Supporting Information

Exploring structures and properties of nickel silicides at pressures of the Earth's inner core

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Computational Details

The structural prediction approach is performed by using a particle-swarm optimization (PSO) based global minimization of free energy surfaces structural search method implemented in the Crystal structure AnaLYsis by Particle Swarm Optimization (CALYPSO) code.[1-2] Our structure search for $Ni_{1-x}Si_x$ (x = 4/5, 3/4, 2/3, 1/2, 1/3, 1/4,1/5, 1/6 and 1/7) compounds is performed with the unit cell containing 1-4 formula units (f.u.) at 0, 50, 100, and 350 GPa, respectively. In the first generation, a population of structures with certain symmetry are constructed randomly. Local optimizations of the generating structures are done with the conjugate gradients method through the VASP code, with an economy set of input parameters and an enthalpy convergence of 1×10^{-5} eV per cell.[3-4] Step in the second generation, 60% of them with lower enthalpies are selected to produce the next generation structures by PSO, and 40% of the structures in the new generation are randomly generated. A structure fingerprinting technique of bond characterization matrix is applied to the generated structures, so that identical structures are strictly forbidden. These procedures significantly enhance the diversity of the structures, which is crucial for the efficiency of the global search of structures. For most of the cases, the structure searching simulation for each calculation was stopped after we generated 900 ~ 1100 structures (e.g., about 20 ~ 30 generations).

Structural optimization and electronic structure calculations were performed with the framework of density functional theory (DFT)[4,5] within the Perdew-Burke-Ernzerhof (PBE)[6]functional of the generalized gradient approximation (GGA),[7] as implemented by the VASP (Vienna *Ab initio* Simulation Package) code. The all-electron projector augmented-wave (PAW)[8] pseudopotentials of Ni and Si treat $3d^8 4s^2$ and $3s^2 3p^2$ electrons as the valence electrons, respectively. The cutoff energy was set at 600 eV, and Monkhorst-Pack scheme[9] with a *k*-point grid of $2\pi \times 0.03$ Å^{-1} in Brillouin zone was selected to ensure that all enthalpy calculations converged to less than 1 meV per atom. The dynamical stability of predicted structures was determined by phonon calculations using a supercell approach with the finite displacement method[10] as implemented in the Phonopy code.[11] Crystal orbital Hamilton population (COHP) analysis giving the information on the interatomic interaction was implemented in the LOBSTER package.[12,13] To make a comparison with the Ni-Si interaction, the COHP of the elemental F_2 solid[14] is calculated. The calculation accuracy is consistent with that of the other parts. Bader's Quantum Theory of Atoms in Molecules (QTAIM) analysis was employed for charge transfer analysis.[15]

Supporting Figures

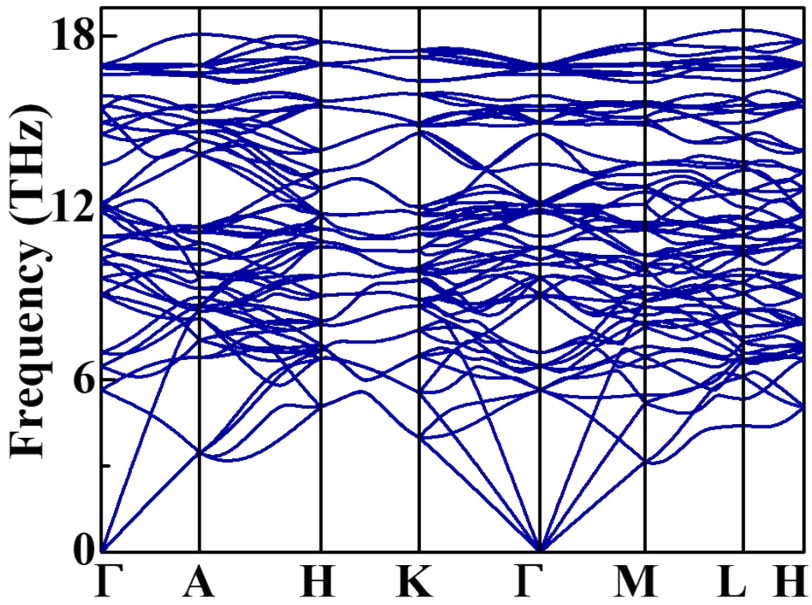


Figure S1. Calculated phonon-dispersion curve for the *Pmmn* structure of NiSi at 350 GPa. The 3 × 3 × 3 supercell was used for the calculation.

