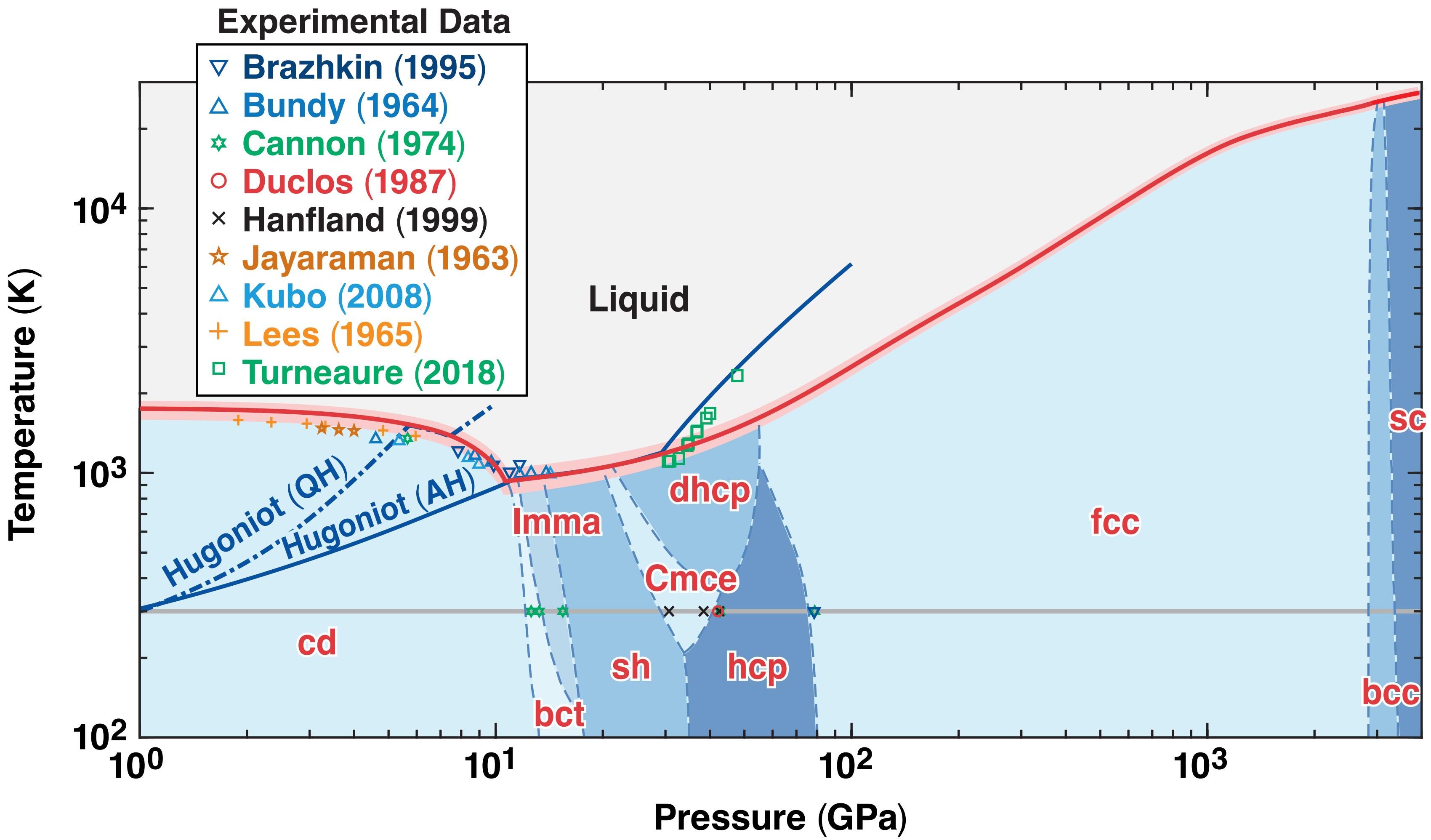
High-Pressure Phase Diagram of Silicon



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Summary

A high-pressure phase diagram of silicon was constructed using density functional theory (DFT) calculations up to a pressure of 4 TPa

- The phases of Imma* and Cmce-16** were predicted on the phase diagram from computations for the first time, consistent with previous experimental observations
- High-pressure anomalous transition of face-centered cubic (fcc) to body-centered cubic (bcc) to simple cubic (sc) was predicted to occur at 2.87 TPa and 3.89 TPa
- Anharmonic contributions to the lattice free energy were determined to be essential for accurate analysis of the cubic diamond and orthorhombic structures

