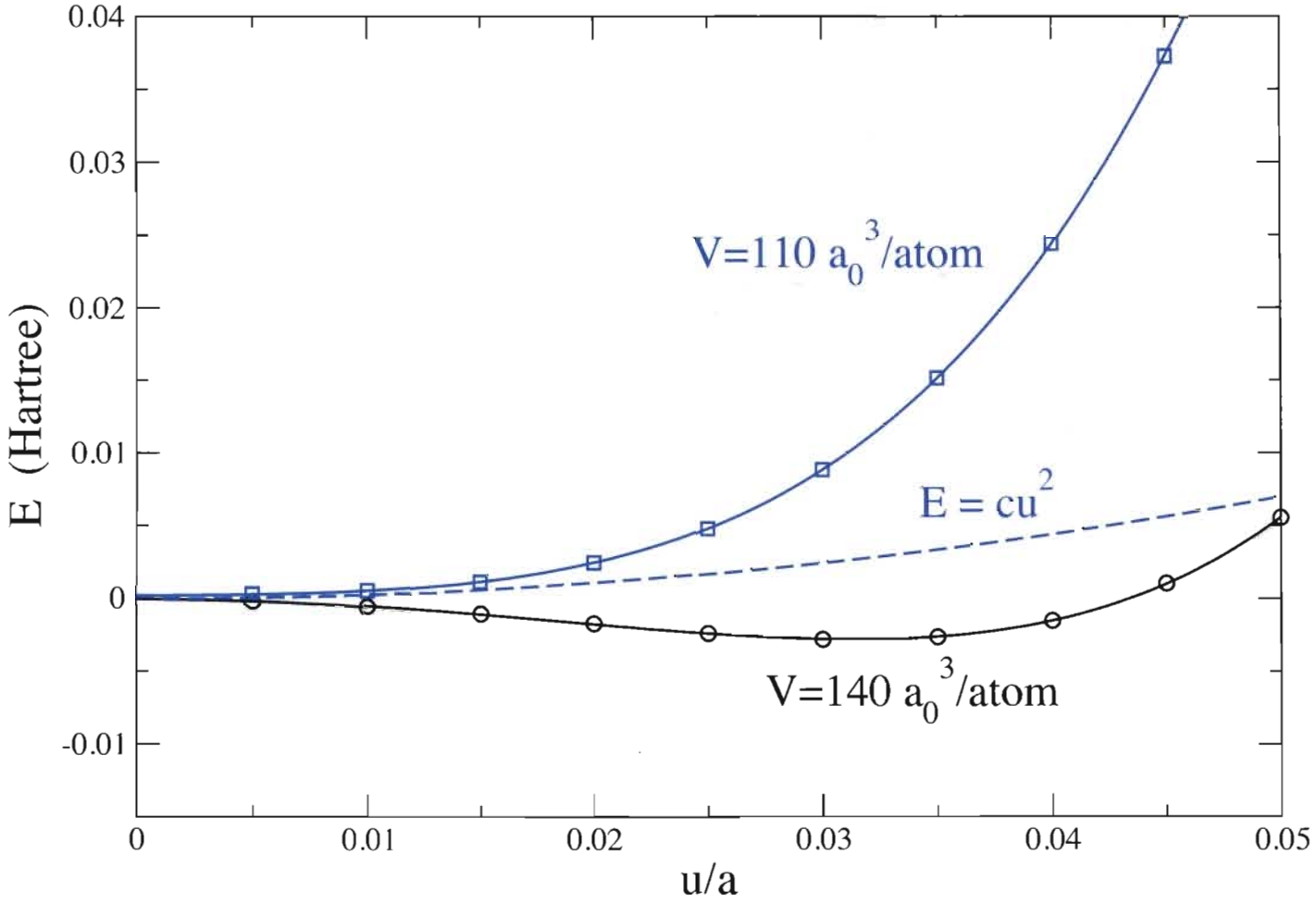
$$= \frac{1}{(2\pi\hbar)^{3N}} \int dP e^{-\beta T_n} \int dR \, e^{-\beta \mathcal{F}_e(R,T)}$$

and we approximate

$$\mathcal{F}_e(R,T) = E_{DFT} + T \sum_i \left[f_i \ln f_i + (1-f_i)\ln(1-f_i) \right]$$

