

***Ab initio* calculation of thermodynamic properties of silicon**

Siqing Wei, Changlin Li, and M. Y. Chou

School of Physics, Georgia Institute of Technology, Atlanta, Georgia 30332-0430

(Received 16 May 1994)

We present a fully *ab initio* calculation of the thermodynamic properties for silicon within the quasiharmonic approximation, making use of volume-dependent phonon frequencies obtained from pseudopotential local-density calculations. The temperature dependence of the thermal-expansion coefficient, specific heat (at constant volume), and other related quantities are studied. We confirm that the thermal-expansion coefficient behaves differently in three temperature regions: positive for temperature below 15 K, negative between 15 and 125 K, and positive again above 125 K. This finding agrees with experiment. The abnormal (negative) thermal-expansion coefficient at low temperatures is explained through a detailed study of mode Grüneisen parameters. Both specific-heat and thermal-expansion-coefficient values calculated are in excellent agreement with experiment up to a few hundred kelvin.

Advances in electronic theories and computer technology have made it possible to predict many physical properties of solids at $T=0$ from first principles, yet there have been few attempts to extend this predictive power to finite-temperature thermal properties. Silicon is a prototype system for this study because accurate measurements on high-purity samples exist over a wide temperature range, and, like other diamond and zinc-blende semiconductors, its anomalous (negative) thermal-expansion coefficient at low temperatures is of fundamental interest. Since the major contribution to entropy comes from phonons, we need a fairly accurate description of lattice dynamics in studying various thermodynamic quantities. Anharmonicity could be included at different levels, the simplest being the quasiharmonic approximation.¹ Within this approximation, atomic force constants and phonon frequencies are renormalized by taking only thermal expansion into account. The necessary input is then zero-temperature phonon frequencies as a function of volume. Recently, thermal expansion of silicon was also studied directly by *ab initio* molecular-dynamics simulations;² this approach is valid only at sufficiently high temperatures (compared with the Debye temperature) where the ion's motion could be treated by classical mechanics.

Previous studies on thermal properties of semiconductors within the quasiharmonic approximation used different methods to determine volume-dependent phonon frequencies. For example, Kagaya, Shoji, and Soma³ used a perturbation treatment with a model pseudopotential to calculate the specific heat and thermal-expansion coefficient for Si and Ge; Biernacki and Scheffler⁴ employed a model of two distortion parameters, which were extracted from local-density pseudopotential calculations, to calculate the thermal-expansion coefficient for Si; and Xu *et al.*⁵ used a tight-binding model to calculate the thermal-expansion coefficient and mode Grüneisen parameters for Si and diamond. The phonon dispersions obtained by these methods all exhibit certain deficiencies (accuracy of optical modes or lack of flatness in the TA modes at the zone boundary). Al-

though the resulting thermal-expansion coefficients were in fair agreement with experiment, namely, with negative values in the right temperature range, it was unclear whether the quasiharmonic approximation or the accuracy of phonon spectra was responsible for the remaining discrepancies.

We recently developed a scheme to extract interatomic force constants from *ab initio* calculations of planar forces,⁶ using the density-functional theory with the local-density approximation (LDA); and calculated accurately the full phonon spectrum for Si. In this work, we apply this method to determine the volume variation of phonon frequencies for the silicon crystal and evaluate its thermal properties, including the thermal expansion coefficient, the specific heat, and the Grüneisen parameters, within the quasiharmonic approximation. To our knowledge, no calculation of the specific heat completely from density-functional theories for Si has been reported. Our results are in excellent agreement with experimental data up to a few hundred K. In particular, the calculated thermal expansion coefficient reproduces not only the negative values below 125 K, but also the positive values at very low temperatures. Another *ab initio* approach developed recently to obtain the phonon dispersion and then the thermodynamical properties uses the linear response theory.⁷ Thermal-expansion coefficient and mode Grüneisen parameters for carbon have been reported.⁸ In comparison, our approach only requires straightforward force calculations using supercells containing about 8–16 atoms for semiconductors.