*M. I. McMahon *et al.*, Phys. Rev. B 50, 739 (1994).
Imma: base-centered orthorhombic
**M. Hanfland *et al.*, Phys. Rev. Lett. 82, 1197 (1999).
Cmce: body-centered orthorhombic

Collaborators

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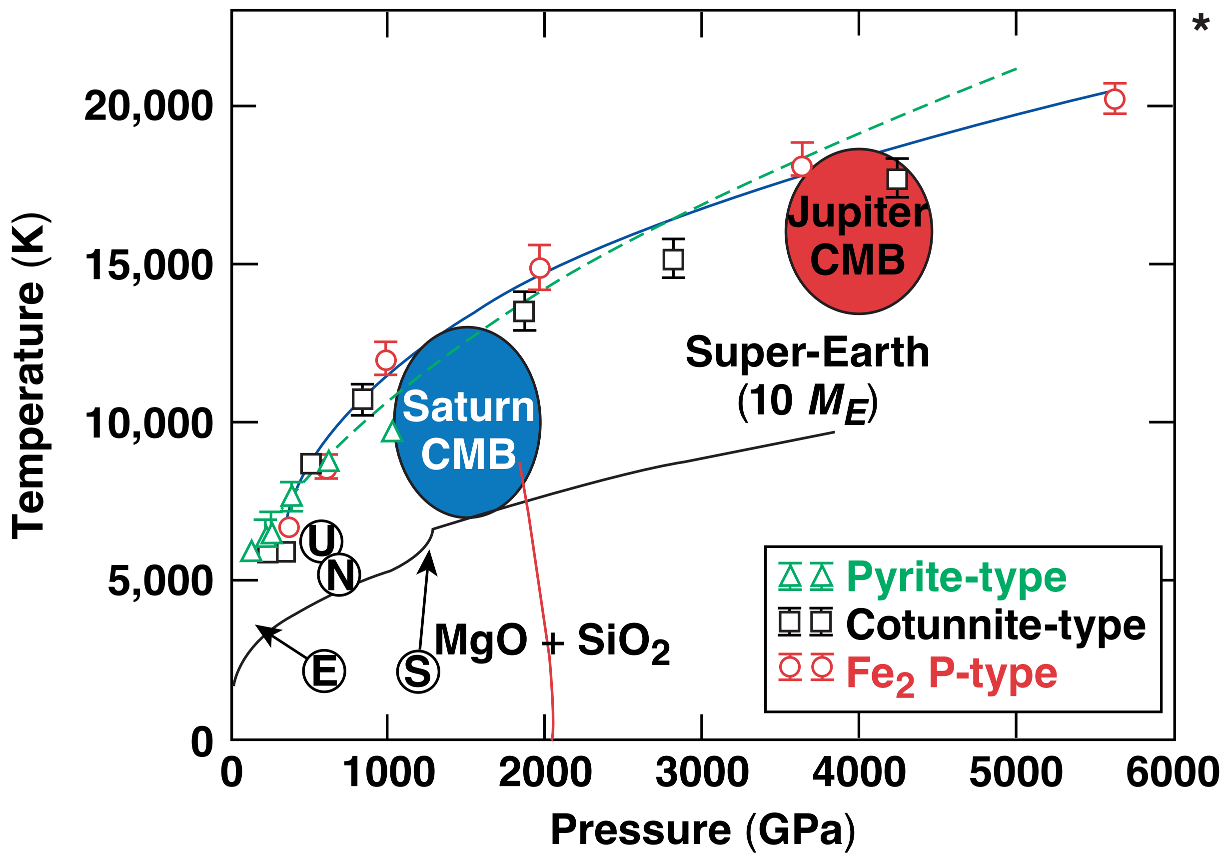
Motivation

Knowledge of the behavior of silicon under high *P–T* conditions is essential for ICF, materials, and planetary sciences



- **Understanding propagation of shock waves through Si is essential for designing ICF using Si-based ablators**
- **For understanding anomalous convection in super-Earths with high concentrations of silicon-based coordination compounds, binary/ternary phase diagrams are required****

