Microscopic Theory of the Phase Transformation and Lattice Dynamics of Si

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An *ab initio* calculation for the solid-solid phase transformation, static structural properties, and the lattice dynamics of Si is presented. A density-functional pseudopotential scheme is used with the atomic number as the only input. The detailed properties of the diamond to β-tin transition are accurately reproduced. The phonon frequencies and mode-Grüneisen parameters at Γ and X, along with the lattice constant, bulk modulus, and cohesive energy, are calculated and found to be in excellent agreement with experiment.

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It has been widely accepted that once the quantum theory of solids is solved accurately, the structural properties of solids can be fully predicted theoretically with only a knowledge of the identities of the constituent elements. The structural properties included (i) the prediction of the most stable crystal structure; (ii) the static properties such as the equilibrium lattice constant, cohesive energy, and bulk modulus; (iii) the prediction and description of the solid-solid phase transformation; and (iv) the dynamic properties such as phonon frequencies and mode-Grüneisen parameters. These are long-standing and fundamental problems in solid-state physics and material science; however, *ab initio* calculations exist for only a few static properties (ii).

This Letter reports on a successful calculation of structural properties [(i) to (iv)] for Si which is used as a prototype material. The only input information is the atomic number, but because it is impossible to test an infinite number of crystal structures, we only consider a subset of plausible crystal structures consisting of the fcc, bcc, hcp, diamond (cubic), hexagonal diamond, and β-tin structures. Our theoretical results reported in the following are, therefore, restricted to this structural subset. To our knowledge, this is the first successful *ab initio* microscopic calculation of a solid-solid phase transformation and of the lattice dynamical frequencies.

To achieve the high accuracy required for structural comparison, we use a frozen-core approximation (FCA). The FCA considers the nuclei plus the core electrons as cores which are nonresponsive ("frozen") to the changes in their chemical environment. This approximation makes the energy calculations more precise since the binding energy of the cores and the valence electrons, as calculated within the FCA, is two orders of magnitude smaller than the binding energy of the nuclei and all the electrons. In addition, the FCA has the computational advantage of dealing with only the valence electrons. This is compatible with the pseudopotential method[1] within the density-functional (DF) formalism.[2]

To justify the use of the FCA for solids, the effective pseudopotential must accurately simulate the interaction of the valence electrons with the cores in the atomic limit. Several schemes for obtaining pseudopotentials of this kind have been developed.[3-6] These *ab initio* pseudopotentials are capable of reproducing excitation energies (within 10^{-3} Ry), valence eigenvalues (within 10^{-3} Ry), and valence wave functions (within 1% outside the core region) when compared with all-electron DF calculations. We have chosen the Si

TABLE I. The volumes at the minimum structural energies ($V_{\min}$, normalized to measured free volume), the minimum energies ($E_{\min}$), and $\Delta E_{\min}$ ($\equiv E_{\min} - E_{\min}{}^{\text{diamond}}$) for the six plausible structures of Si.

	Diamond	Hexagonal diamond	β-tin	hcp	bcc	fcc
$V_{\min}$	1.012	1.015	0.773	0.723	0.826	0.824
$E_{\min}$ (Ry)	-7.9086	-7.9074	-7.8888	-7.8681	-7.8260	-7.8171
$\Delta E_{\min}$ (eV)	0	0.016	0.27	0.55	1.12	1.25

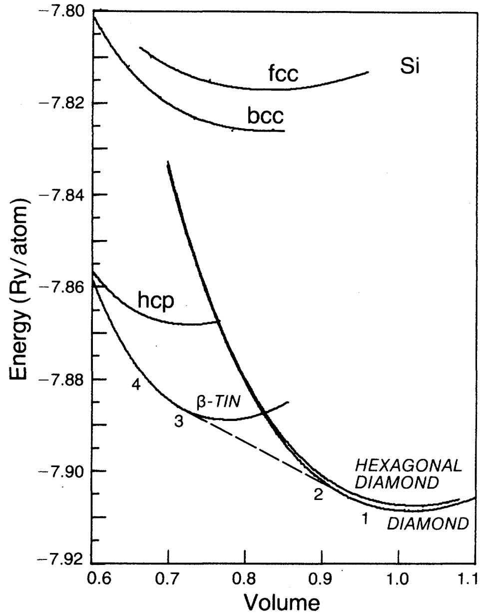

FIG. 1. The diamond, hexagonal diamond, and β-tin, hcp, bcc, and fcc structural energies (in units of Ry/atom) as a function of the atomic volume [normalized to the measured free volume (Ref. 16)] for Si. The dashed line is the common tangent of the energy curves for the diamond and the β-tin structures.

potential of Hamann, Schlüter, and Chiang[5] which gives accurate results compared with all-electron calculations for various atomic configurations over a 2-Ry range within the DF formalism. This helps to ensure the transferability of the pseudopotential from atom to solid and from structure to structure. This potential has an additional important feature of being relatively weak and, thus, it is easier to use with plane-wave expansions of the wave functions. We use the Wigner interpolation formula[7] for the exchange and correlation energy, $E_{xc}[\rho]$, in both the atomic and crystal calculation.

