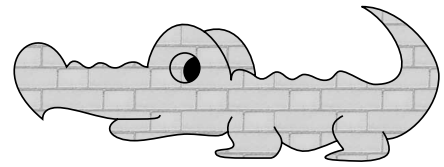
Density functional theory and quantum Monte Carlo calculations of solid molecular hydrogen

Jonathan Lloyd-Williams[1], Bartomeu Monserrat[1], Pablo López Ríos[1], Neil Drummond[2], and Richard Needs[1]



[1]Theory of Condensed Matter Group, Cavendish Laboratory, University of Cambridge, UK
[2]Condensed Matter Theory Group, Department of Physics, Lancaster University, UK

QMC in the Apuan Alps IX – Tuesday 29th July, 2014

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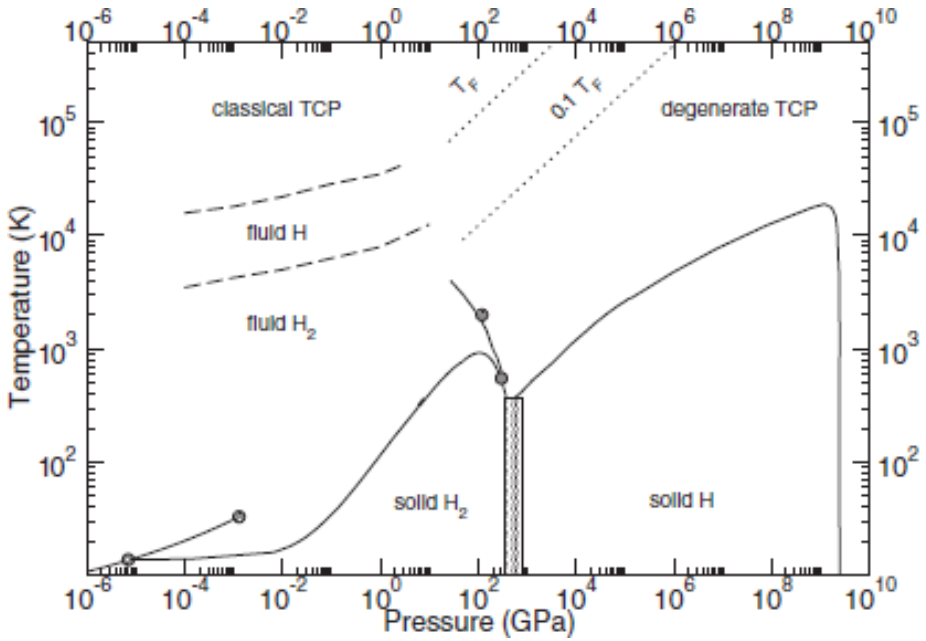
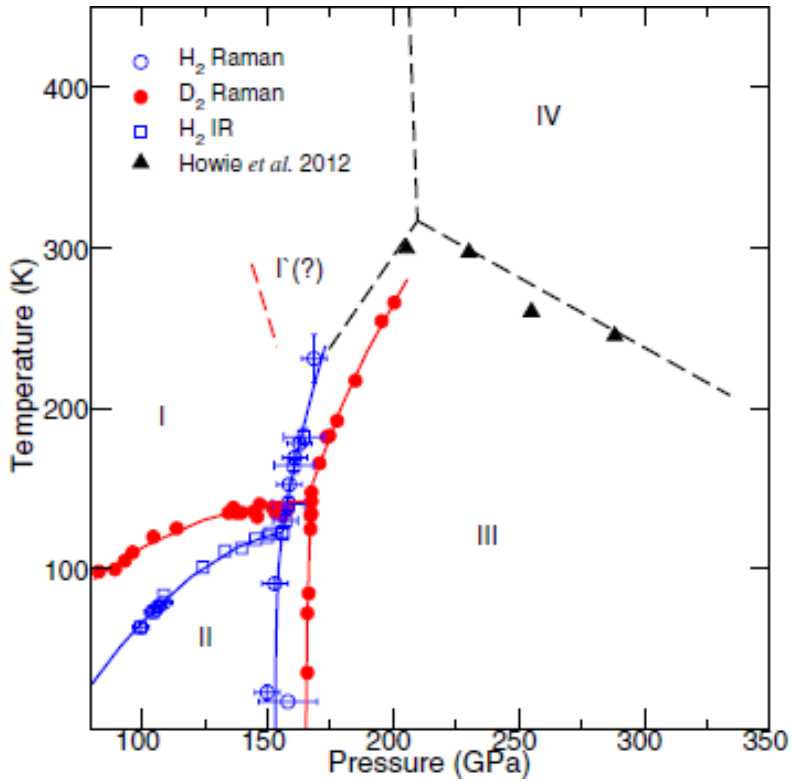
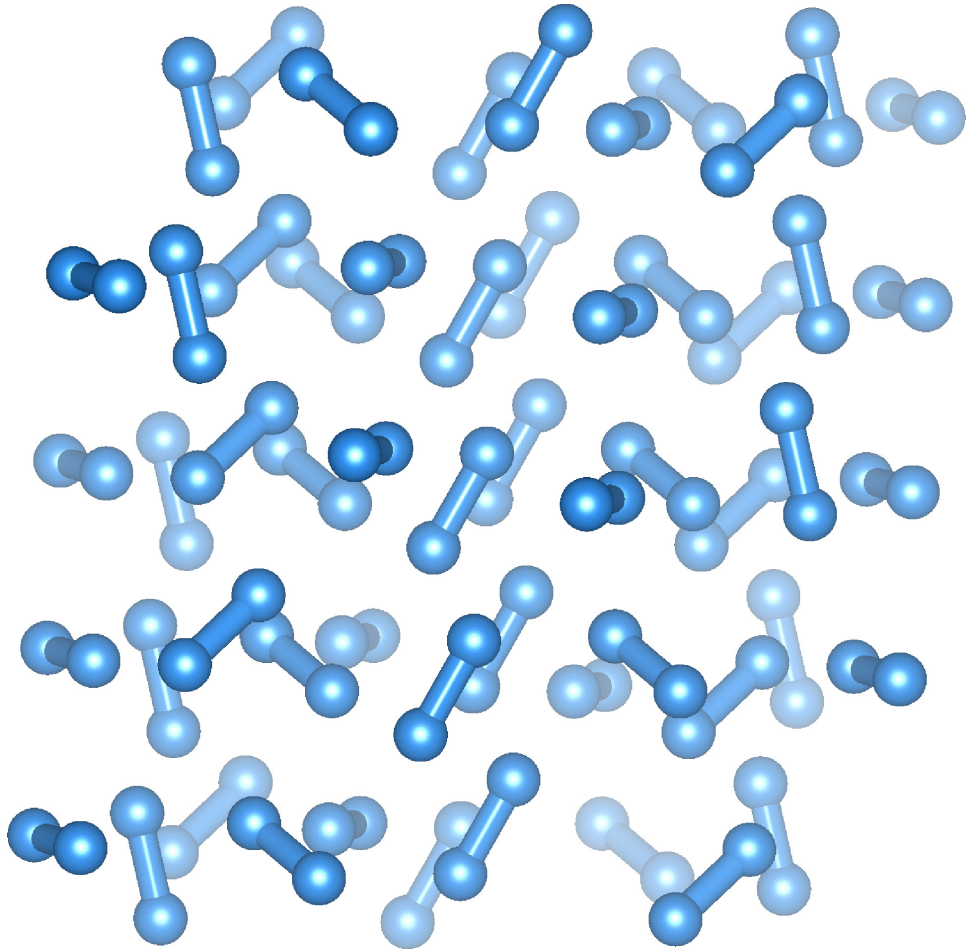
Hydrogen phase diagram