Within the quasiharmonic approximation,¹ the free-energy of a crystal is

$$F(T, V) = E(V) + \frac{1}{2} \sum_{\mathbf{k}, n} \hbar \omega_n(\mathbf{k}, V) + k_B T \sum_{\mathbf{k}, n} \ln \left[1 - \exp \left(- \frac{\hbar \omega_n(\mathbf{k}, V)}{k_B T} \right) \right], \quad (1)$$

where $E(V)$ is the energy of a static lattice and $\omega_n(\mathbf{k}, V)$ the phonon frequency of mode n and wave vector \mathbf{k} for a

given volume V . The equilibrium volume is obtained by minimizing the free energy at a fixed temperature; one then determines the linear thermal expansion coefficient $\alpha(T)$. Alternatively, α may be written as⁹

$$\alpha(T) = \frac{1}{3B(T)} \sum_{\mathbf{k}, n} \gamma_n(\mathbf{k}) c_{vn}(\mathbf{k}, T), \quad (2)$$

where $B(T)$ is the isothermal bulk modulus, $\gamma_n(\mathbf{k})$ the mode Grüneisen parameter defined as

$$\gamma_n(\mathbf{k}) = - \frac{d[\ln\omega_n(\mathbf{k}, V)]}{d[\ln V]}, \quad (3)$$

and $c_{vn}(\mathbf{k}, T)$ is the mode contribution to the specific heat defined as

$$c_{vn}(\mathbf{k}, T) = \frac{\hbar\omega_n(\mathbf{k}, V)}{V} \frac{d}{dT} \left[\exp\left(\frac{\hbar\omega_n(\mathbf{k}, V)}{k_B T}\right) - 1 \right]^{-1}. \quad (4)$$

The total specific heat of the crystal will be the sum of all modes over the Brillouin zone

$$C_v(T) = \sum_{\mathbf{k}, n} c_{vn}(\mathbf{k}, T). \quad (5)$$

The overall Grüneisen parameter is the weighted average of mode Grüneisen parameters

$$\gamma(T) = \frac{1}{C_v(T)} \sum_{\mathbf{k}, n} \gamma_n(\mathbf{k}) c_{vn}(\mathbf{k}, T) = 3B(T) \frac{\alpha(T)}{C_v(T)}. \quad (6)$$

In our calculation, we first extract the interatomic force constants from planar Hellmann-Feynman forces¹⁰ obtained by direct supercell LDA calculations.⁶ Phonon frequencies are then obtained by diagonalizing the dynamical matrix, which is the Fourier transform of these real-space force constants. The real-space cutoff is set at the eighth-nearest neighbor to ensure the real space convergence (for details of the force constants calculation, see Ref. 6). We use an energy cutoff of 18 Ry for the plane-wave expansion and an equivalent ten special k points in the diamond structure for the Brillouin-zone integration. The calculated zero-temperature bulk modulus B and equilibrium volume V_0 are 0.950 Mbar (experiment 0.99) and 156.07 \AA^3 (experiment 160.10), respectively. Phonon frequencies for 408 special k points in the irreducible Brillouin zone (equivalent to a total of 16384 k points in the whole Brillouin zone) are evaluated. Their volume variation is determined by a linear fit through the calculated frequency values for three volumes: V_0 and $(1 \pm 3\%)V_0$.

The calculated phonon dispersion curves along three high-symmetry directions ($[100]$, $[110]$, and $[111]$) for the equilibrium volume V_0 are shown in Fig. 1(a). Also shown is the calculated density of states (DOS). The experimental data^{11,12} are marked by circles and crosses in the figure. Our calculated curves are in excellent agreement with the experimental data. The flattening of the TA modes at the zone boundary (X and L points) in the calculated results indicates that the real-space convergence has been reached. (See Ref. 6 for the full phonon spectrum.)

