Computed phase stability and phase transition mechanisms in $CaCO_3$ at finite temperature and pressure

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First-principles calculations on the seven known $CaCO_3$ polymorphs (calcite I, II, III, IIIb, VI, aragonite and vaterite) have been performed using hybrid exchange density functional theory in the all-electron linear combination of atomic orbitals approximation. The variation of the Gibbs free energy with pressure and temperature has been computed in the quasi-harmonic approximation based on well-converged and validated phonon calculations. The resultant theoretical phase diagram is compared to the available measurements. In addition, the mechanism of several phase transitions between polymorphs are examined. For example, negative phonon frequencies in the aragonite phase suggest pathways to three distinct alternative phases that involve symmetry breaking and distortion of the unit cell. Predictions of the structure for these phases will be reported along with their computed Gibbs free energies.