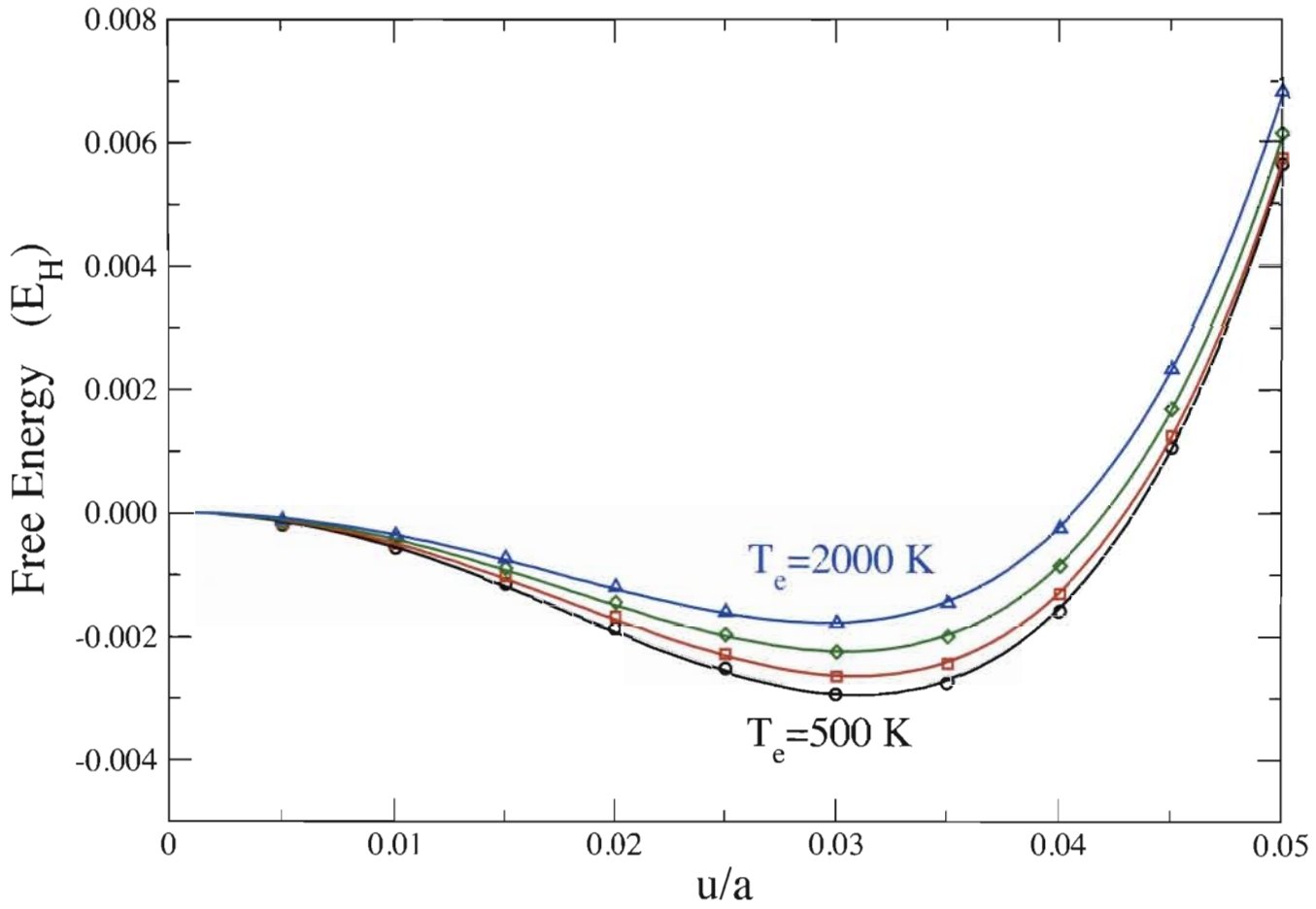


Phonon instability: effect of compression



Compression to ~50 GPa stabilizes mode, but strong anharmonicty remains.