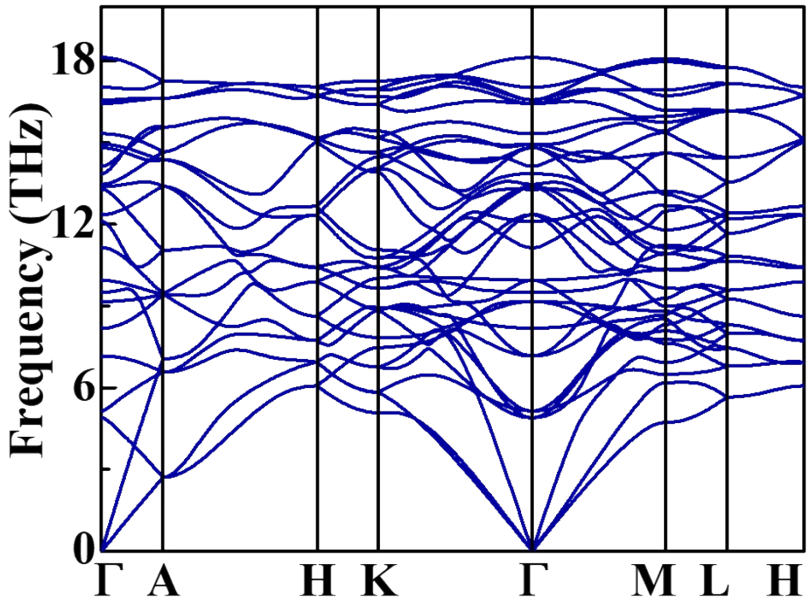


Figure S2. Calculated phonon-dispersion curve for the *Pmmn* structure of Ni_2Si at 350 GPa. The 3 × 3 × 3 supercell was used for the calculation.

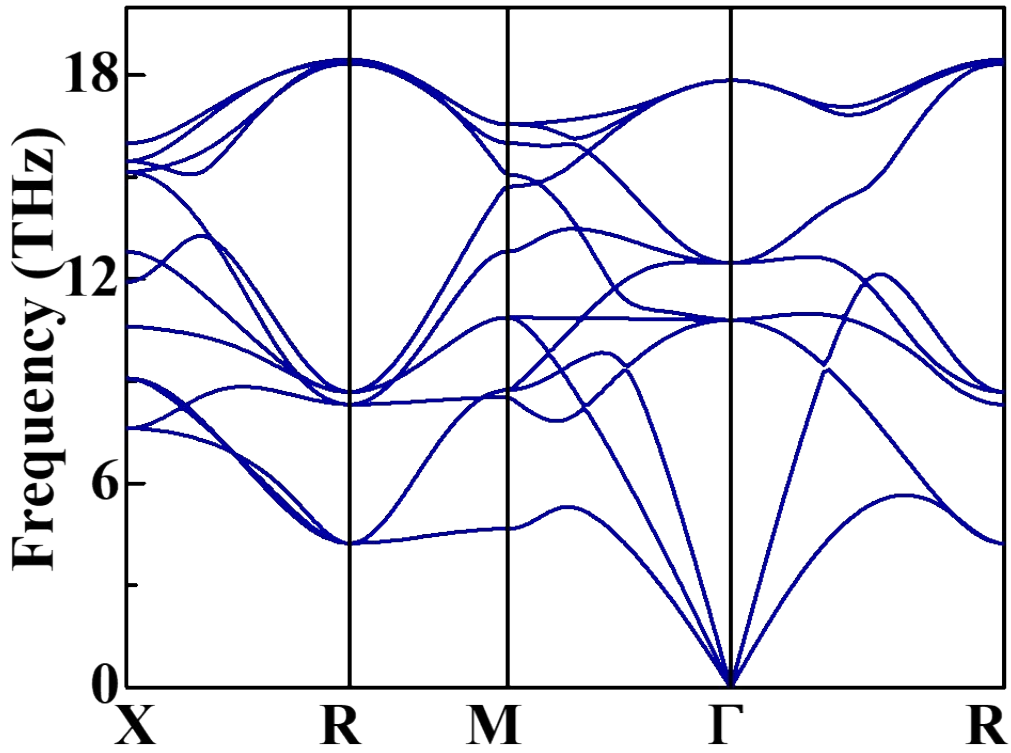


Figure S3. Calculated phonon-dispersion curve for the *Pmmn* structure of Ni_3Si at 350 GPa. The 2 × 2 × 2 supercell was used for the calculation.