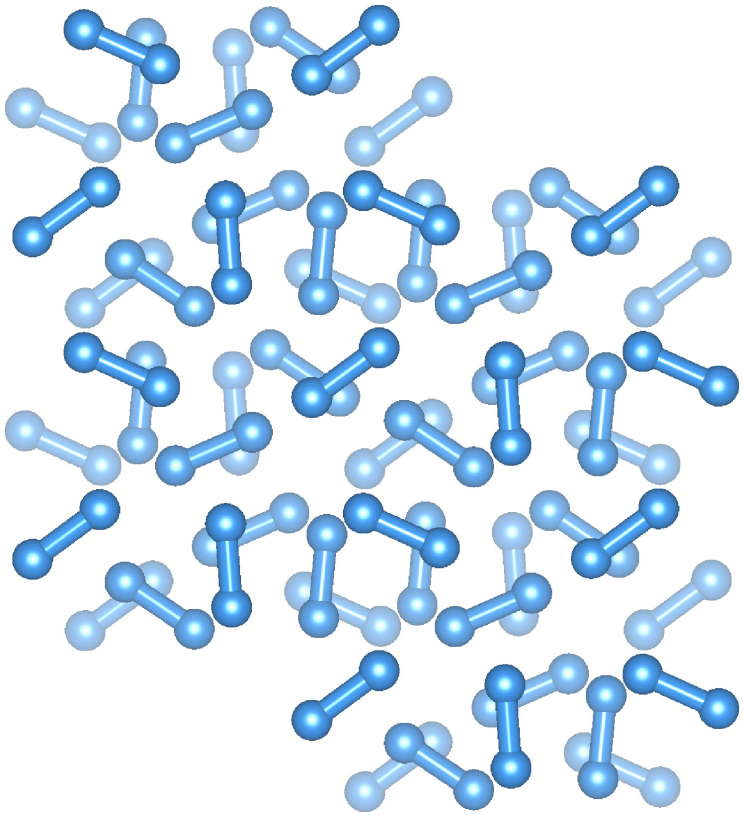


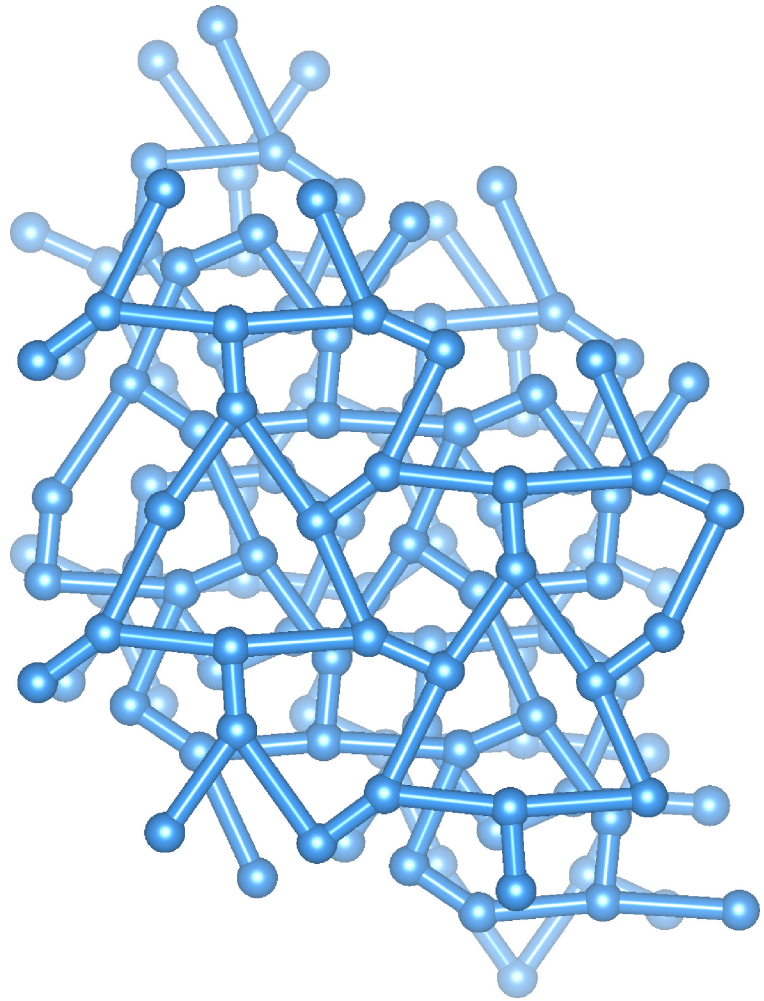
Figures from: J. M. McMahon, M. A. Morales, C. Pierleoni, and D. Ceperley, Rev. Mod. Phys. **84**, 1607 (2012).