Phonon instability: effect of electron T



Electron-ion coupling is significant, but does not qualitatively change the situation.

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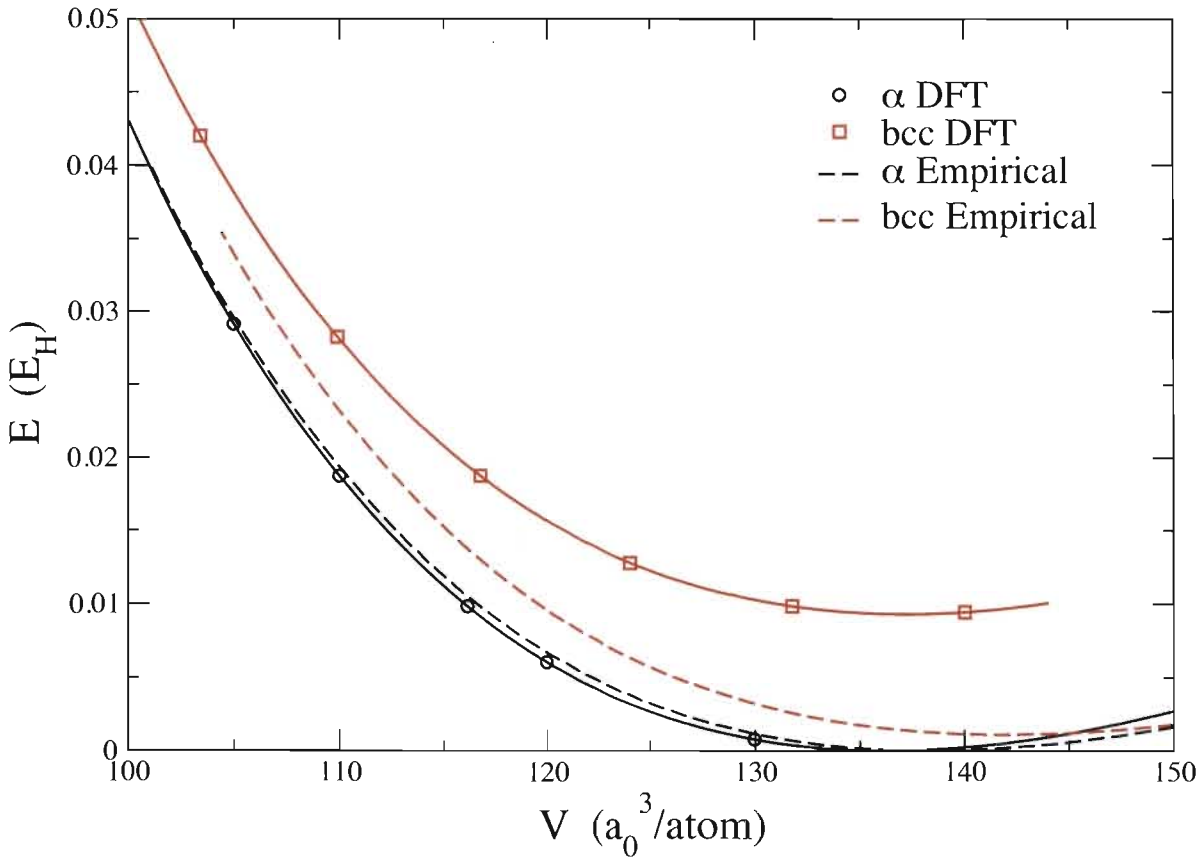
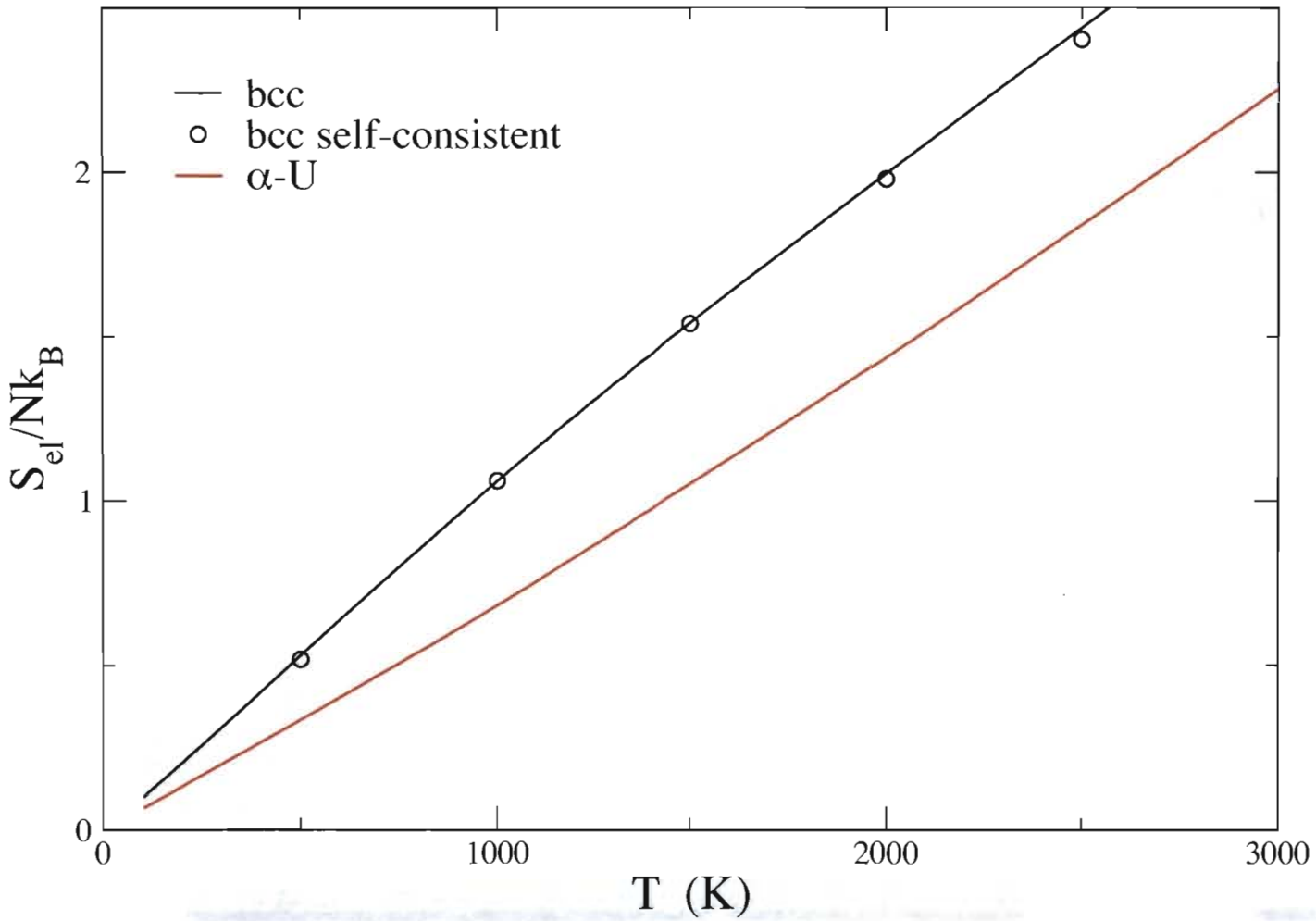
Energy difference for bcc phase