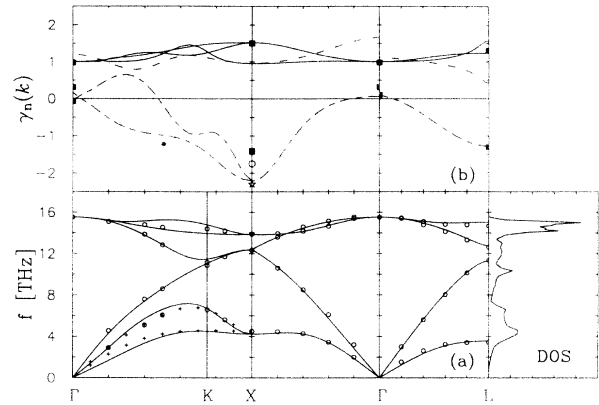


FIG. 1. (a) Phonon dispersion and density of states at the equilibrium volume of Si. Experimental phonon frequencies are denoted by open circles (Dolling, Ref. 11) and crosses (Nilsson and Nelin, Ref. 12). (b) Mode Grüneisen parameters for Si. Dashed lines correspond to TA modes, dotted lines to LA modes, solid lines to optical modes, and the star corresponds to the frozen phonon calculation for the TA mode at X . The experimental data are denoted by solid squares (Weinstein and Piermarini, Ref. 15) and open circles (Chandrasekhar, Renucci, and Cardona, Ref. 16).

Our calculated thermal expansion coefficient $\alpha(T)$ of silicon is shown in Fig. 2. Two experimental results are also plotted (circles and crosses).^{13,14} The inset shows the detail for temperatures below 20 K. From Fig. 2 we can see that our calculation reproduces accurately the anomalous negative thermal expansion coefficient between 15 and 125 K, and also correctly gives the positive behavior at very low temperatures (below 15 K), as observed experimentally. From Eqs. (2)–(4) it is apparent that for very low temperatures, only the very-low-frequency phonons contribute to the summation, since the high-frequency contribution decays exponentially. As illustrated in Fig. 1(a) only the zone-center acoustic modes have energy low enough ($1 \text{ THz} \approx 47 \text{ K}$) to contribute. The correct results at very low temperatures indicate that the low-frequency phonon mode's volume dependence is correctly determined in our calculations.

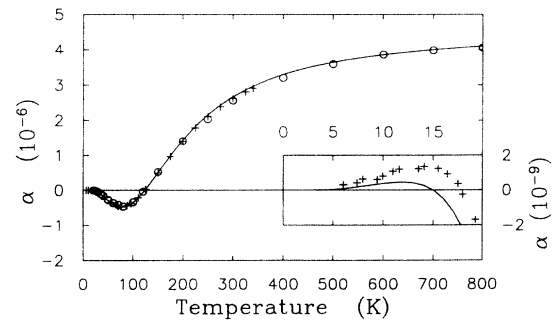


FIG. 2. Temperature dependence of the thermal expansion coefficient, $\alpha(T)$, of Si. The inset gives the details for temperatures below 20 K. Experimental data are denoted by open circles (Ref. 13) and crosses (Ref. 14).

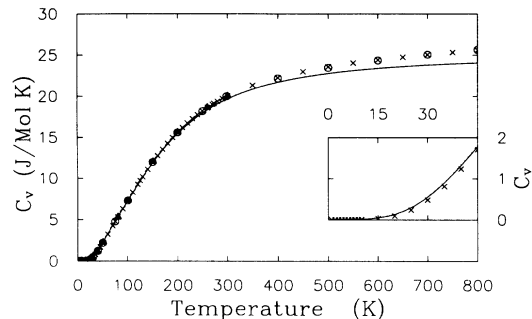


FIG. 3. Temperature dependence of the specific heat, $C_v(T)$, of Si. The inset shows the details at low temperatures. Experimental data are denoted by solid triangles (Flubacher, Leadbetter, and Morrison, Ref. 17), open circles (Hultgren, Ref. 18), and crosses (Desai, Ref. 19).

