Crystalline Phase Transitions and Vibrational Spectra of Silicon up to Multi-TPa Pressures

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This article presents the *first-principles* construction of a high pressure–temperature (*P–T*) phase diagram of Si up to 4 TPa and 26,000 K, which revealed new stable phases at these multi-TPa conditions. The methodology employed in this work was a combination of different first-principles approaches centered on the use of Mermin's extension of Kohn–Sham density functional theory (DFT)[1,2] and *ab initio* lattice dynamics of perfect crystals.[3]

The upper bound of the solid-state phase diagram was established using quantum molecular dynamics (QMD) simulations, within the Born–Oppenheimer approximation, with a canonical ensemble to determine the melting points. VASP[4] was used for these calculations, with the temperature being controlled via a Nosé–Hoover thermostat. Instead of using Monkhorst–Pack *k* mesh, we resorted to the use of a single special *k* point (1/4, 1/4, 1/4) for sampling the Brillouin zone (1BZ). As with all such finite-temperature computations involving electronic structure theory and lattice dynamics, however, the main challenge is the accurate determination of the effects of anharmonicity (AH) beyond the quasiharmonic (QH) approximation of phonon dynamics for the solid state, which is the principal emphasis of this work.

The anharmonic solid-state ionic-thermal contribution F_{AH}, for an optimal axial ratio γ_T at a given specific volume and temperature (V, T), was evaluated by breaking it up into two separate components and performing thermodynamic integration, with T being the ionic temperature. The first component tracks the change in Helmholtz free energy, while moving along an isochore, from $T = 0$ K to some finite temperature keeping the cold-curve axial ratio γ_0 constant, which is obtained from statistically averaging internal energy $U(T)$ from QMD and QH phonon calculations. The second term tracks the free energy change when the axial ratio is changed from γ_0 to γ_T at that temperature, from the anisotropic stress tensor of the ensemble. These terms are shown in Eqs. (1) and (2):

$$\left\langle F_{\mathrm{AH}}\left(V,T;\gamma=\gamma_0\right)\right\rangle\Big|_V = -T\int \frac{\left\langle U(T)\right\rangle_{\mathrm{QMD}} - \left[U(T)_{\mathrm{QH}} - \frac{3}{2}N_{\mathrm{a}}k_{\mathrm{B}}T\right]}{T^2}\Bigg|_V \mathrm{d}T, \tag{1}$$

$$F_{\mathrm{AH}}\left(V,T;\gamma_0 \longrightarrow \gamma_T\right) = -\left(\frac{2V}{3\gamma_T}\right)^2 \frac{\left\langle \sigma_{\mathrm{total}}^{\mathrm{anisotropic}}(T)\right\rangle \left\langle \sigma_{\mathrm{AH}}^{\mathrm{anisotropic}}(T)\right\rangle}{\dfrac{\partial^2}{\partial \gamma^2} F_{\mathrm{QH}}(T)\Big|_{\gamma_0}}. \tag{2}$$

The phase diagram (Fig. 1) shows the existence of high-pressure body-centered cubic (bcc) and simple cubic (sc) phases beyond 2.8 TPa, as well as a pocket of double hexagonal close-packed (dhcp) in the low-pressure region. The lower-symmetry orthorhombic phases of Cmce and Imma can be accurately determined only when the anharmonicity is included. The comparison to experimental results demonstrates the absolute necessity of incorporating the said effects. Similarly, the correct slope of the principal Hugoniot can be determined only when the anharmonic contribution to the Helmholtz free energy is included. The method employed in this summary presents an approach developed for the accurate construction of first-principles equation of state, phase diagrams, or deriving any property that depends on thermodynamic state variables. A remarkable observation is the increasing localization of the electron density in the face-centered cubic (fcc) phase with increasing pressure from ~100 GPa to ~2.8 TPa, leading to a dip in the electronic density of states and formation of interstitial blobs of electrons; although the dip never develops to a band gap as seen in electrides.

Supplementing the structural calculations, second- and third-order interatomic force constants were evaluated, using a combination of density functional perturbation theory (DFPT)[4] and the power spectrum constructed from phonon eigenvector-projected atomic velocities, to compute the phonon vibration modes and linewidths, respectively. This allowed for an elaborate analysis of the Raman and infrared spectra for all of the structures of silicon identified along the 500-K isotherm.

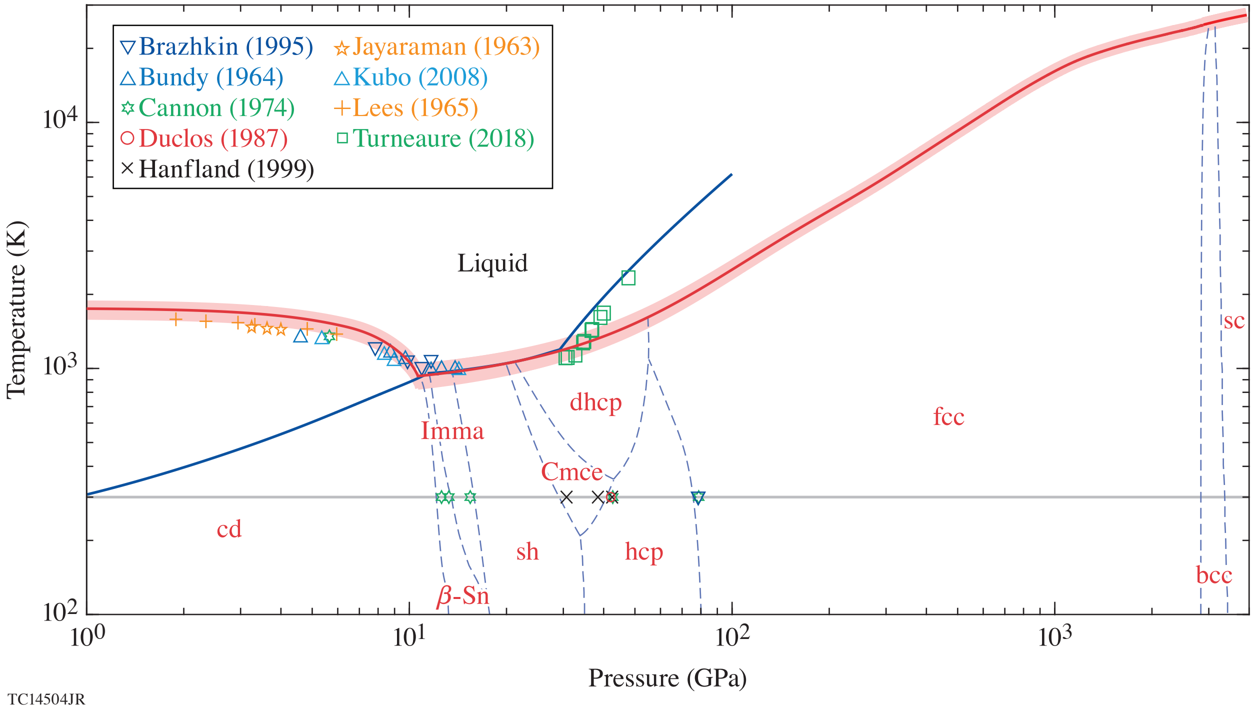

Figure 1
Pressure–temperature (P–T) phase diagram of silicon predicted using first-principles methodology. Here, the gray horizontal line represents the 300-K isotherm, whereas the solid blue line represents the principal shock Hugoniot. The discrete data points, which are also labeled in the legend, correspond to experimentally observed phase transition points.

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