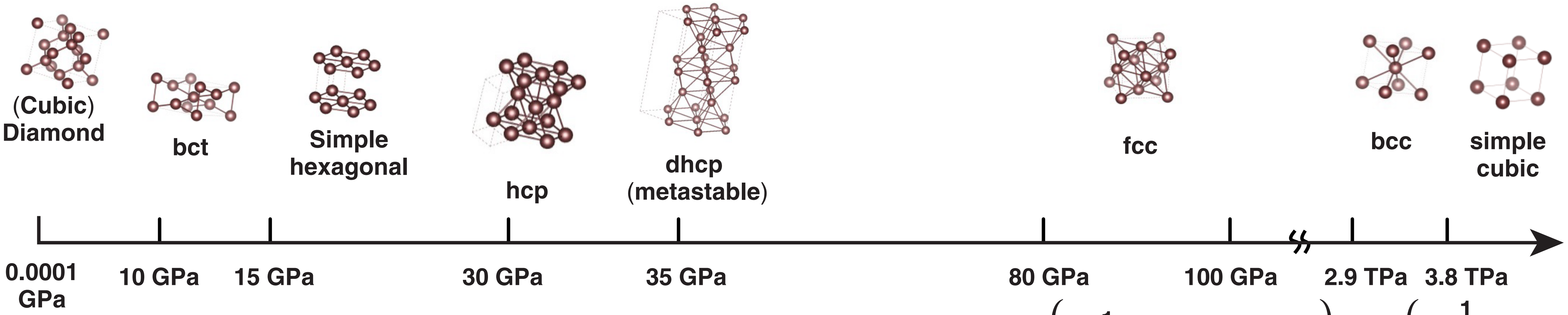
*F. González-Cataldo, S. Davis, and G. Gutiérrez, Sci. Rep. 6, 26537 (2016).
**F. Soubiran *et al.*, Phys. Plasma 24, 041401 (2017).
D. C. Swift *et al.*, Phys. Rev. B 64, 214107 (2001);
B. Militzer and K. P. Driver, Phys. Rev. Lett. 115, 176403 (2015);
S. X. Hu *et al.*, Phys. Rev. B 94, 094109 (2016); S. X. Hu *et al.*, Phys. Rev. E 95, 043210 (2017).

ICF: inertial confinement fusion
CMB: cosmic microwave background

Method

An evolutionary algorithm-based structure search with USPEX* was employed to identify possible structures at zero Kelvin

- The methodology involves random structure searching with 1, 2, 4, 6, 8, 9, 12, and 16 Si atoms in a conventional unit cell looking for minimum enthalpy at a given pressure



- Transformation matrices using the strain parameter ε were used to scale each structure across the pressure domain

$$\begin{pmatrix} 1+\varepsilon & 0 & 0 \\ 0 & 1+\varepsilon & 0 \\ 0 & 0 & 1+\varepsilon \end{pmatrix}, \quad \begin{pmatrix} \frac{1}{\sqrt{1+\varepsilon}} & 0 & 0 \\ 0 & \frac{1}{\sqrt{1+\varepsilon}} & 0 \\ 0 & 0 & 1+\varepsilon \end{pmatrix}, \quad \begin{pmatrix} \frac{1}{\sqrt{1+\varepsilon}} & 0 & 0 \\ 0 & 1+\varepsilon & 0 \\ 0 & 0 & \frac{1}{\sqrt{1+\varepsilon}} \end{pmatrix}$$

Scales: Volume; c/a, b/a: Axial ratios

*A. R. Oganov and C. W. Glass, J. Phys. Chem. 124, 244704 (2006).
hcp: hexagonal close packed
dhcp: double-hexagonal close-packed
bct: body centered tetragonal