Candidate structures - $P2_1/c$-24

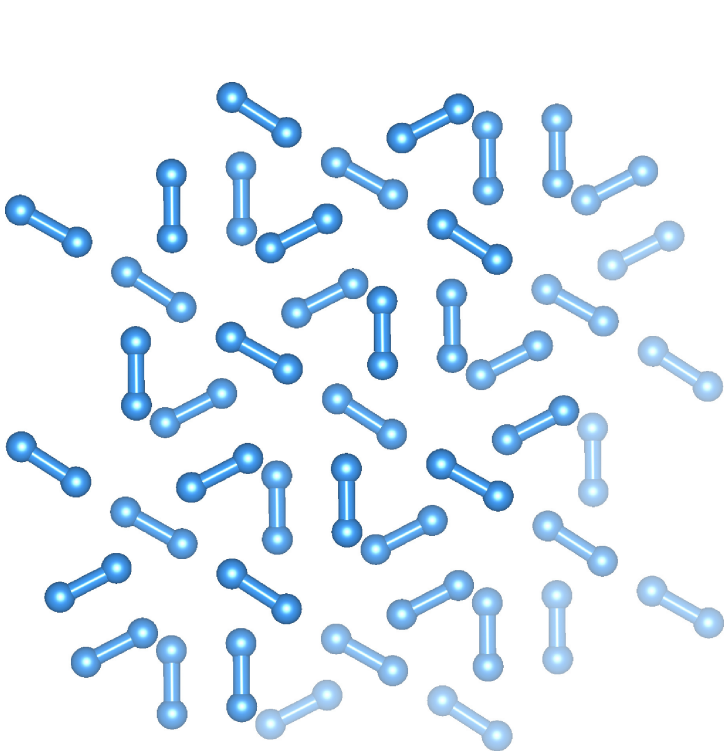


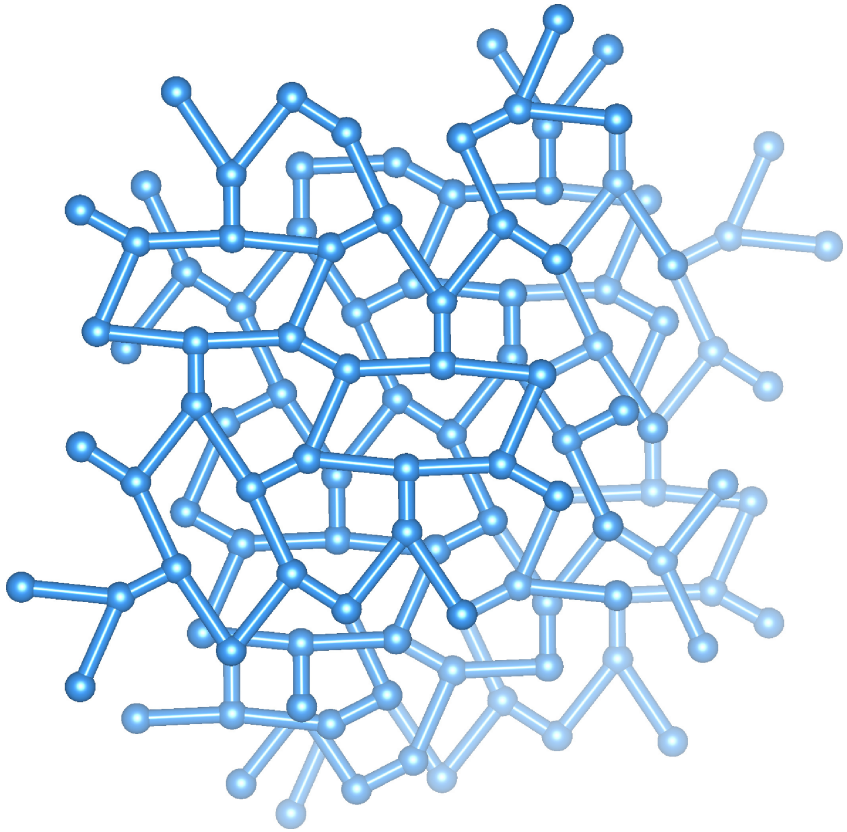
Candidate structures - C2/c-24



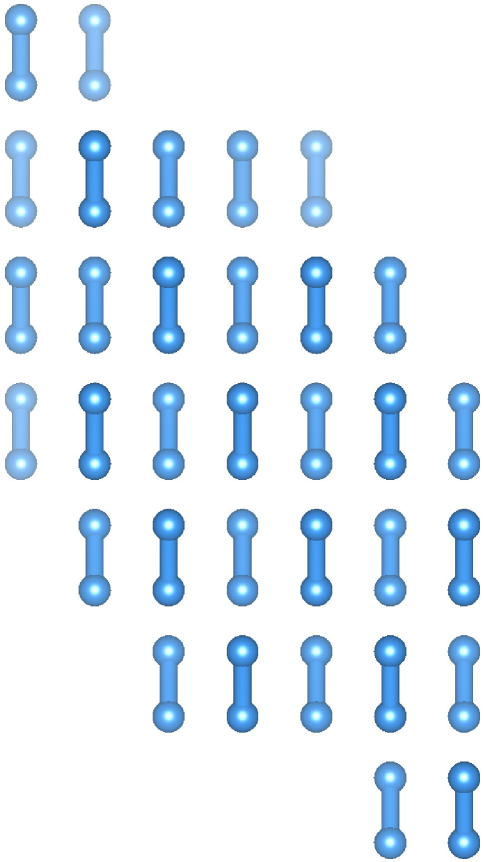


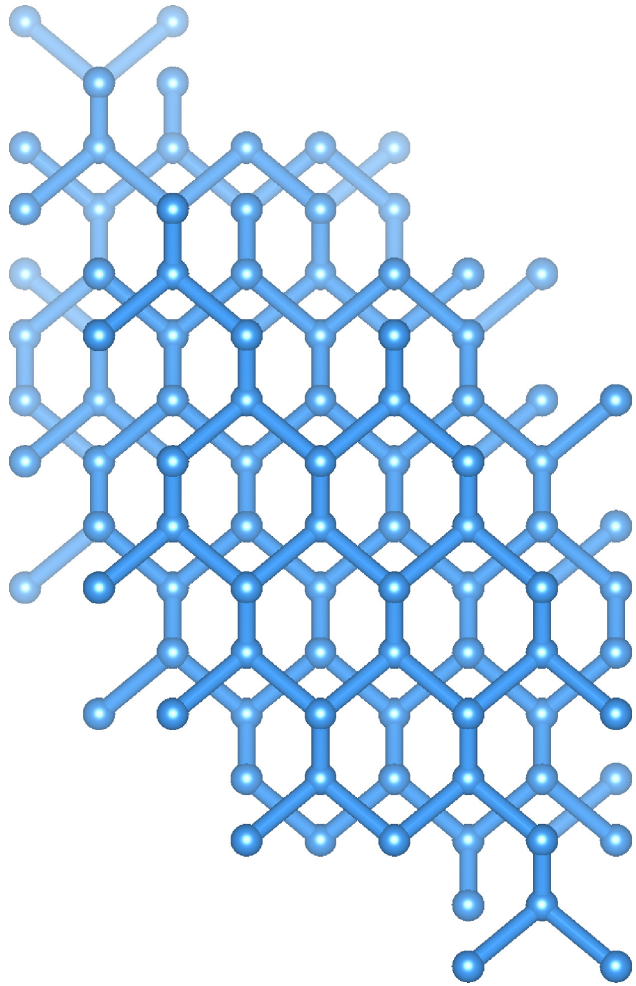
Candidate structures - Cmca-12



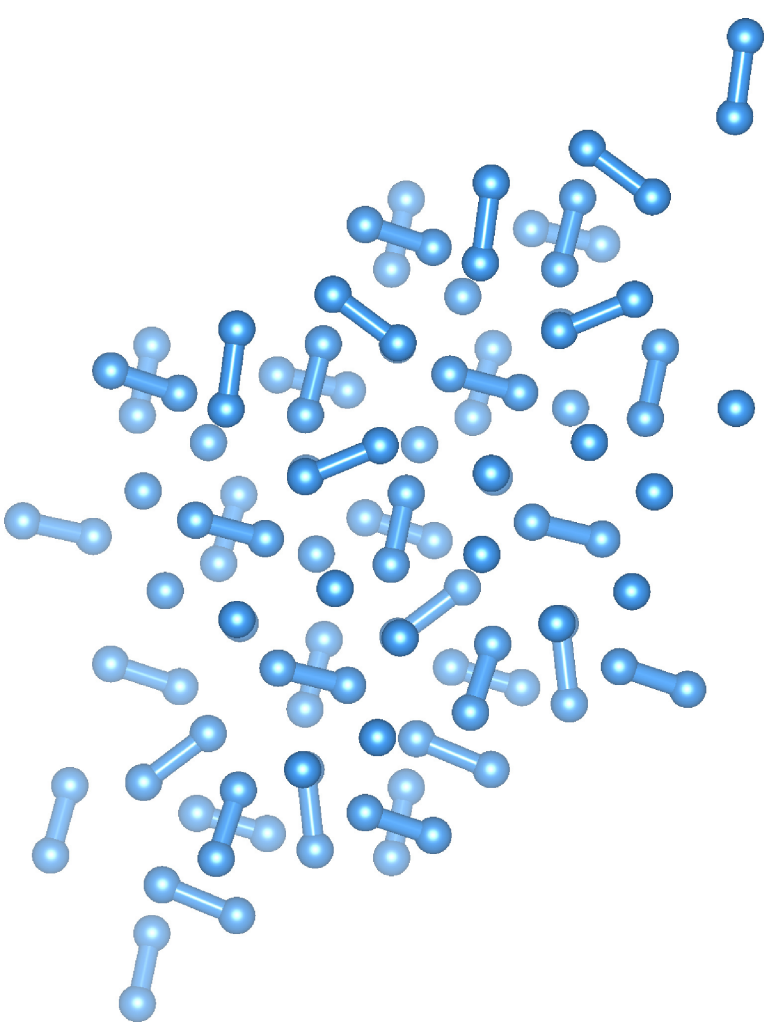


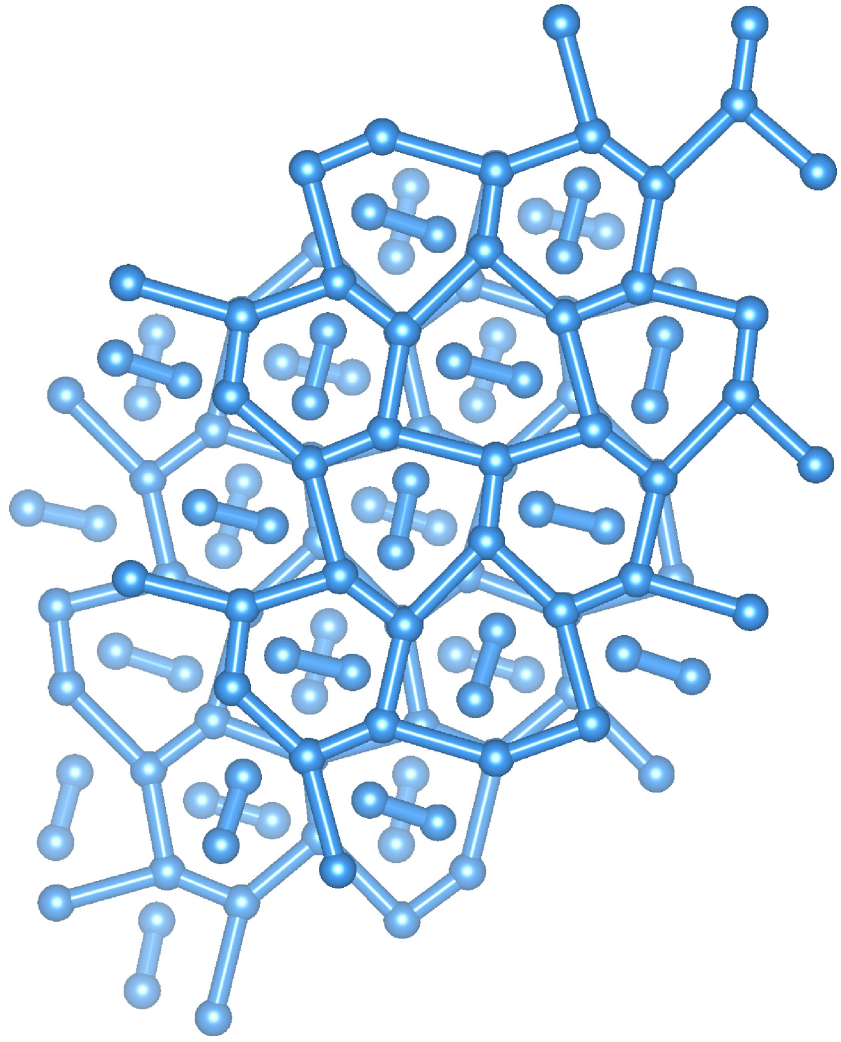