To determine where the negative thermal expansion originates, we focus on the logarithmic volume derivation of the phonon dispersion—the mode Grüneisen parameter defined in Eq. (3). Since $c_{nv}(\mathbf{k}, T)$ as defined in Eq. (4) is always positive, from Eq. (2) the only negative contribution to α has to come from the mode Grüneisen parameter. In Fig. 1(b) the dispersion of the mode Grüneisen parameter is plotted along three high-symmetry directions ([110], [110], and [111]), solid squares and circles being two different experimental results.^{15,16} The dashed lines represent the acoustic TA modes, dotted lines the acoustic LA modes, and solid lines the optical modes. Except for the TA mode at X , the agreement between our calculation and experiment is excellent. We also performed a direct frozen phonon calculation of the mode Grüneisen parameter for TA(X) and the result [denoted by the star in Fig. 1(b)] is consistent with that obtained from force-constant calculations. It is clear from Fig. 1(b) that the largest negative contribution to α comes from the zone boundary TA modes (X and L). These negative values of the mode Grüneisen parameter were attributed to a larger contribution by the central force than the angular force.⁵ The Grüneisen parameters for the zone-center modes are mostly positive, which explains the positive thermal-expansion coefficients at very low temperatures, where only the phonons in the acoustic modes near the zero center (Γ point) are excited.

As the temperature increases, between 15 and 125 K, the excitation of other TA modes increases. From the DOS plot in Fig. 1(a), we can see a peak of the DOS around 4 THz whose contribution to α is negative, leading to a negative thermal-expansion coefficient for this temperature range. As the temperature increases further, higher-energy states (mostly optical modes which have positive Grüneisen parameters) start to contribute; the thermal-expansion coefficient changes sign again to positive and increases with temperature. The quasiharmonic result is expected to saturate at high temperature for neglecting phonon-phonon interactions, yet the agreement with experiment is very good up to 800 K.

In Fig. 3, the calculated specific heat according to Eq. (5) is compared with experiments.^{17–19} The inset shows the detail at low temperatures. The agreement between theory and experiment is excellent below 300, and fair up

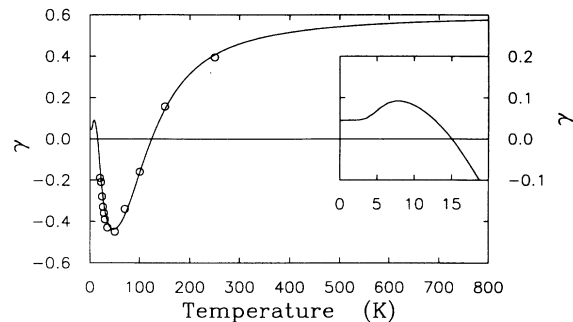


FIG. 4. Overall Grüneisen parameter $\gamma(T)$ of Si. The inset gives the details for temperatures below 20 K. Experimental data are denoted by open circles (Ref. 13).

to 800 K. When the temperature increases, the quasiharmonic result is expected to approach a constant $3Nk_B$, and the agreement with experiment will deteriorate at high temperatures where anharmonicity becomes important. At 800 K, the difference between the quasiharmonic result and experiment is about 10%. For the whole temperature range, the isothermal bulk modulus changes only by a few percent.

Finally, from Eq. (6) the overall Grüneisen parameter $\gamma(T)$ is calculated for silicon. In Fig. 4, the calculated value is plotted and compared with experiment. The agreement with experiment¹³ is excellent. The inset shows the detail for temperatures below 20 K (where no reliable experimental data are available). As the temperature goes to zero, the overall Grüneisen parameter approaches a constant in our calculation. The nonzero value at 0 K indicates that the thermal-expansion coefficient and the specific heat approach zero in the same asymptotic way. In fact, $\gamma(0)$ is proportional to the logarithmic derivative of the T^3 coefficient in the specific heat with respect to volume.²⁰

In conclusion, we have presented a pseudopotential local-density calculation of thermodynamic properties of Si within the quasiharmonic approximation. The calculated thermal expansion coefficient, specific heat, and the overall Grüneisen parameter agree perfectly with experiment below 300 K. The agreement is still good up to 800 K. A detailed study of the mode Grüneisen parameter shows clearly that the (negative) anomaly in the thermal-expansion coefficient at low temperatures results from the zero-boundary TA phonons, in agreement with previous observations. Our calculation also confirms a positive thermal-expansion coefficient at very low temperatures, in agreement with experiment.

