

First-Principles Thermodynamical Properties of Semiconductors

The thermodynamical potentials of semiconductors in a large range of temperatures are determined mainly by phonons and their dependence on temperature and pressure. Therefore a precise and efficient tool for phonon frequencies calculation, at arbitrary wavelength and crystal lattice constant, is necessary for their investigations.

In a recent Letter,¹ the thermal expansion of crystalline silicon was obtained through the minimization of the Gibbs free energy, and carefully analyzed with respect to entropy and internal-energy contributions. As a tool to get the phonon frequencies in the whole Brillouin zone (BZ) and their dependence on the lattice parameter, the method involved a two-parameter analytic expression. The values of the parameters were determined from accurate *ab initio* total-energy calculations of the perfect and specifically distorted crystal (supercell method).

In this Comment we would like to present another tool, in which phonons at arbitrary wavelength are obtained in a more direct way. The scheme is efficient enough to be used for more complex geometries, such as surface phonons or vibrations at defects. It relies on the perturbed density-functional theory (PDFT), as proposed by Baroni, Gianozzi, and Testa,² for linear-response coefficients, and by Gonze and Vigneron³ for higher-order coefficients. Using PDFT, phonon dynamical matrices for any wave vector are obtained efficiently, without any supercell calculation. In particular, the knowledge of the dynamical matrices for a dense, uniform mesh of points over the 1BZ leads to the interatomic force constants in real space, as a result of a Fourier transform. From these force constants, it is a trivial problem to perform thermodynamical sums over a practically unlimited number of phonons. As an example, we calculated the thermal expansion coefficient of silicon, using norm-conserving pseudopotentials, a plane-wave basis set (maximum kinetic energy of 15 Ry), and 32 special points for the electronic integration over the Brillouin zone. The dynamical matrix was determined at ten different wavelengths in the 1BZ using slightly modified⁴ Eqs. (43) and (44) of Ref. 3, and this allowed the calculation of real-space interatomic force constants for the sixteen first shells of atoms, at various lattice constants. We used the force constants to get dynamical matrices and phonon frequencies at 182 different wavelengths in the 1BZ. As in Ref. 1, the Gibbs free energy was calculated and minimized with respect to the lattice constant. In Fig. 1, we compare the thermal-expansion coefficient from experiment, from Ref. 1, and from this work.⁵

In conclusion, we would like to stress that with the present calculational scheme, fully *ab initio* thermodynamic properties of semiconductors are accessible without any model-analytic expression or supercell cal-

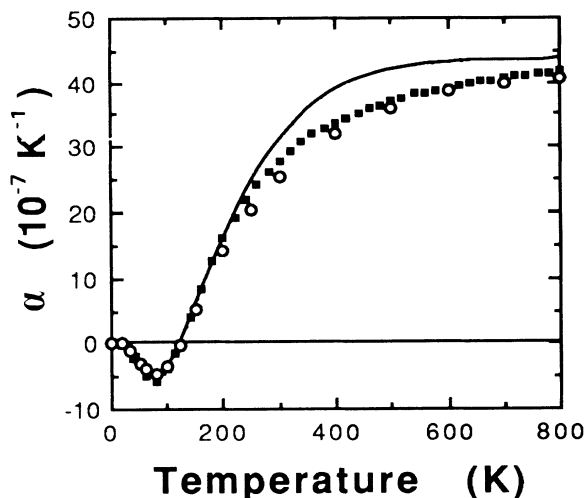


FIG. 1. Coefficient of thermal expansion for crystalline silicon as a function of temperature. Circles: experimental results (Ref. 2 of our Ref. 1); solid line: Ref. 1; squares: this work.

ulation.

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⁴The introduction of a projector operator, as described in Ref. 2, was found to be important for the convergence of the calculation. On the other hand, the Grüneisen parameters could have also been calculated directly in the framework of the nonlinear-response formalism, along the lines given in Ref. 3.

⁵Further details in A. Fleszar and X. Gonze (to be published).