Candidate structures - Cmca-4



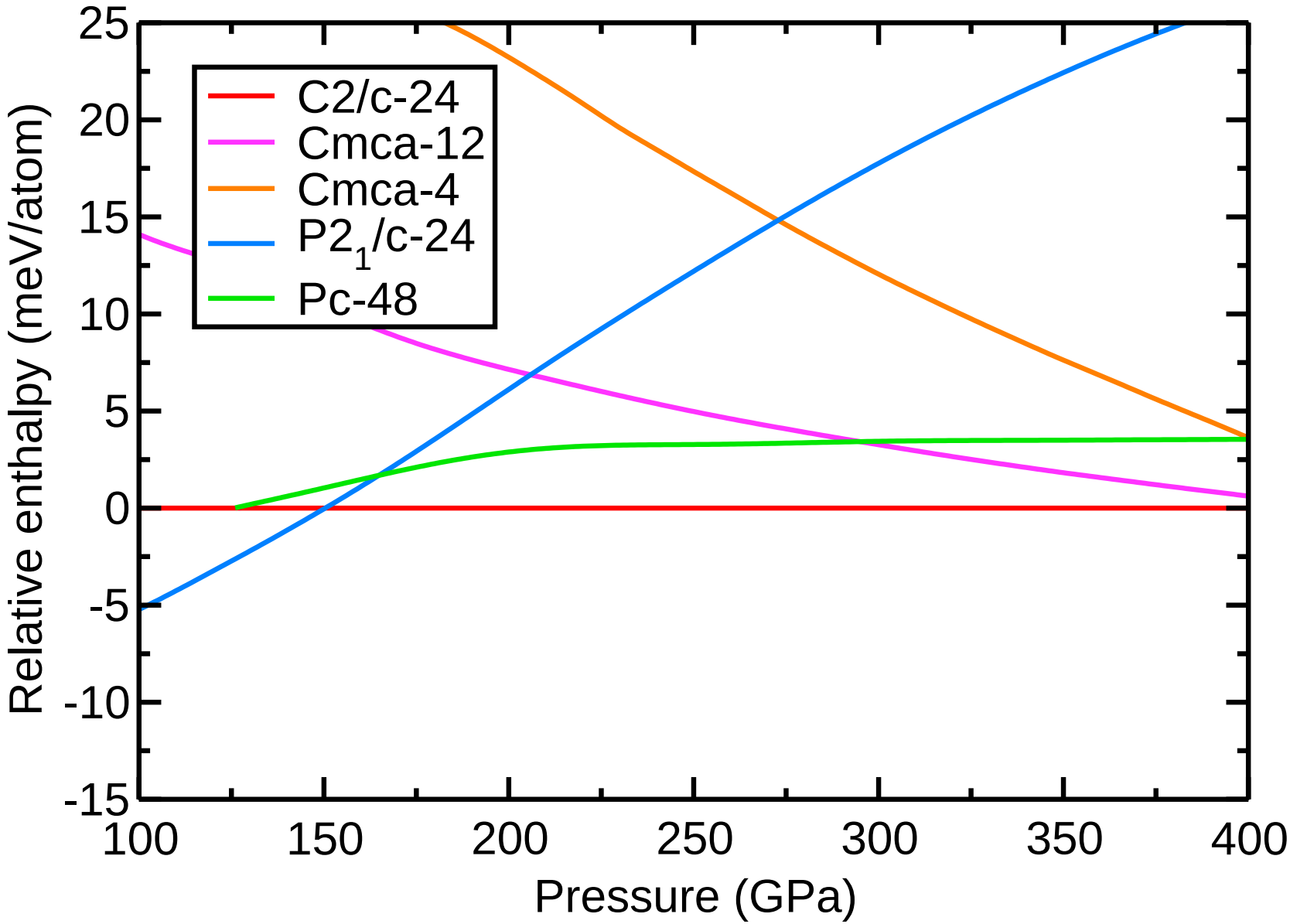


Candidate structures - Pc-48

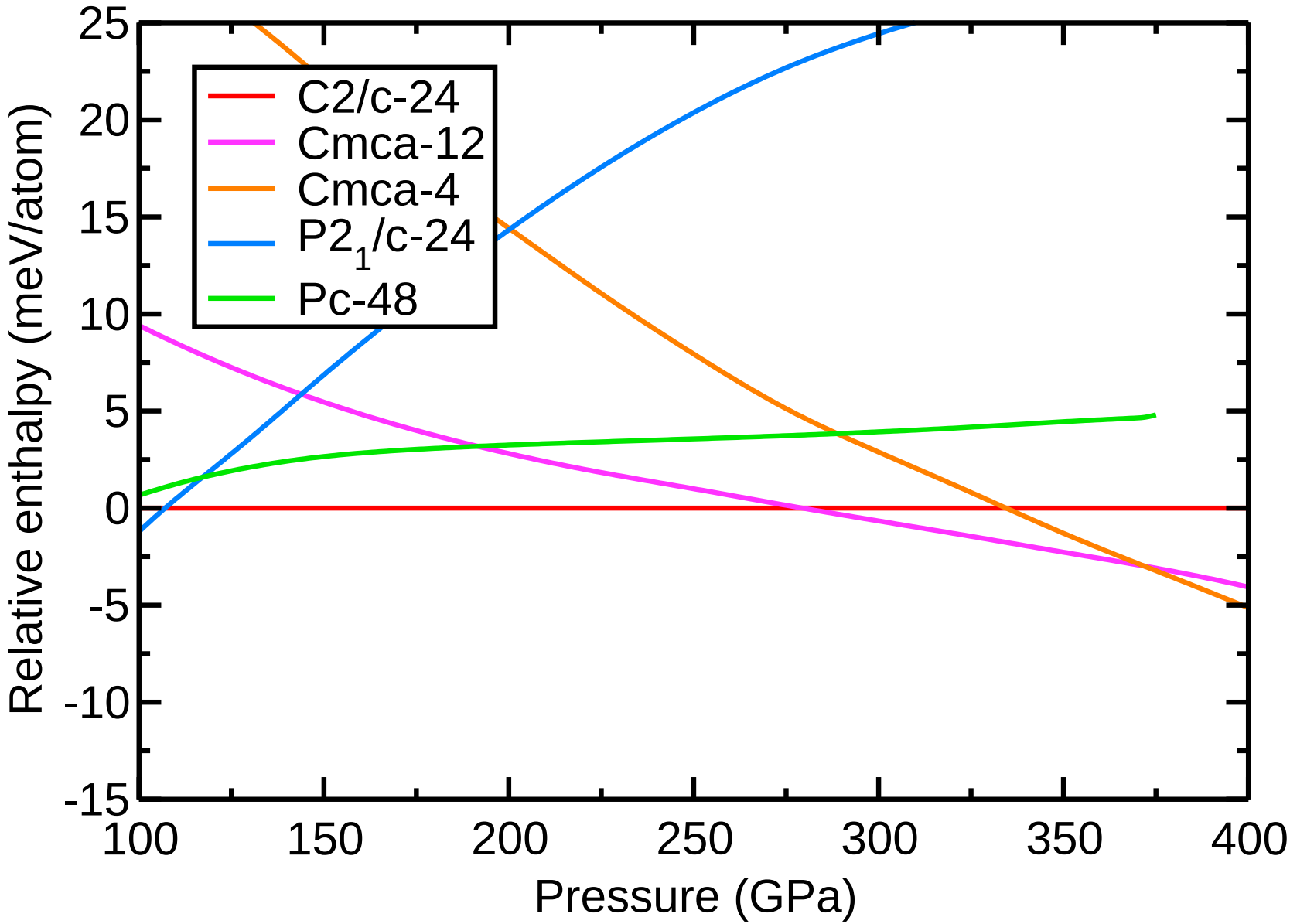




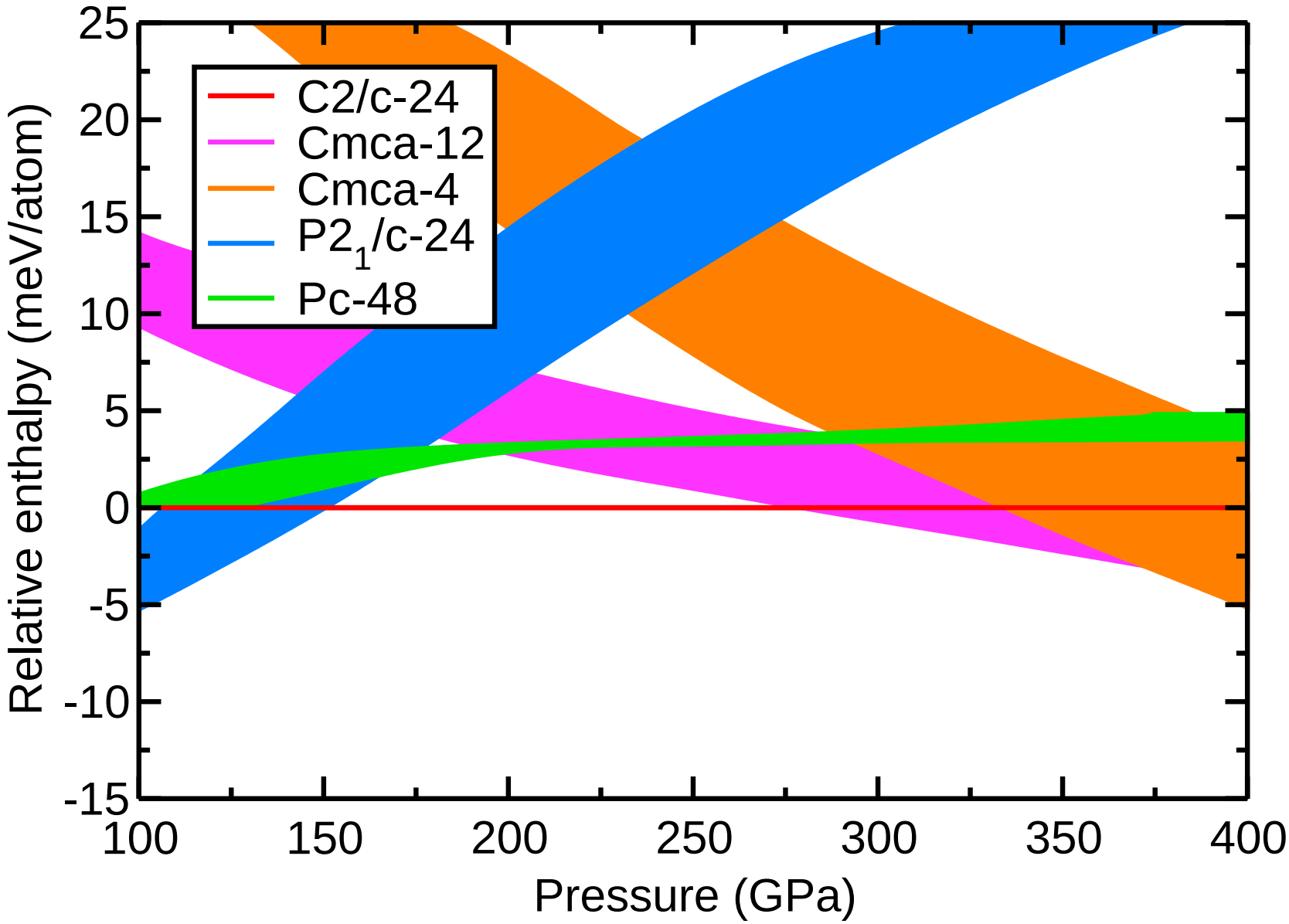
DFT phase diagram - BLYP



DFT phase diagram - PBE



DFT phase diagram



Brief digression - choice of supercell

- Superlattice basis vectors:

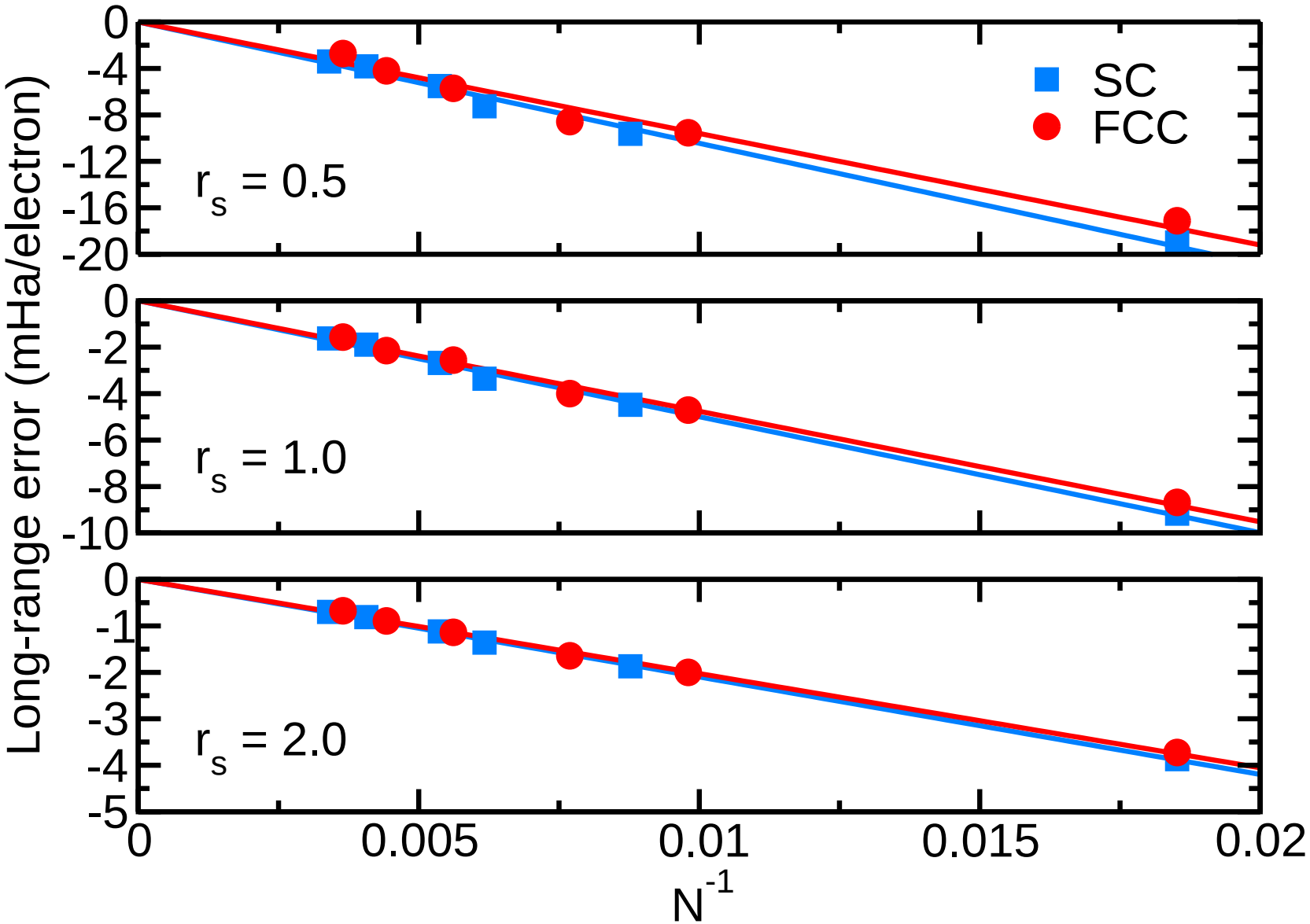
$$\begin{pmatrix} \mathbf{a}_{s_1} \\ \mathbf{a}_{s_2} \\ \mathbf{a}_{s_3} \end{pmatrix} = \begin{pmatrix} S_{11} & S_{12} & S_{13} \\ S_{21} & S_{22} & S_{23} \\ S_{31} & S_{32} & S_{33} \end{pmatrix} \begin{pmatrix} \mathbf{a}_{p_1} \\ \mathbf{a}_{p_2} \\ \mathbf{a}_{p_3} \end{pmatrix}$$

$$S_{ij} \in \mathbb{Z}$$

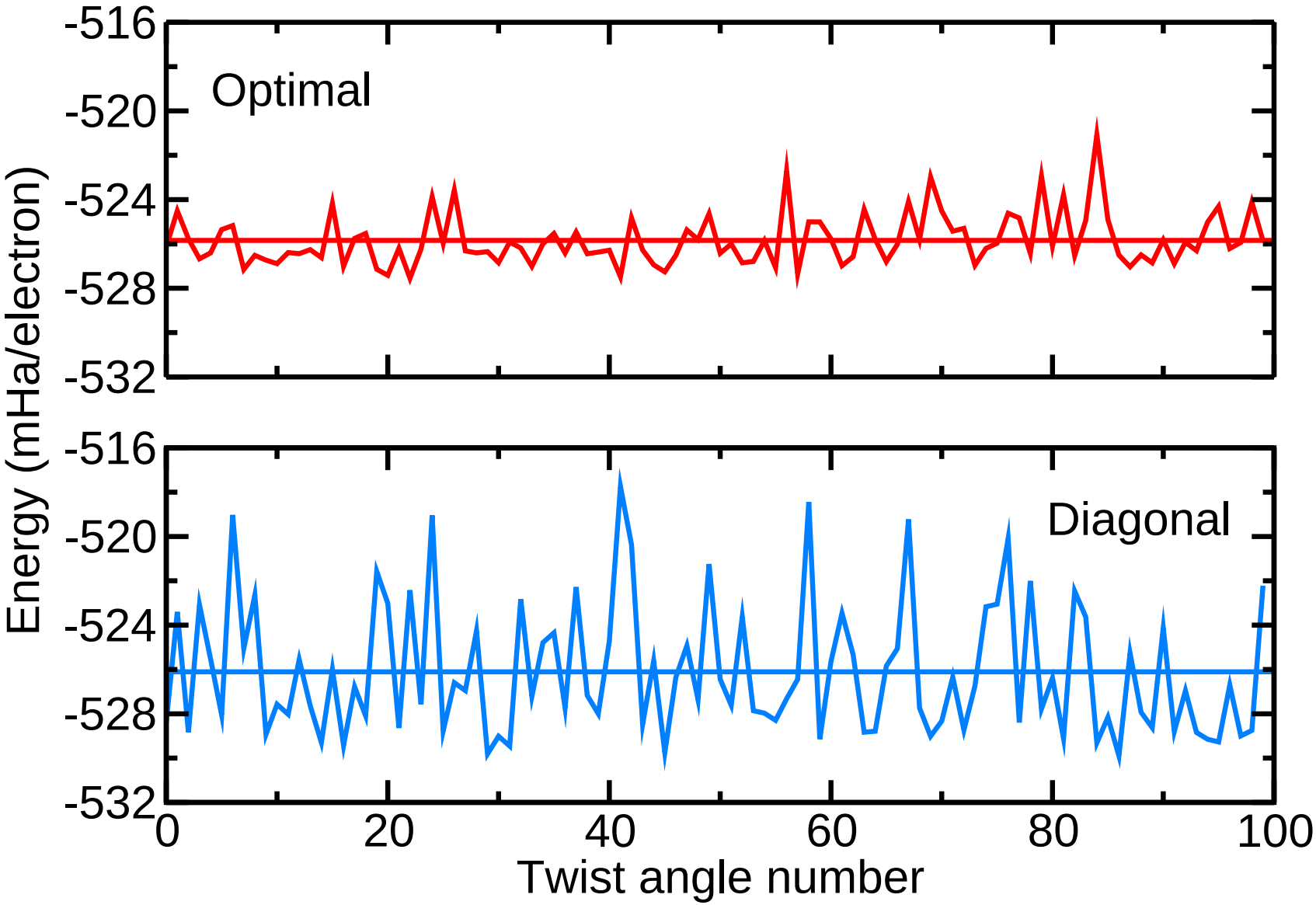
- Two different supercell matrices S and S' generate different bases for the same superlattice if S' can be reduced to S by integer row operations.
- The canonical form for such operations is the upper-triangular Hermite normal form:

$$\begin{pmatrix} a & b & d \\ 0 & c & e \\ 0 & 0 & f \end{pmatrix}, \quad 0 \leq b < c\,, \quad 0 \leq d, e < f\,.$$

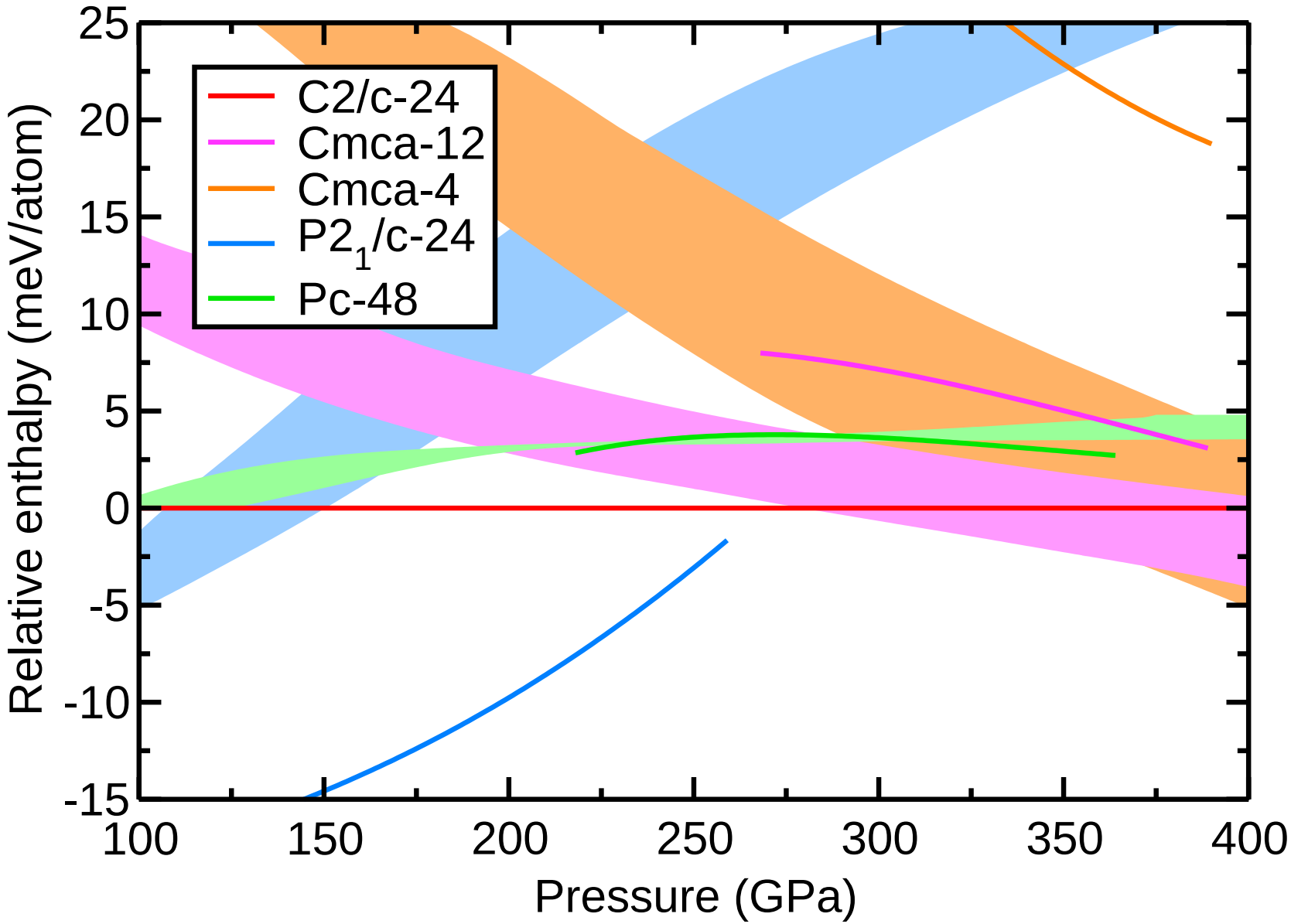
Brief digression - long-range finite-size errors