Calculated bcc-α is much larger than empirical model.

Model matches data for entropy at transition.

Electronic entropy of α and γ U



Thermal excitations of electrons contribute significantly to transition entropy.

Occupying states from low-T dos gives same result as self-consistent finite T calculation.

Summary

For α-U, we are doing pretty well.

- DFT predicts structure.
- PBE cold curve is accurate.
- Quasi-harmonic lattice dynamics consistent with thermodynamics.

For γ (bcc) there are several issues

- Unstable modes invalidate quasi-harmonic approximation.
- Electron-ion coupling is not negligible.
- Large DFT energy difference from α is not easily reconciled with phase diagram.

What can we say about bcc U?

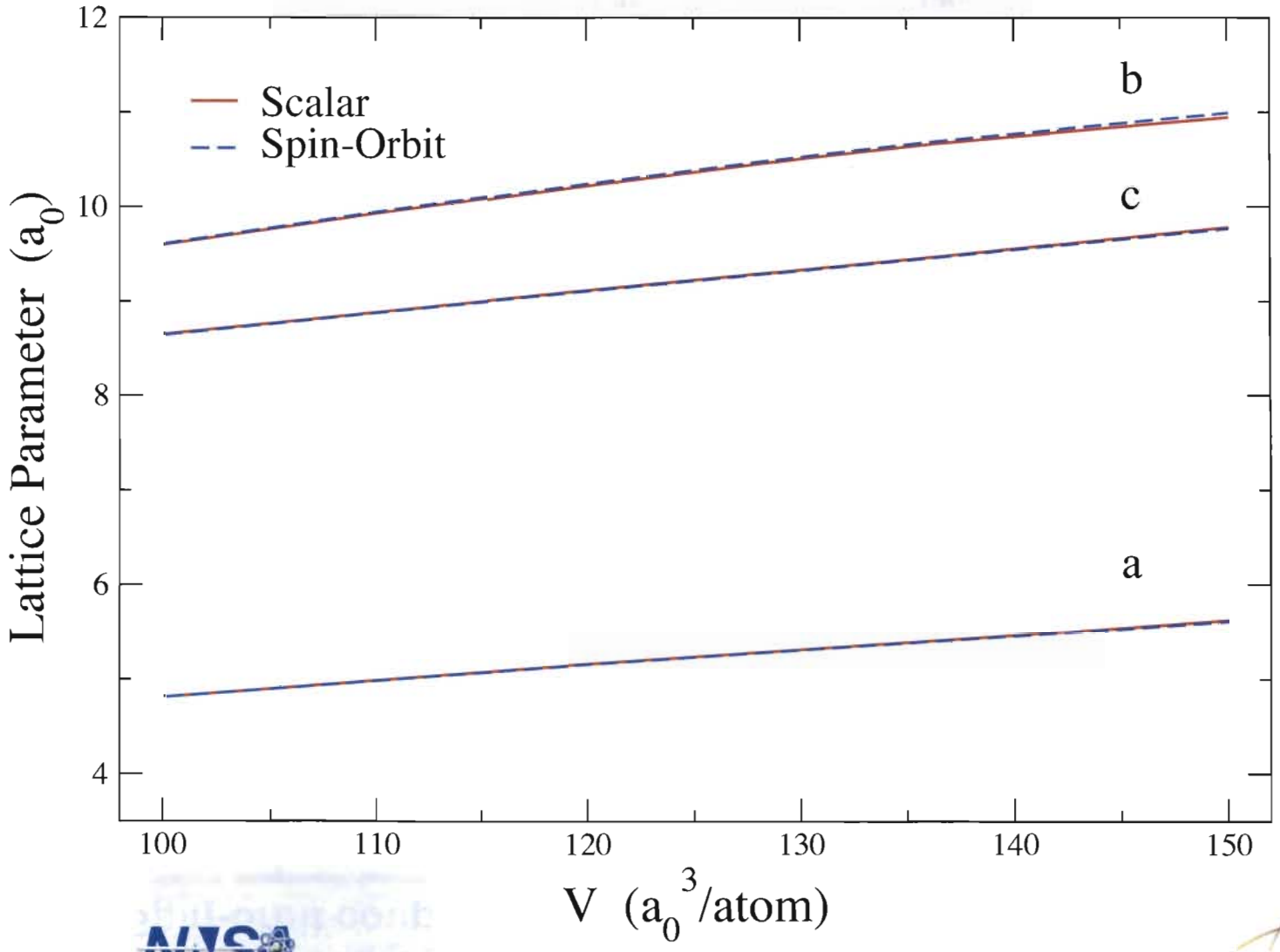
Empirical EOS models have:

U = cold energy + 3kT + electron thermal energy.

It is possible that strong anharmonicity causes this to be significantly in error.