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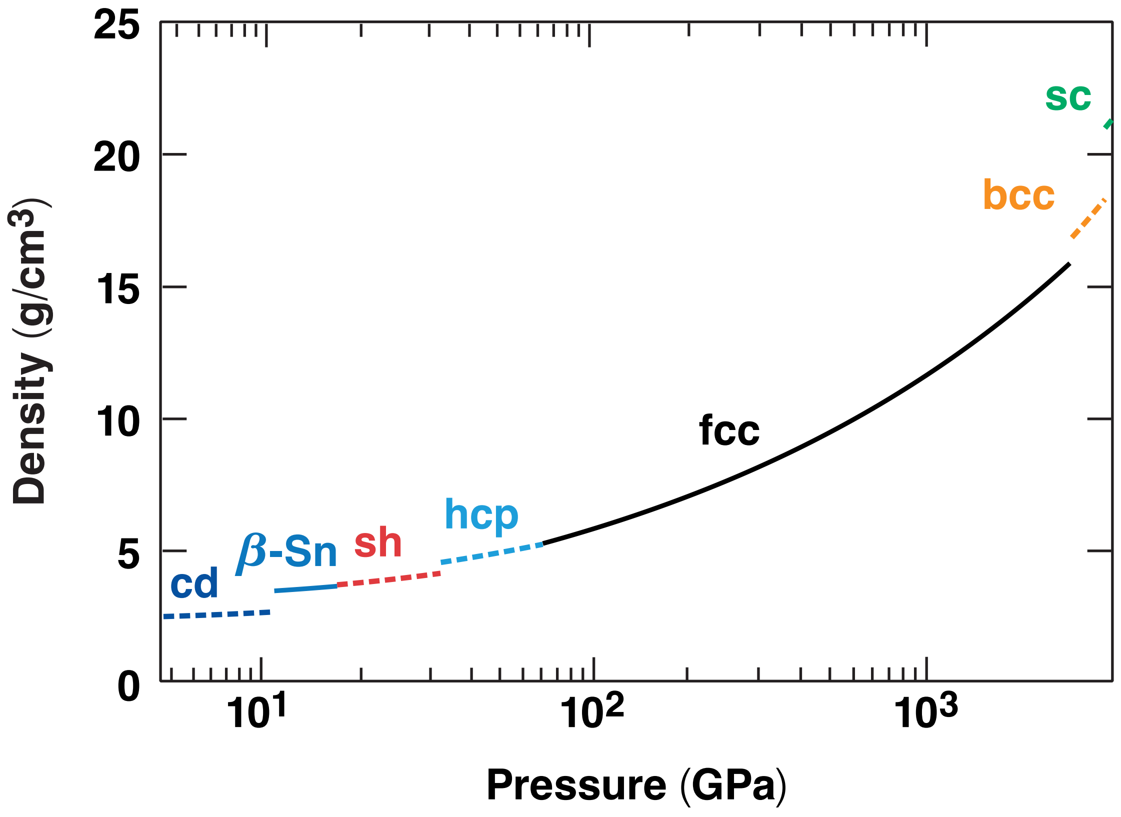
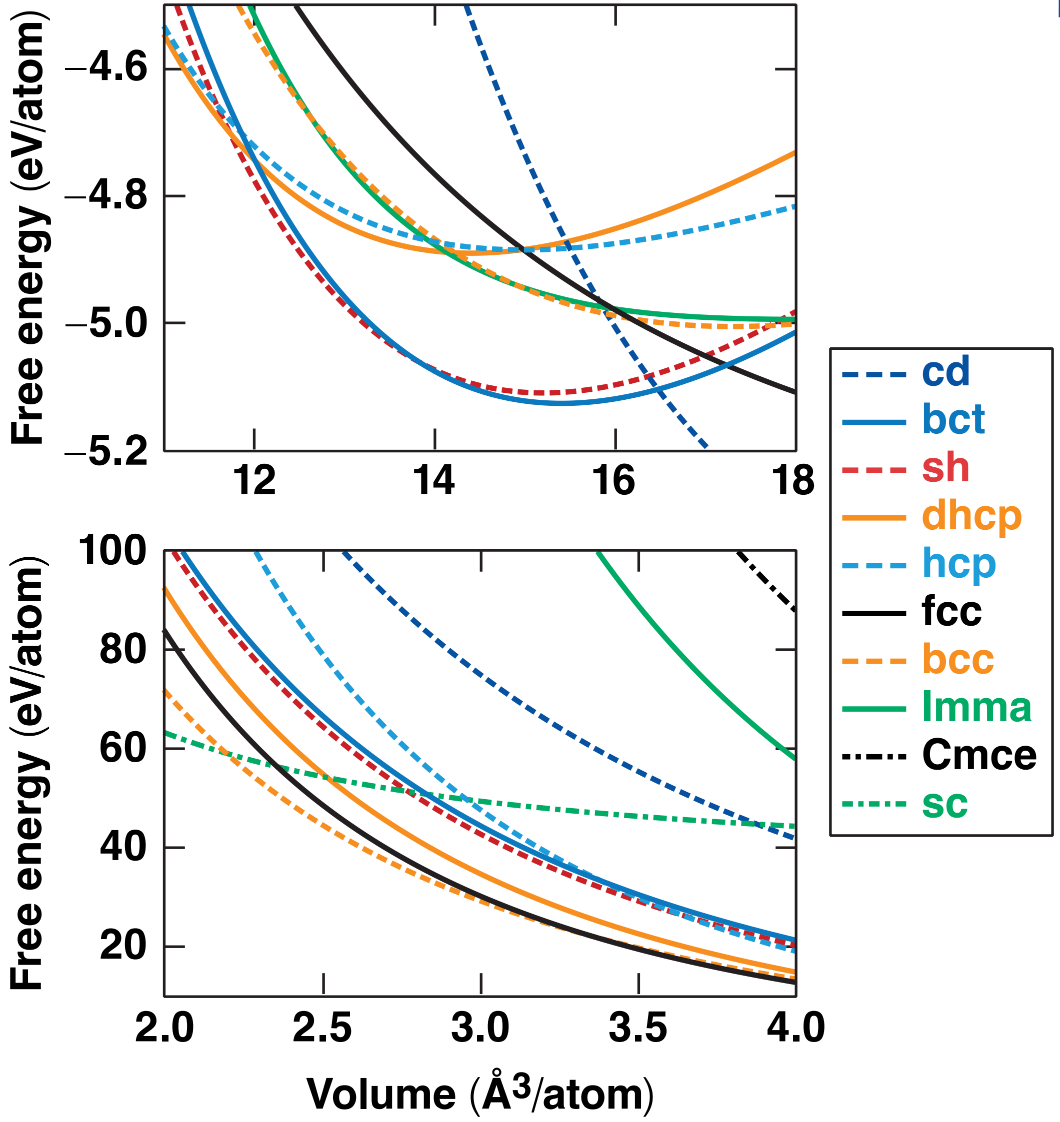
DFT calculations were performed for each structure to compare thermodynamic stability at 0 K