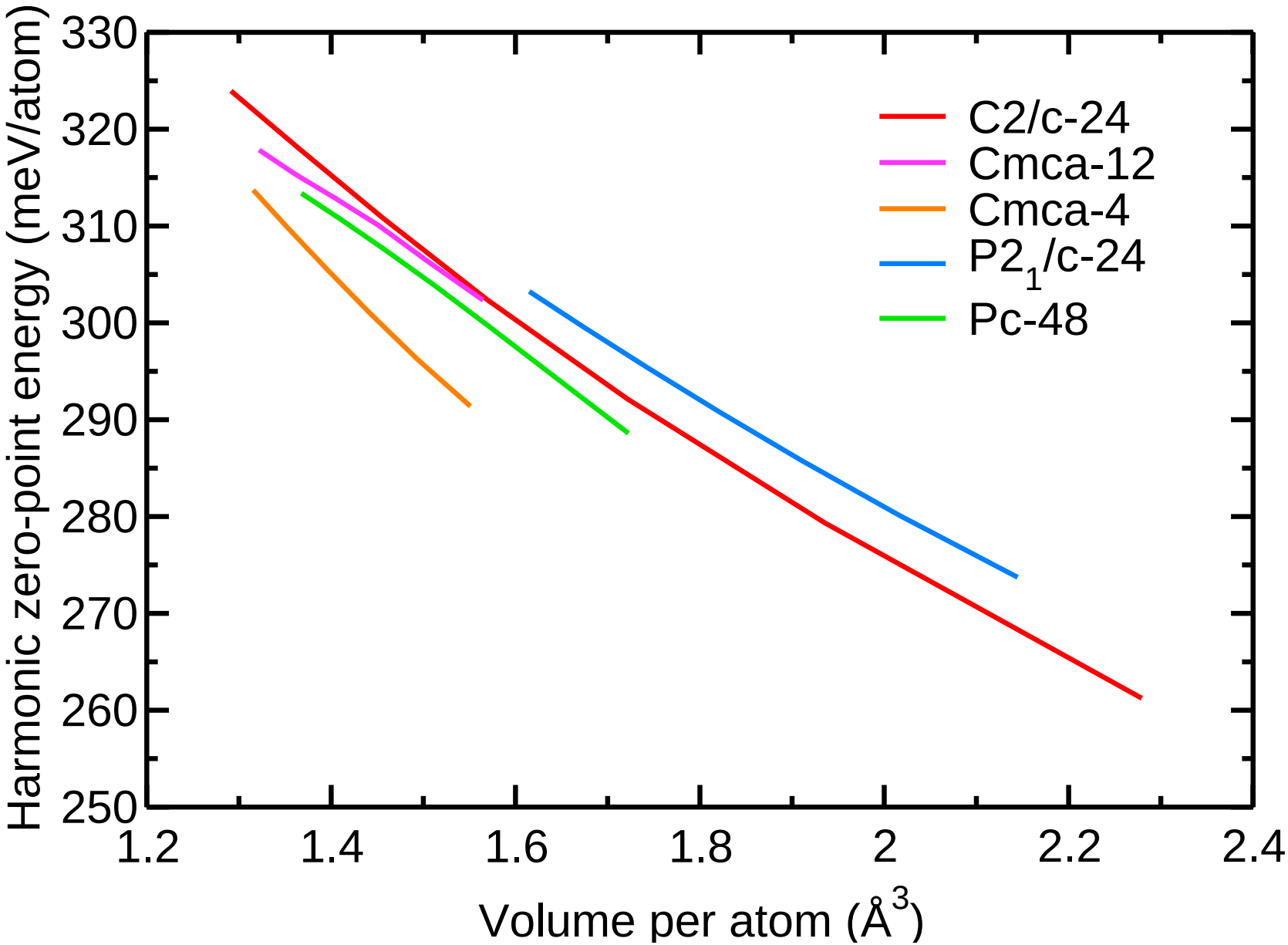
Brief digression - single-particle fluctuations



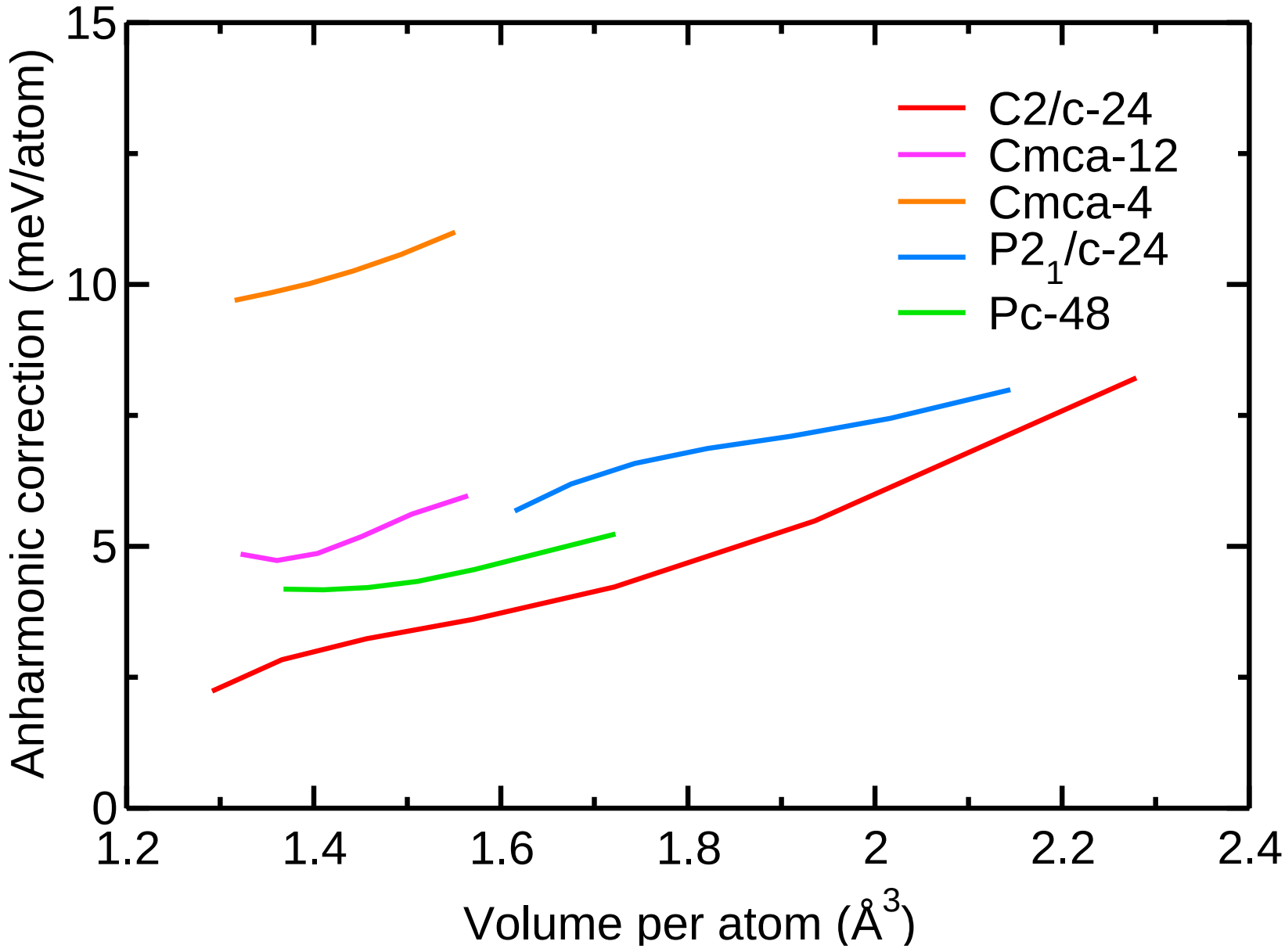
Comparison of static lattice phase diagrams