Or it could be that DFT energy difference is misleading.

Spin-orbit coupling influence on α-U lattice parameters



α-U geometry optimized with and without spin-orbit coupling.

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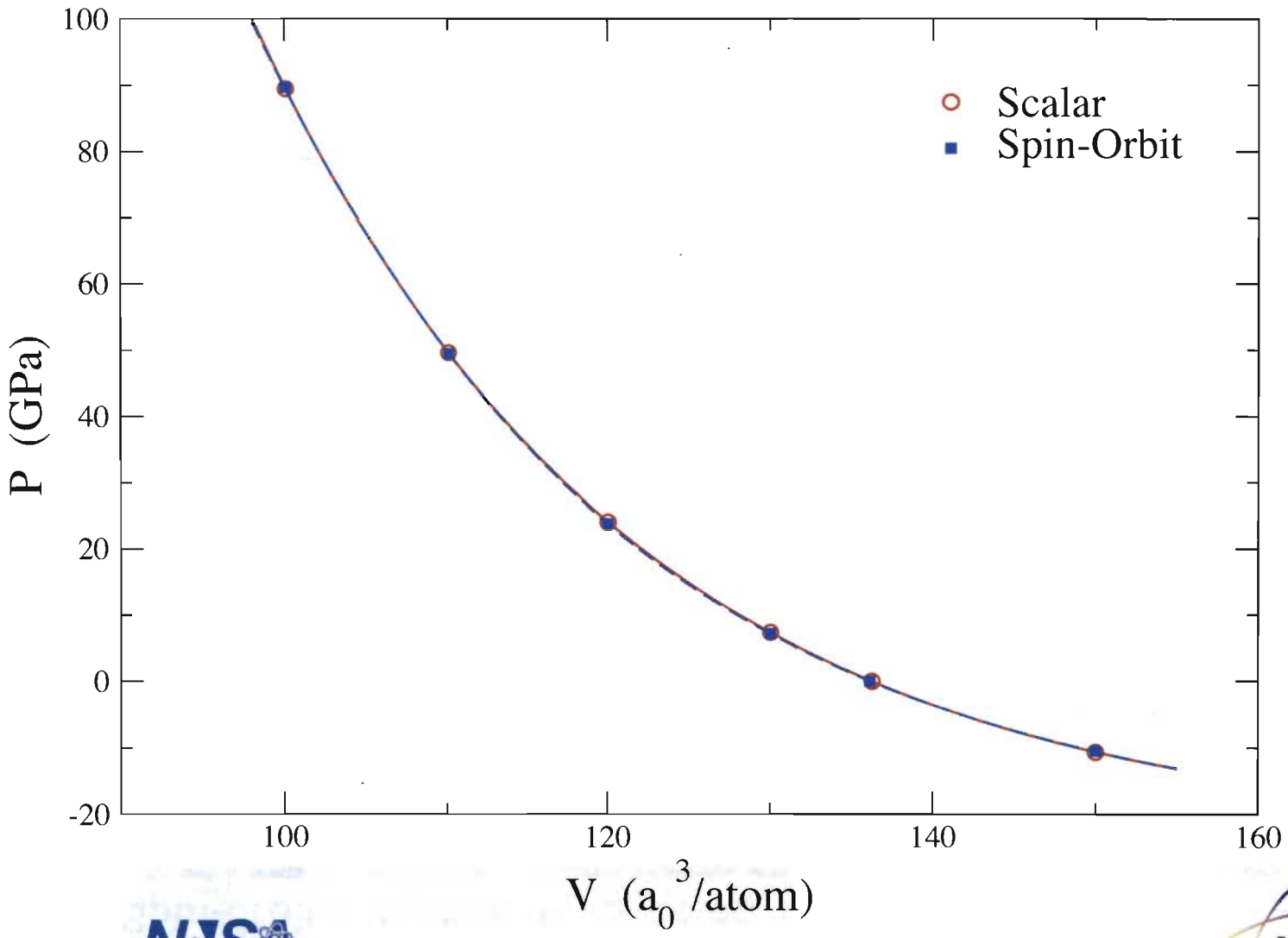
Spin-orbit coupling influence on α-U cold pressure