The pseudopotential calculation is carried to self-consistency,[8] and the structural energy, E_{struc}, is then calculated.[1] The number of special k points[9] used in the iteration and the number of plane waves used in the wave function expansion are increased until E_{struc} converges to within the desired precision. In this way, E_{struc}'s are calculated for five to ten lattice constants for each structure in the structural subset. Applying a nonlinear least-squares fit for E_{struc} to Murnaghan's[10] equation of state, we obtain the minimum structural energy per atom (E_{min}) and the corresponding atomic volume (V_{min}) for each structure as shown in Table I and Fig. 1. The diamond structure is found to be the stablest, and the zero-pressure static properties are given in Table II. The cohesive energy was obtained by subtracting the pseudoatomic energy including the spin-polarized correction[11] and the zero-point vibrational energy from E_{struc}. The results are as good or better than previous calculations for static properties (using either pseudopotentials fitted to band structure[12-14] or *ab initio* pseudopotentials[15,16]) when compared to experiment.[17-19]

This calculation also shows that Si will transform[20] to the β-tin structure under high pressure (Table I and Fig. 1). With increasing hydrostatic pressure, the crystal will follow the path $1\rightarrow 2 \rightarrow 3 \rightarrow 4$ as shown in Fig. 1. The phase transition occurs along the path $2 \rightarrow 3$ which is the common tangent of the $E_{\text{struc}}(V)$ curves for the diamond and β-tin structures. This region represents a mixture of these two phases. The tangent points determine the transition volumes, V_t^d and V_t^β, and the slope is the transition pressure, P_t. The calculated $V_t^{d,\beta}$ and P_t are shown in Table III together with the measured values.[21,22] The agreement for the volumes is excellent. The transition pressure has a larger uncertainty in our calculation because of the incomplete convergence of the calculated structural energies. The exper-

TABLE II. Comparison of calculated and measured static properties of silicon.

	Lattice constant (Å)	Crystal energy (Ry)	Cohesive energy (eV)	Bulk modulus (Mbar)
Calculation	5.451	-7.909	4.67	0.98
Experiment	5.429[a]	-7.919[b]	4.63[b]	0.99[c]
Percent difference	0.4%	-0.1%	0.9%	-1%

[a] Ref. 17. [b] Ref. 18. [c] Ref. 19 (at 77 K).

TABLE III. Comparison of the calculated and measured[a] volumes ($V_t^{d,\beta}$) of the diamond and β-tin phases at the transition pressure, their ratios (V_t^{β}/V_t^{d}), and the transition pressure itself. The volumes are normalized to the measured zero-pressure volume.

	V_t^d	V_t^β	V_t^β/V_t^d	P_t (kbar)
Calculation	0.928	0.718	0.774	99
Experiment[a]	0.918	0.710	0.773	125
Deviation	1.1%	1.1%	0.1%	-20%

[a] Refs. 21 and 22.

TABLE IV. Comparison of the calculated phonon frequencies (f_{calc}) and the mode-Grüneisen parameters (γ_{calc}) with experiment[a] ($f_{\text{expt}}, \gamma_{\text{expt}}$). The deviations from f_{expt}'s are also presented. All frequencies are in units of 10^{12} Hz.

	LTO(Γ)	TA(X)	TO(X)	LOA(X)
f_{calc}	15.16	4.45	13.48	12.16
f_{expt}[a]	15.53	4.49	13.90	13.32
Percent difference	-2.4%	-0.9%	-3.0%	-1.3%
γ_{calc}	0.92	-1.50	1.34	0.92
γ_{expt}[b]	0.98	-1.4	1.5	0.9

[a] Ref. 25 (measured at 296 K).

[b] Ref. 22; γ_{expt} of LOA(X) is estimated from the thermal expansion coefficient.

imental data were taken at room temperature. Using the phase diagrams shown in Ref. 23, we estimate the transition pressure to change by $\lesssim \pm 15\%$ from room temperature to 0 K. If we also consider possible superstress effects, the agreement of the calculated transition pressure with experiment is satisfactory.

In Fig. 1, the hexagonal structure lies above the cubic structure before the diamond–β-tin transformation. This result is consistent with the experimental observations on the metastability of Si in the hexagonal diamond structure.[24]

For the lattice dynamics, we have investigated the phonon frequencies at Γ and X where the polarizations are determined using group-theoretic methods. E_{struc}'s are calculated for the ideal and the phonon-distorted lattices. The phonon frequencies can then be obtained by calculating the change in E_{struc}. The calculated and measured[25, 22] results for the phonon frequencies and mode-Grüneisen parameters ($\gamma \equiv -d\ln\omega/d\ln V$) are tabulated in Table IV. We have also tested the dependence of the results on the functional form[26] of $E_{\text{xc}}[\rho]$ and find a maximum change of less than 5%.

To illustrate the need for an accurate pseudopotential, we note that our *ab initio* results are more accurate than those of Wendel and Martin,[13] who used an empirically fitted pseudopotential and an *ad hoc* linear repulsive force parameter. This indicates that pseudopotentials fitted to excitation spectra do not necessarily guarantee accurate structural properties and that self-consistency is important for accurate results.

The DF approach was developed to deal with ground-state properties but not with the electronic excitation spectra. The calculated band gap of 0.5 eV, which is consistent with the all-electron crystal calculation,[27] has no direct connection within the DF formalism with the measured excitation gap of 1.17 eV. This discrepancy implies that we need a modified or entirely new formalism to study the electronic excitational spectra.

A few observations can be made in light of this calculation. Since no input information beyond the atomic number (and the consideration of only a subset of crystal structures) were used to obtain excellent structural properties for Si, this result can be regarded as an important confirmation of the DF approach for studying structural properties. The scheme is not limited to Si. Our preliminary results for Ge appear to be as accurate as those for Si. Furthermore, the successes strongly suggest that this approach can also be applied to the study of defects in solids, structural properties of surfaces, and more complex phase transitions.

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