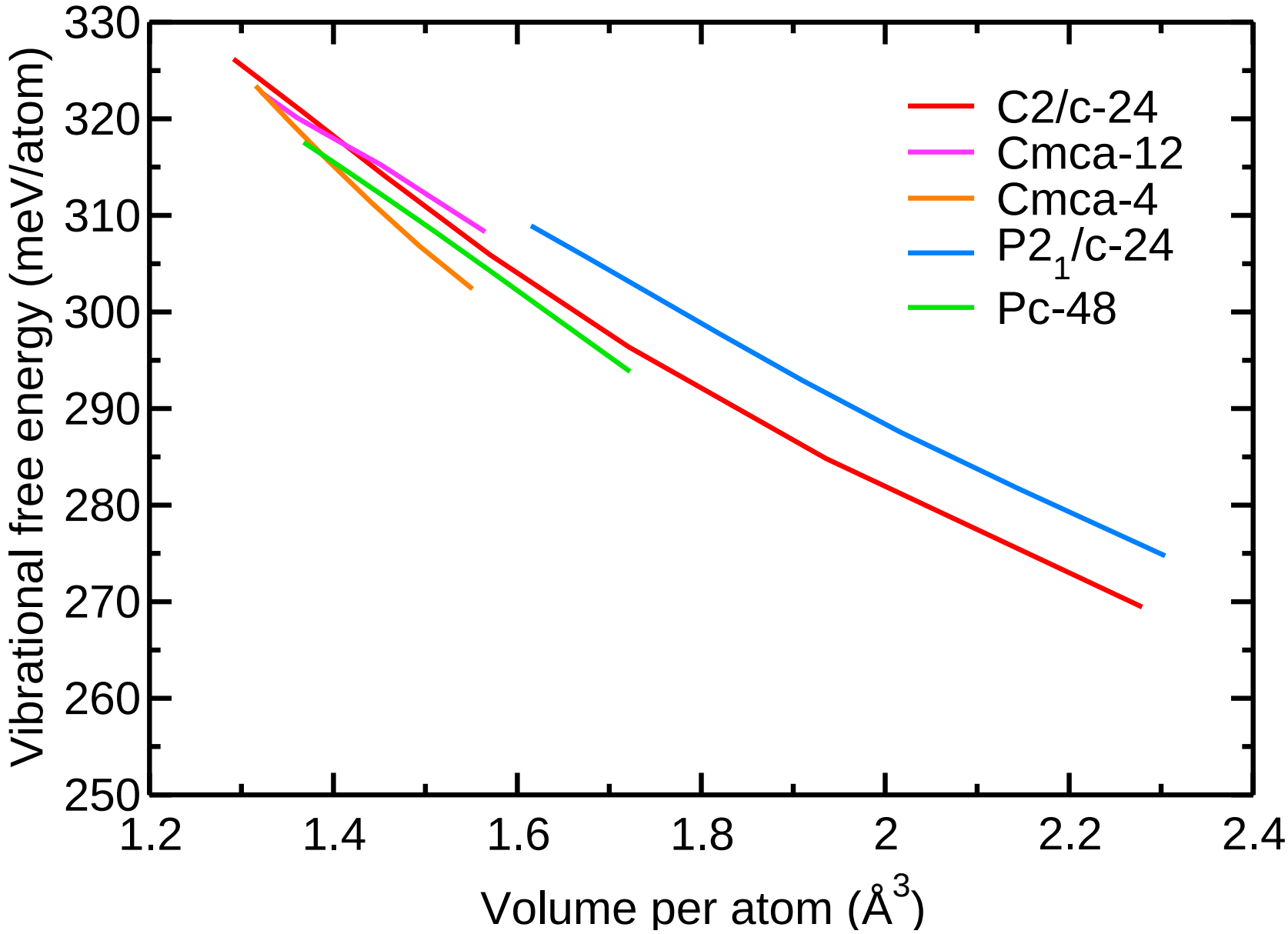
Zero-point energies - harmonic approximation



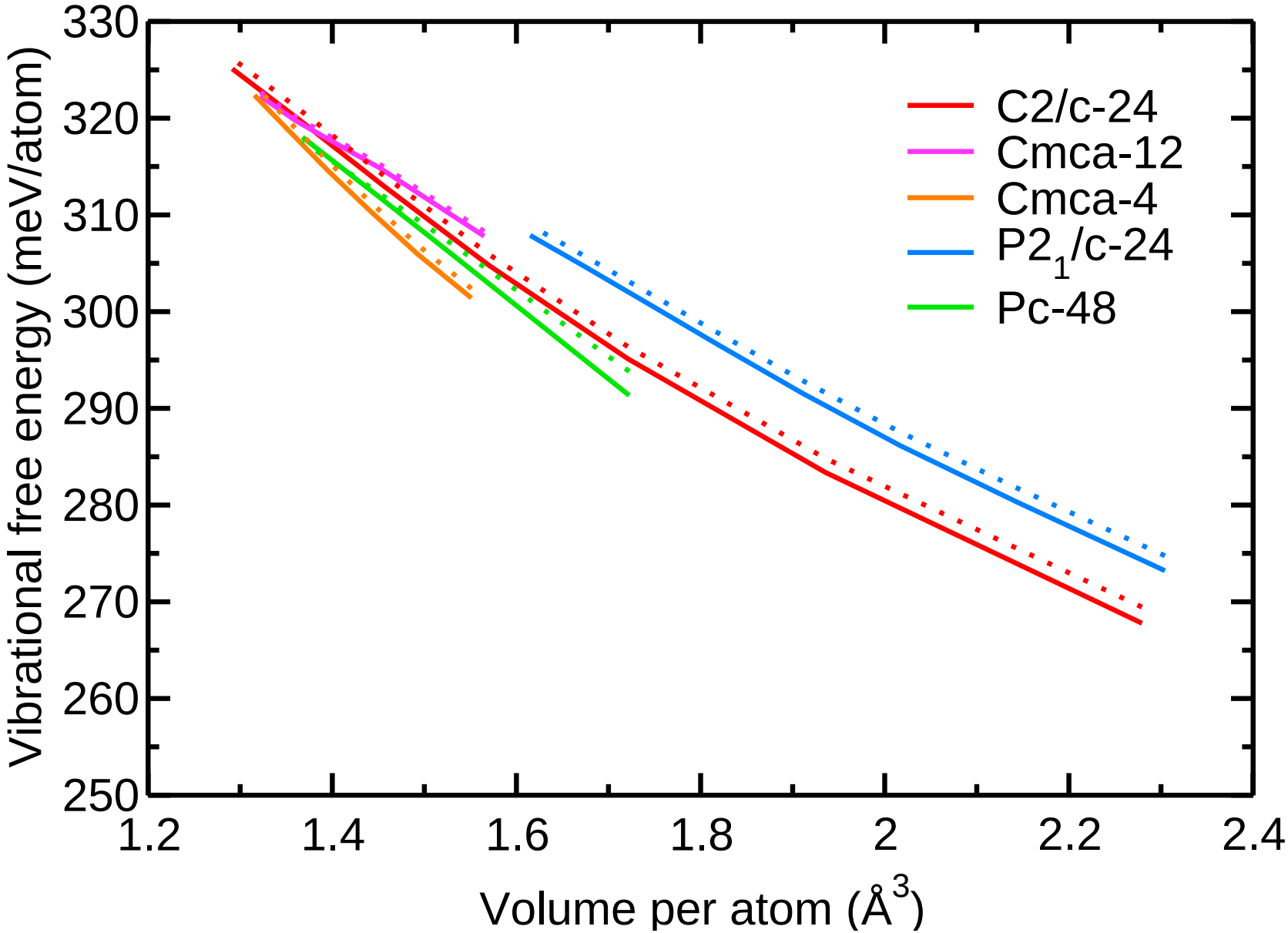
Zero-point energies - anharmonic correction