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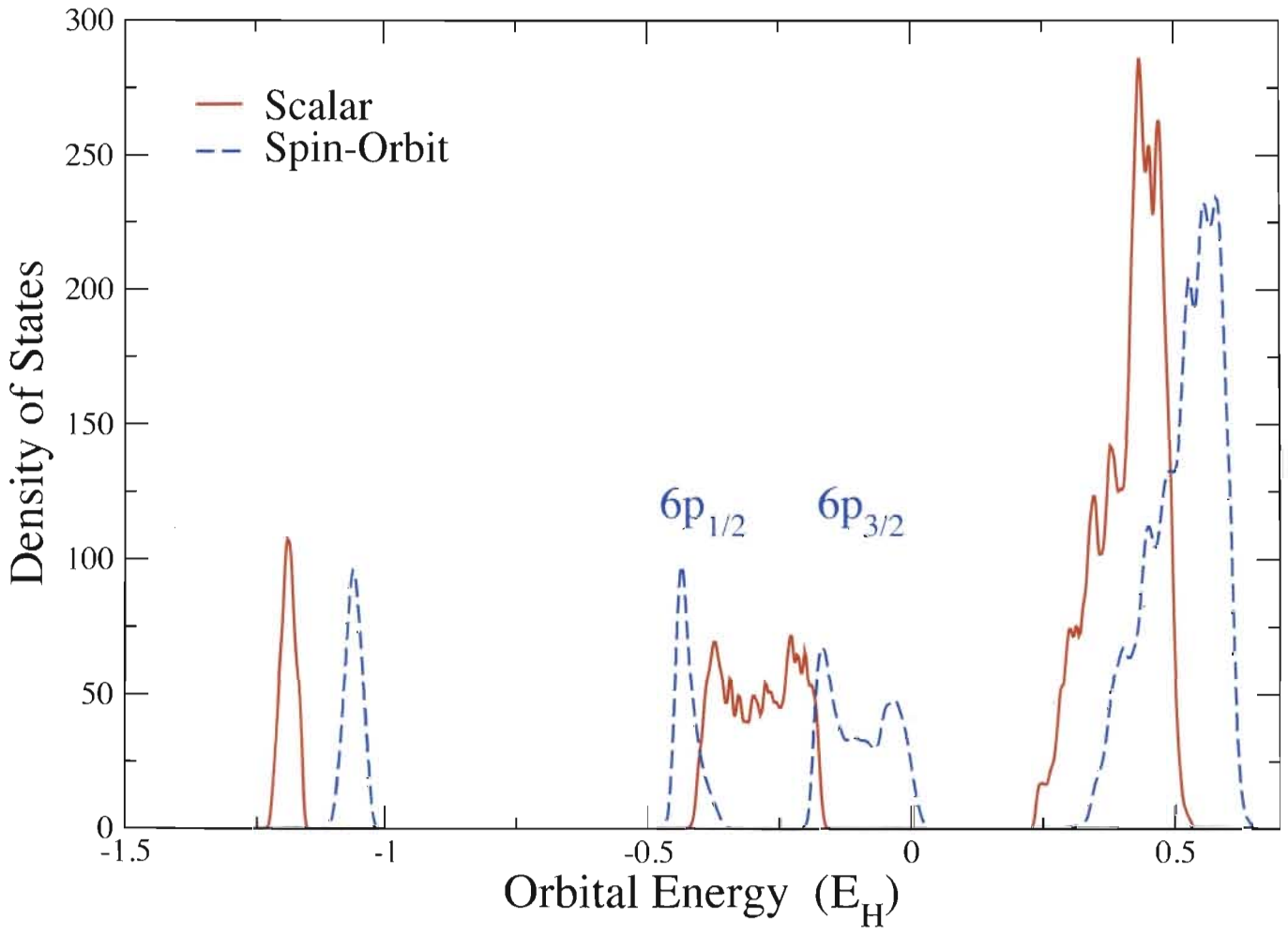
Spin-orbit coupling: effect on density of states



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