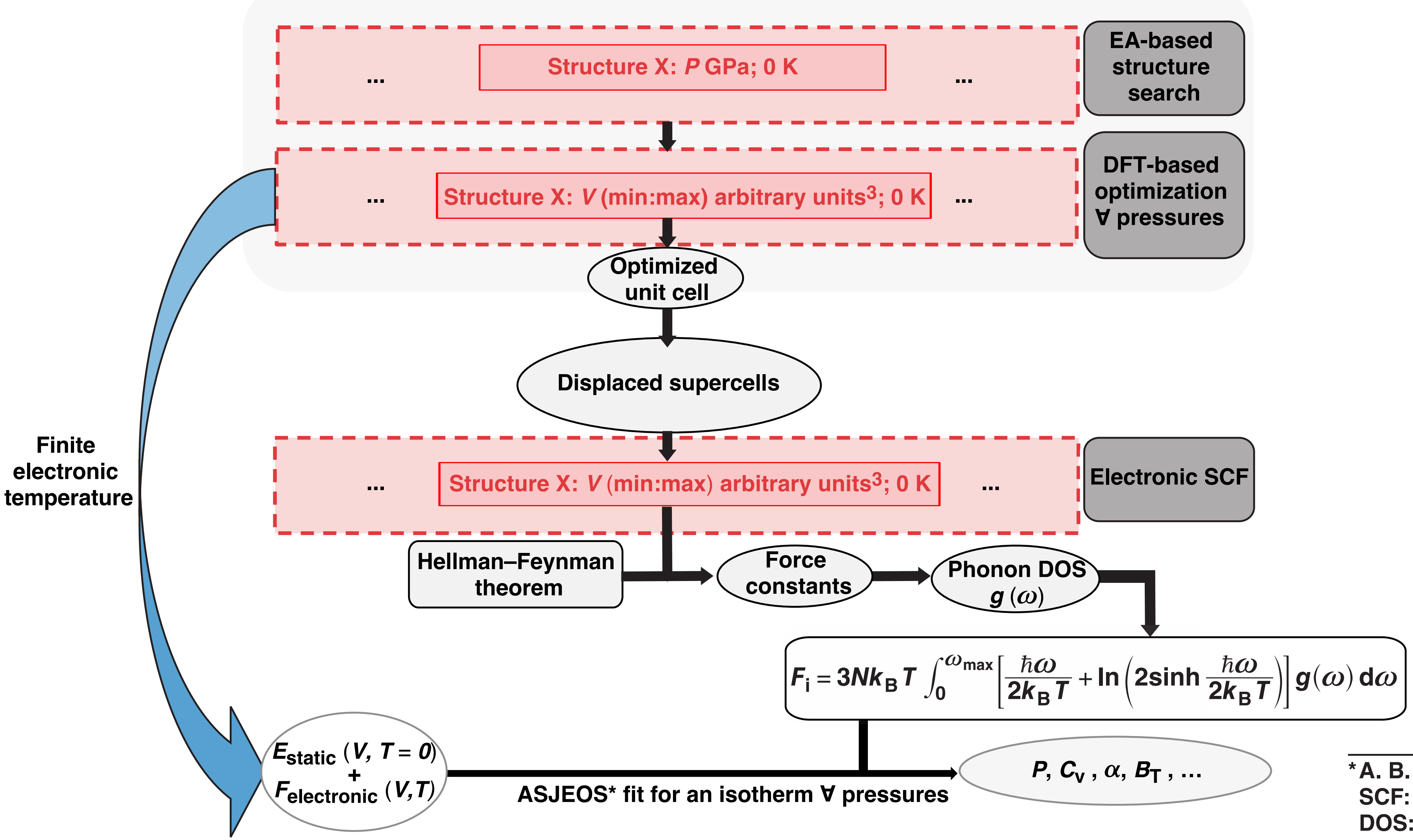
- The obtained discrete data of Gibbs free energy were fitted with an augmented stabilized jellium equation of state (ASJEOS)*