Note added in proof. It was brought to our attention by Dr. T. W. Barbee III that in a comment²¹ to Ref. 4, Fleszer and Gonge presented the calculated thermal-expansion coefficient for Si from the perturbed density-functional theory.⁷ The agreement with experiment was also very good.

This work was supported in part by the NSF and DOE. M.Y.C. acknowledges the Packard Foundation for the support. A grant for supercomputer time from the Livermore National Supercomputer Center is also acknowledged.

- ¹G. Leibfried and W. Ludwig, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1961), Vol. 12, p. 275; L. L. Boyer, *Phys. Rev. Lett.* **42**, 584 (1979).
- ²F. Buda, R. Car, and M. Parrinello, *Phys. Rev. B* **41**, 1680 (1990).
- ³M.-M. Kagaya, N. Shuoji, and T. Soma, *Solid State Commun.* **65**, 1445 (1988); T. Soma, *Phys. Status Solidi B* **87**, 345 (1978).
- ⁴S. Biernacki and M. Scheffler, *Phys. Rev. Lett.* **63**, 290 (1989).
- ⁵C. H. Xu, C. Z. Wang, C. T. Chan, and K. M. Ho, *Phys. Rev. B* **43**, 5024 (1991).
- ⁶S. Wei and M. Y. Chou, *Phys. Rev. Lett.* **69**, 2799 (1992); *Phys. Rev. B* **50**, 2221 (1994).
- ⁷S. Baroni, P. Giannozzi, and A. Testa, *Phys. Rev. Lett.* **58**, 1861 (1987).
- ⁸P. Pavone, K. Karch, O. Schütt, W. Windl, D. Strauch, P. Giannozzi, and S. Baroni, *Phys. Rev. B* **48**, 3156 (1993).
- ⁹N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Saunders College, Philadelphia, 1976), p. 492.
- ¹⁰R. P. Feynman, *Phys. Rev.* **56**, 340 (1939); J. C. Slater, *J. Chem. Phys.* **57**, 2389 (1972); J. Ihm, A. Zunger, and M. L. Cohen, *J. Phys. C* **12**, 4409 (1979).
- ¹¹G. Dolling, in *Inelastic Scattering of Neutrons in Solids and Liquids*, edited by S. Eklund (IAEA, Vienna, 1963), Vol. II, p. 37.
- ¹²G. Nilsson and G. Nelin, *Phys. Rev. B* **6**, 3777 (1972).
- ¹³H. Ibach, *Phys. Status Solidi* **31**, 625 (1969).
- ¹⁴K. G. Lyon, G. L. Salinger, C. A. Swenson, and G. K. White, *J. Appl. Phys.* **48**, 865 (1977).
- ¹⁵B. A. Weinstein and G. J. Piermarini, *Phys. Rev. B* **12**, 1172 (1975).
- ¹⁶M. Chandrasekhar, J. B. Renucci, and M. Cardona, *Phys. Rev. B* **17**, 1623 (1978).
- ¹⁷P. Flubacher, A. J. Leadbetter, and J. A. Morrison, *Philos. Mag.* **4**, 273 (1959).
- ¹⁸R. Hultgren, *Selected Values of Thermodynamic Properties of Elements* (ASM, Metals Park, 1973).
- ¹⁹P. D. Desai, *J. Phys. Chem. Ref. Data* **15**, 967 (1986).
- ²⁰B. Yates, *Thermal Expansion* (Plenum, New York, 1972), p. 84.
- ²¹A. Fleszer and X. Gonze, *Phys. Rev. Lett.* **64**, 2961 (1990).