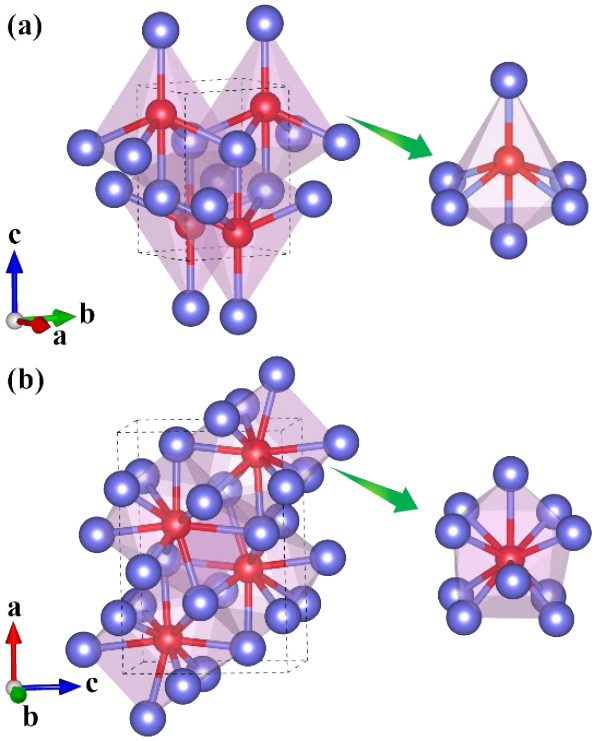
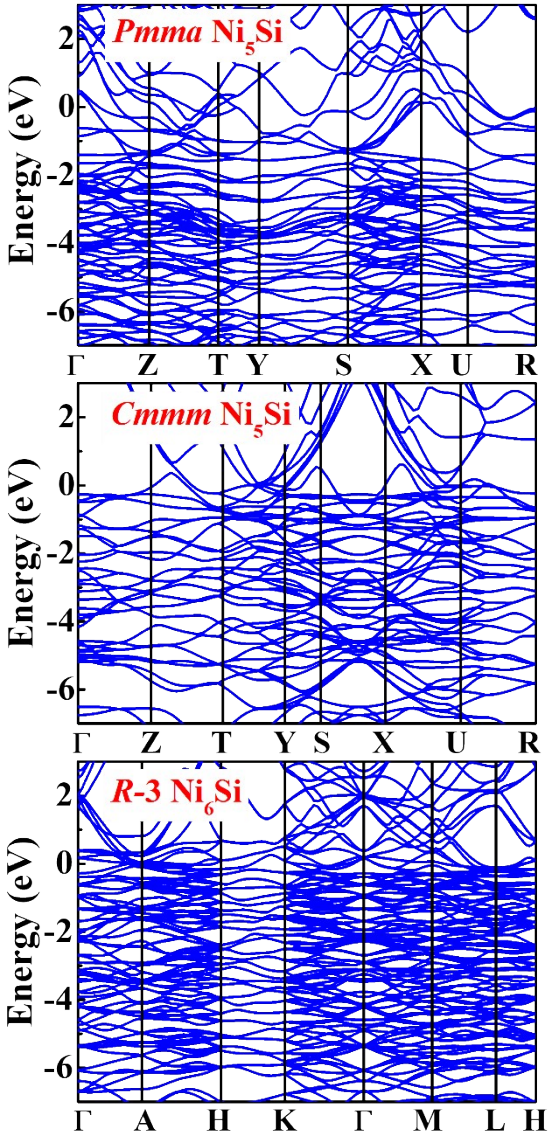


Figure S4. Crystal structures of (a) *Pmmn* NiSi. (b) *Pbnm* Ni_2Si at 50 GPa.



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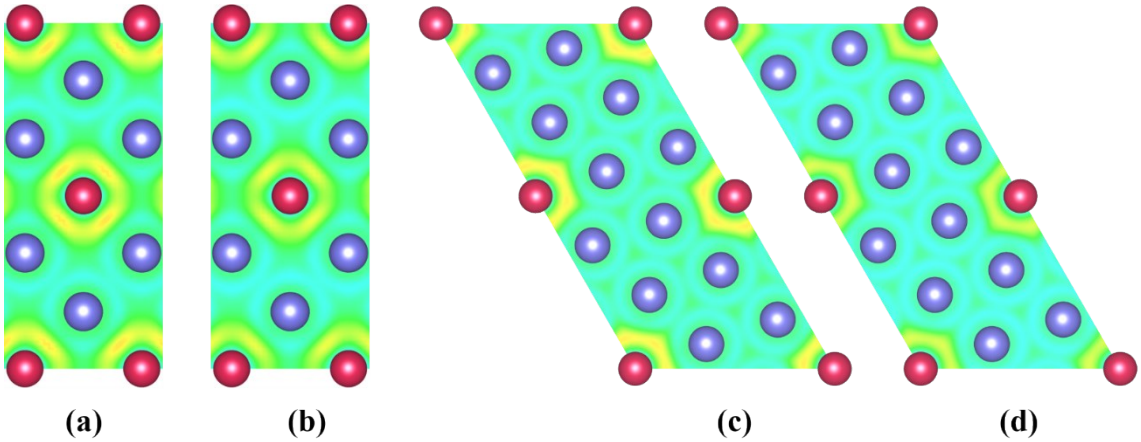

Figure S6. The calculated electron localization functions (ELF) for *Cmmm* Ni_5Si phase at (a) 200 GPa and (b) 350 GPa and *R*-3 Ni6Si phase at (c) 200 GPa and (d) 350 GPa.

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