*A. B. Alchagirov *et al.*, Phys. Rev. B 63, 224115 (2001).
sh: simple hexagonal

Finite-temperature thermodynamic variables were obtained using first-principles electronic and phonon calculations



$$F_i = 3Nk_B T \int_0^{\omega_{max}} \left[\frac{\hbar\omega}{2k_B T} + \ln\left(2\sinh\frac{\hbar\omega}{2k_B T}\right)\right] g(\omega)\, d\omega$$

*A. B. Alchagirov *et al.*, Phys. Rev. B 63, 224115 (2001).
SCF: self-consistent field
DOS: density of states
EA: evolutionary algoritms

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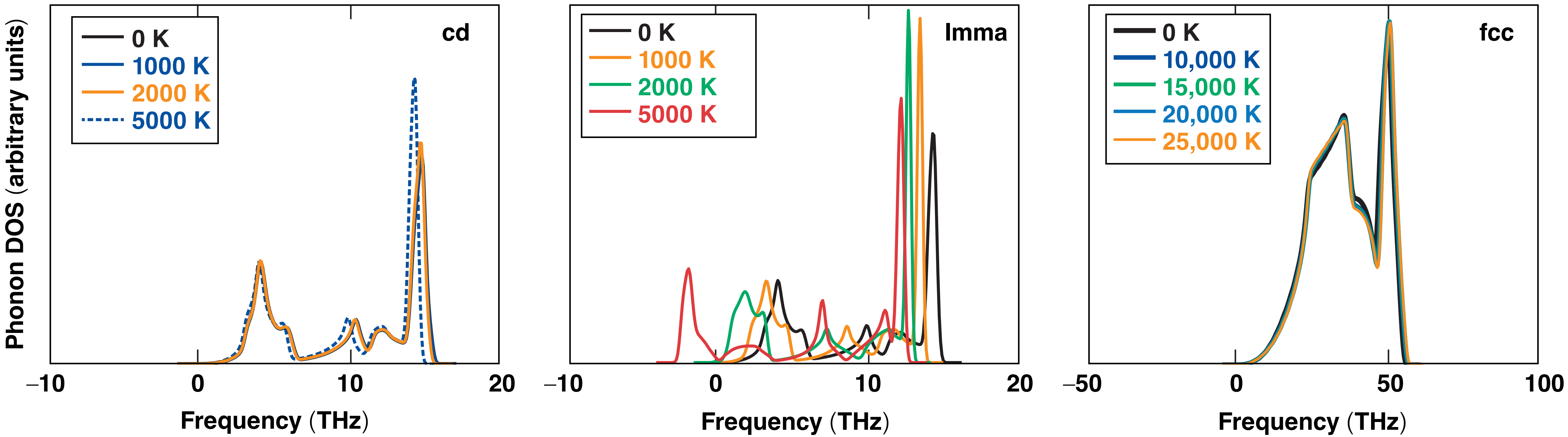
Results

Phonon density-of-state calculations* were performed at nonzero electron temperatures for checking anharmonicity

- Limit of validity of the quasi-harmonic (QH) approximation at finite temperatures



The negative thermal expansion coefficient of cubic diamond and temperature-dependence of the axial ratios of orthorhombic structures necessitate anharmonic correction F_{anh}.**

$$F_{anh}(T)\big|_v = F_{anh}(T_{ref})\big|_v \frac{T}{T_{ref}} - T_f \int_{T_{ref}}^{T} \frac{U_{FT\text{–}QMD}(T) - U_{QH}(T)}{T^2}\bigg|_v dT$$