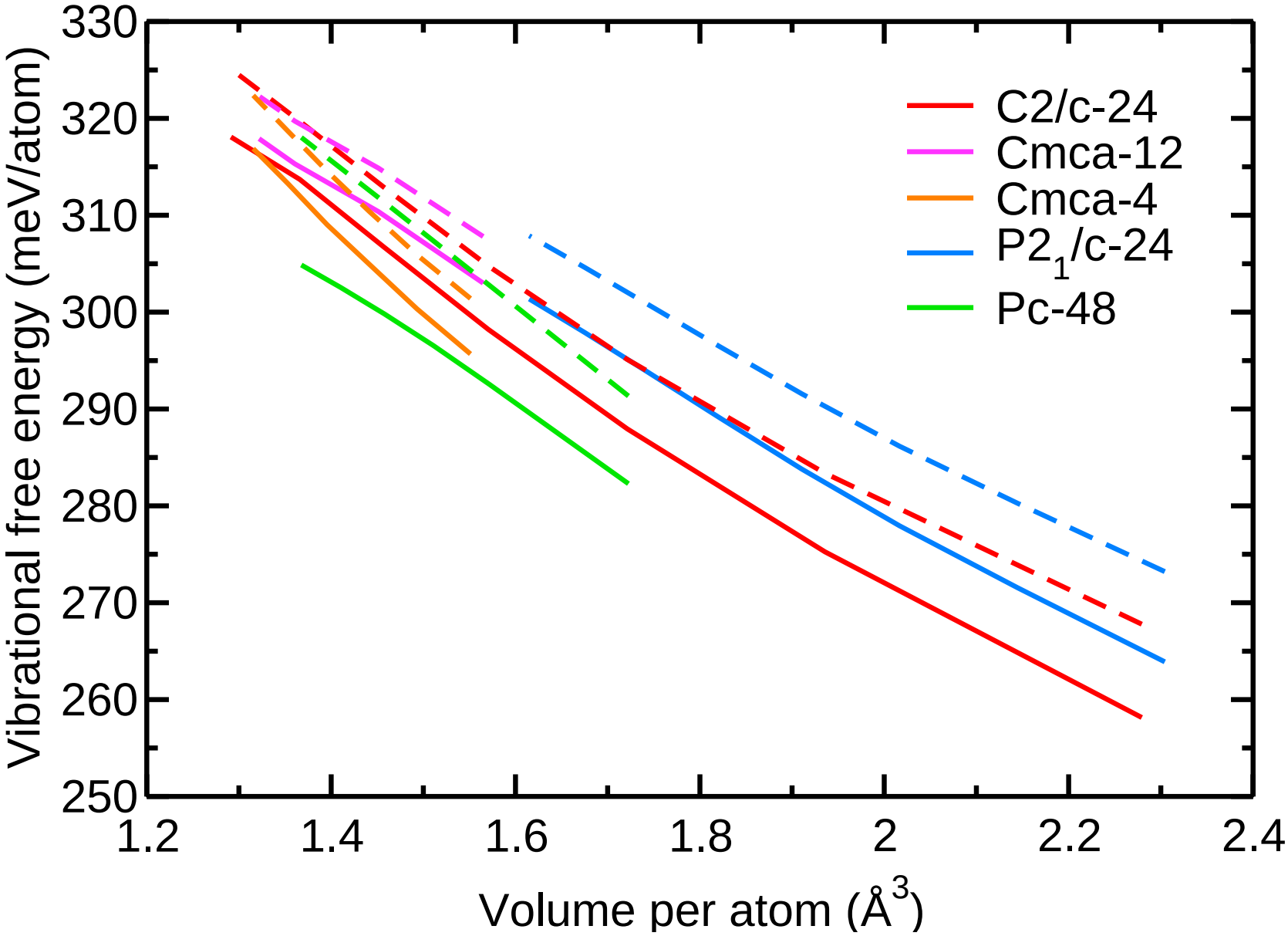
Vibrational free energy - 0 K



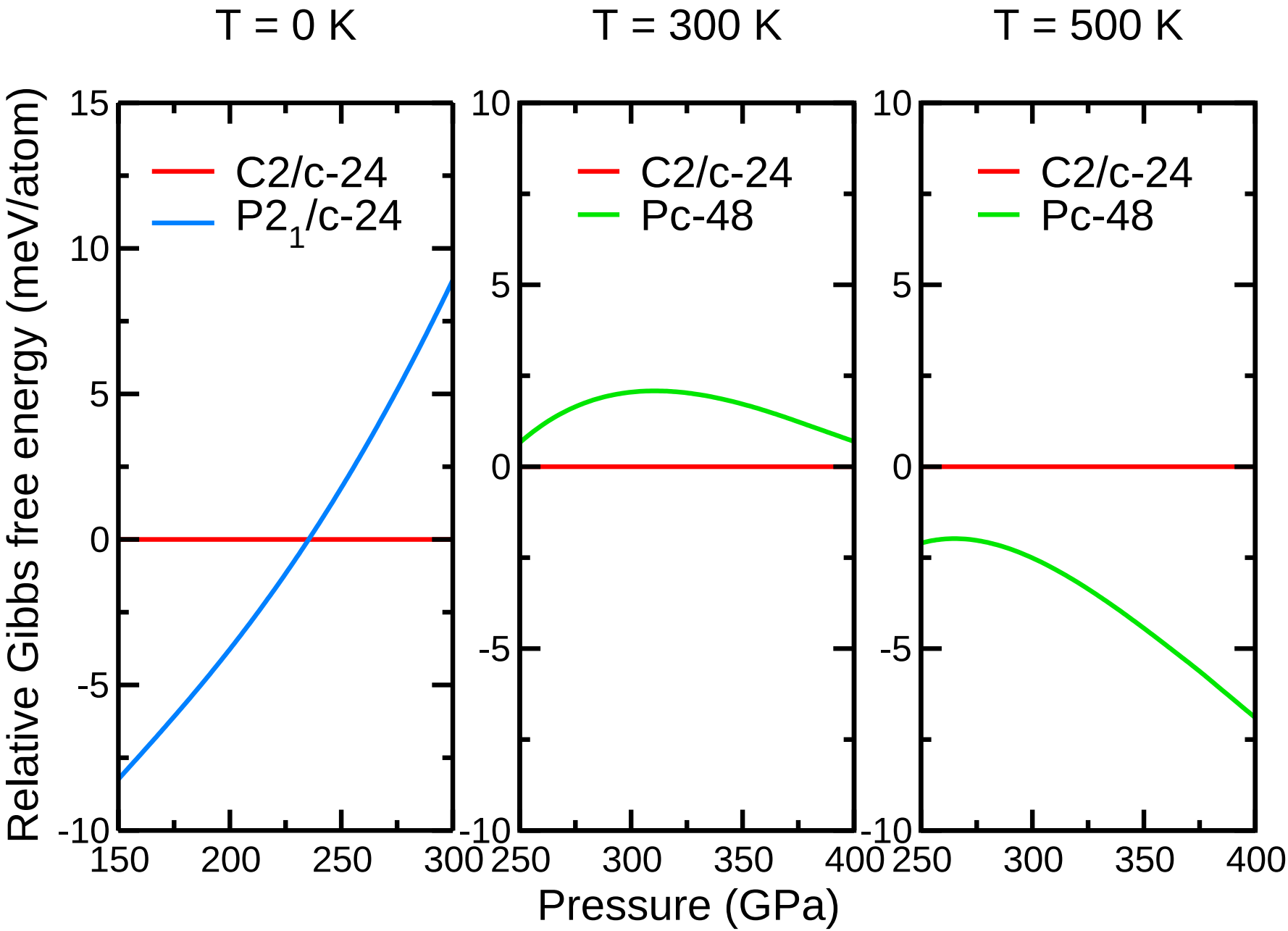
Vibrational free energy - 300 K



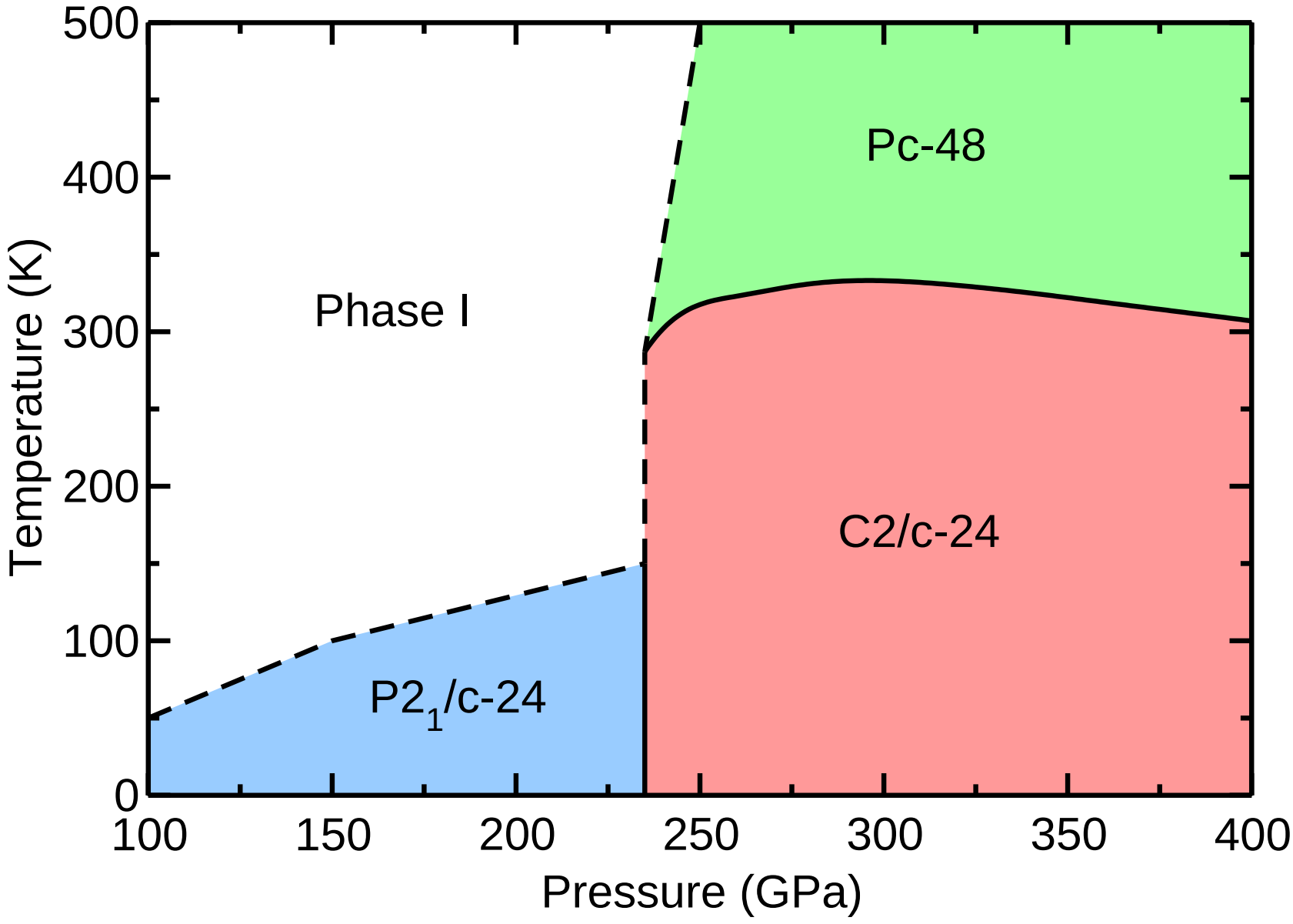
Vibrational free energy - 500 K



Phase transitions



Phase diagram



Conclusions

- Combination of DMC and anharmonicity removes Cmca-12 and Cmca-4 from the picture (up to 400 GPa).
- Calculated $P2_1/c$-24 to $C2/c$-24 transition pressure is around 75 GPa higher than that observed for transition from phase II to phase III.
  - Nuclear spin effects important?
  - Better phase III structure?
- Pc-48 is stabilized by temperature at pressures above 250 GPa, suggesting that it is a good structural model for phase IV.

Acknowledgements

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EPSRC
Pioneering research and skills

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