*A. Togo and I. Tanaka, Scr. Mater. 108, 1 (2015).
**S. G. Moustafa *et al.*, Phys. Rev. B 96, 014117 (2017).
FT-QMD: finite-temperature quantum molecular dynamics

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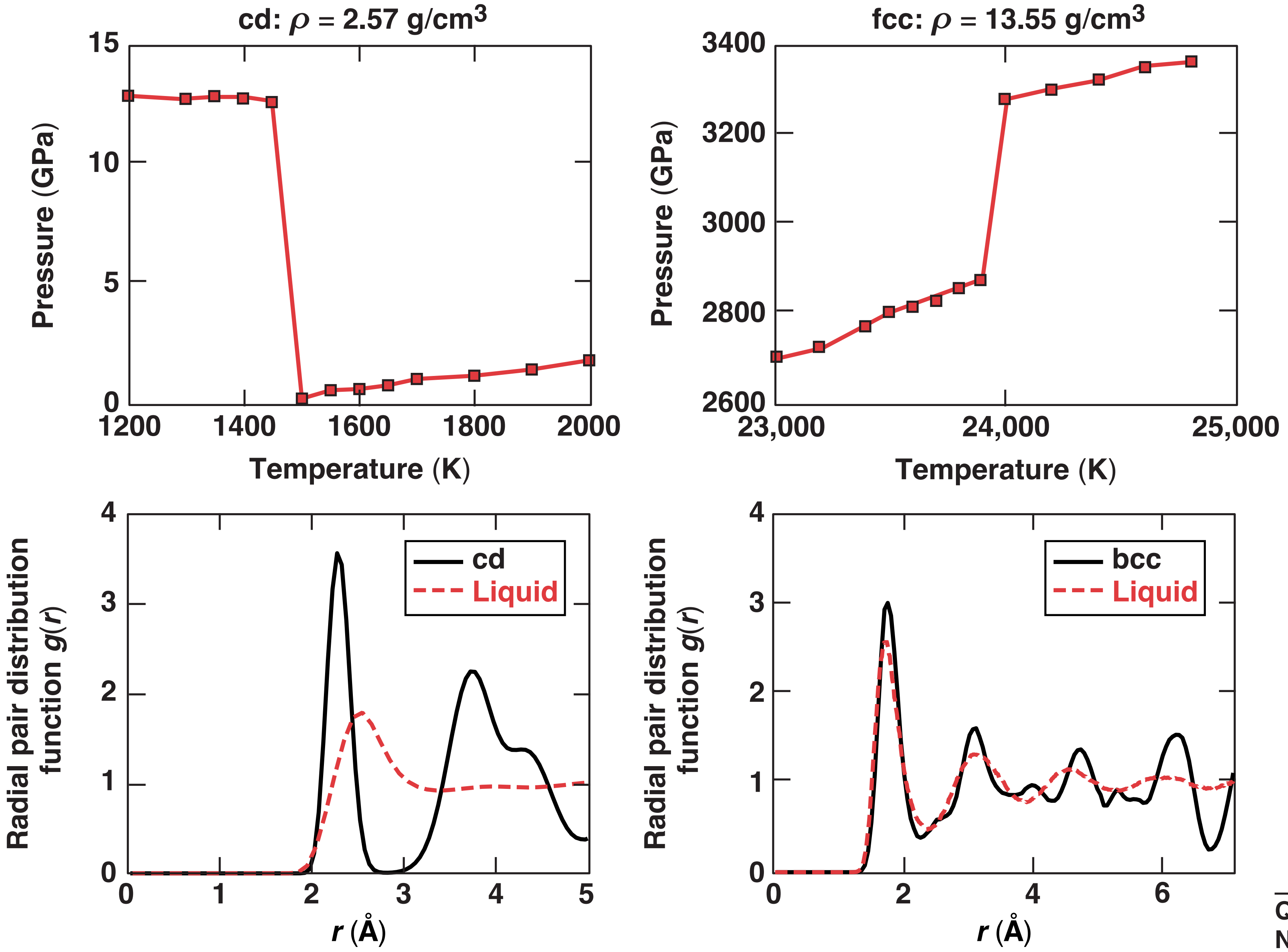
QMD calculations using an *NVT* ensemble with Nosé–Hoover thermostat were applied to determine the melting line



- A pressure *drop* in the cd and *jump* in the fcc branches is indicative of the reversal in slope of the melting line consistent with the Clausius–Clapeyron relation

$$\frac{dP}{dT} = \frac{1}{T_m}\frac{L_m}{\Delta v}$$

L_m: latent heat of melting
T_m: melting temperature
Δv: volume change on melting

QMD: quantum molecular dynamics
NVT: number of atoms (*N*), volume (*V*), and temperature (*T*)

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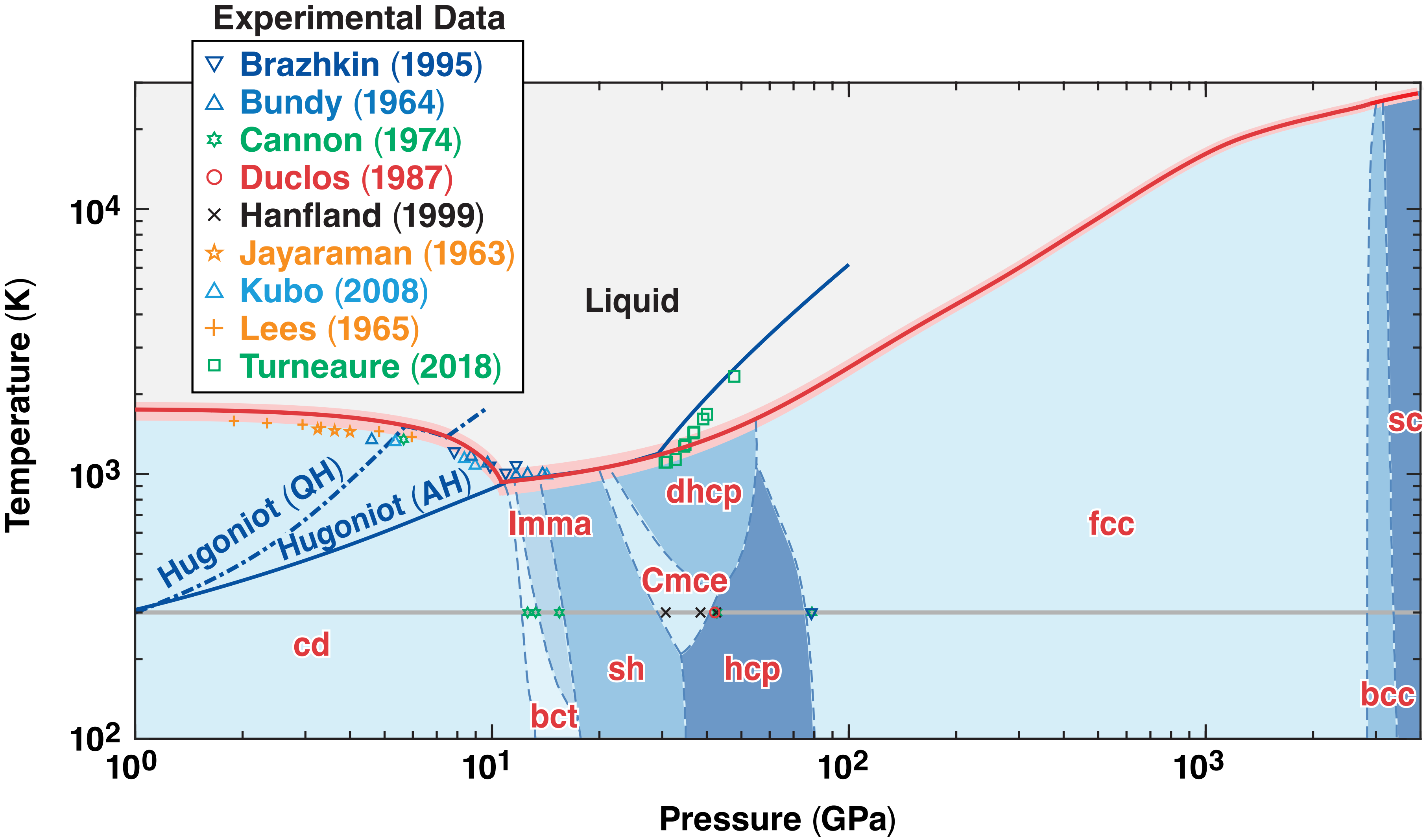
Results

Substantial differences in the Hugoniot and orthorhombic phase boundaries were observed as a result of anharmonic effects*



QH: quasiharmonic
AH: anharmonic
*R. Paul, S. X. Hu, and V. V. Karasiev (in preparation).

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A high-pressure phase diagram of silicon was constructed using density functional theory (DFT) calculations up to a pressure of 4 TPa

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