Ab initio calculation of the phonon dispersion relation: Application to Si

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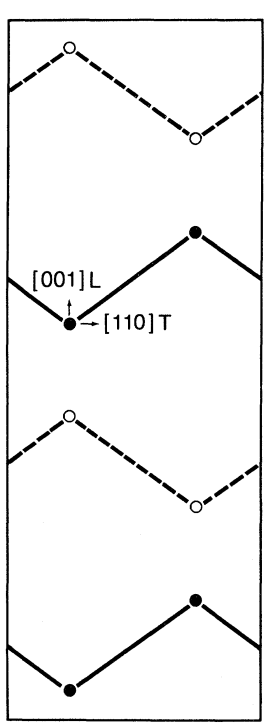
We demonstrate that by using atomic numbers and masses of constituent elements and crystal structures as the only input information, phonon dispersion curves of crystals can be calculated from first principles within the local-density-functional formalism. As shown by an exemplary calculation for the [001]-direction phonon dispersion curves of Si, the agreement with experiment is excellent. The calculation is carried out using the *ab initio* pseudopotential method and the Hellmann-Feynman theorem.

An *ab initio* calculation of the phonon frequencies for Si at high-symmetry points has recently been demonstrated[1] to yield results in excellent agreement with experiment. The calculation was carried out using the pseudopotential method within the local-density-functional formalism.[2] A frozen-phonon approach was employed, and the phonon frequencies were obtained by comparisons of total energies of the ideal lattice and the phonon-distorted lattices. In principle, this approach can be used to calculate the phonon frequencies at nonsymmetry points. However, the calculation would be very difficult computationally because of the large supercell size involved. In this Communication, we use another approach and show that, by calculating the force constants between atomic layers, the phonon dispersion relation along the direction normal to the atomic layers can be obtained from first principles.

Si is chosen as a prototype material. One of the interesting features[3] of the phonon dispersion relation of Si as well as other semiconductors in diamond or cubic ZnS structures is that the TA dispersion curves are low lying and become flat away from the zone center. It is shown[4] from the phenomenologic force-constant model that the interatomic forces extend to fifth-nearest neighbors, and it takes 15 parameters to achieve a reasonable fit to the dispersion curves. Successful fittings of the dipersion curves of Si have been reported using six parameters in the valence force field model[5] and four parameters in the adiabatic bond charge model.[6] A microscopic calculation[7] of the phonon dispersion relation of Si has been carried out using dielectric matrix formulation,[8] and the agreement with experiment is fair. However, the accuracy of the use of a continued-fraction series in the dielectric matrix calculation is not known, and the results are sensitive to the choice of the pseudopotential as well as the value used for the first moment.[7] In the present study, the phonon dispersion relation of Si along the [001] direction is calculated using only the Si atomic number, atomic mass, and the diamond crystal structure as input information. This represents the first *ab initio* calculation of phonon dispersion curves of Si.

In our calculations, we use the pseudopotential method[1] within the local-density-functional formalism.[2] The *ab initio* pseudopotential of Si is generated through the Hamann-Schlüter-Chiang scheme[9] and is shown [1] to give ground-state structural properties in excellent agreement with experiment. A 12-(001) layer supercell geometry is chosen. To preserve the inversion symmetry of the system which facilitates the computation, we displace two inversion-symmetry-associated atoms (instead of just one atom) from their ideal crystalline positions by an equal amount (about 1% of the lattice constant) in opposite directions. Plane waves up to $E_{pw}=6$ Ry in kinetic energy are included in the basis set for the wave-function expansion.[10] This corresponds to about 400 plane waves in the supercell calculations. The Schrödinger equation is solved iteratively to self-consistency at which point the input and output screening potentials differ by only 10^{-5} Ry and the Hellmann-Feynman forces on each atomic layer stabilize to 2×10^{-5} Ry/a.u. The calculations of Hellmann-Feynman forces are conveniently performed in the momentum space.[11] The Wigner interpolation formula[12] for exchange and correlation energies is used.

The interlayer force constants for longitudinal (transverse) phonons are deduced from the Hellmann-Feynman forces acting on individual atomic layers when dual layers are displaced along the [001] ([110]) direction. Figure 1 contains definitions and calculated values of interlayer force constants. Here we make an assumption that interlayer force constants are negligible beyond the third-nearest layers.[13] This assumption is checked in four ways: (i) The translational invariance condition[14] is satisfied to 0.5% (see Fig. 1); (ii) if different dual layers are displaced, the Hellmann-Feynman forces calculated from solving the Schrödinger equation agree to



Longitudinal	Transverse
$k_3 = -0.001$	$k_3 = -0.001$
$k_2 = -0.021$	$k_2 = 0.005$
$k_1 = -0.121$	$k_1 = -0.192$
$k_0 = 0.286$	$k_0 = 0.228$
	$k_{\bar{1}} = -0.037$
	$k_{\bar{2}} = 0.005$
	$k_{\bar{3}} = -0.010$

FIG. 1. Interlayer force constants (k) of Si. (The subscripts represent the order of nearness; e.g., k_1 is the first-nearest-layer force constant, etc.) The atomic positions in the $(1\bar{1}0)$ plane are denoted with black dots. The solid lines denote the atomic chain on the plane. The open dots and dashed lines denote the projections of the atoms and atomic chains a distance $\sqrt{2}a/4$ away from the plane where a is the lattice constant. The upper central atom is displaced in the [001] direction in the longitudinal (L) case and in the [110] direction in the transverse (T) case. The corresponding interlayer force constants in Rydberg units are given on the right. The positive sign means the force is in the direction opposite to the displacement.

within 3% with the results obtained using the force constants; (iii) the calculated frequencies of LO(Γ) and TO(Γ) agree to less than 1%; and (iv) the calculated phonon frequencies of LO(Γ), TO(Γ), LOA(X), and TO(X) agree to within 1% with the corresponding results calculated using the frozen-phonon approach in which all the interlayer force constants are taken into consideration (see Table I). The 4% difference in the TA(X) mode is also rather small considering the small magnitude of the TA(X) frequency itself.

By symmetry, the longitudinal (interlayer) force constants are symmetric with respect to the displaced layer, and the second-nearest-layer force constants in the transverse case are the same ($k_2 = k_{\bar{2}}$). The longitudinal force constants die off rapidly with respect to the interlayer spacing. The value of the third-nearest-layer force constant (k_3) is only 1% of the first-nearest-layer force constants (k_1). The transverse force constants show large variations. One of the first-nearest-layer force constant (k_1) is much larger than the other one ($k_{\bar{1}}$) because only the bond-bending forces are involved in $k_{\bar{1}}$, which are small compared to the bond-stretching forces involved in k_1. The negative value of the second-nearest-layer force constant ($k_2, k_{\bar{2}}$) is a manifestation of the bond-bending forces which tend to preserve the regular tetrahedral angles. The large difference between $k_{\bar{3}}$ and k_3 can be interpreted in the valence force field picture[5] where the fifth-nearest-neighbor interatomic interaction is modeled through the bending of bond angles in the atomic chain connecting one atom and its fifth-nearest neighbor. This interatomic interaction is transmitted more effectively for atoms associated with $k_{\bar{3}}$ than the atoms associated with k_3.

From these *ab initio* interlayer force constants, the phonon frequencies of Si in the [001] direction can be readily calculated. As shown in Fig. 2, the calculated dispersion curves (dash lines) reproduce prom-

TABLE I. Comparison of the calculated phonon frequencies (in THz) at Γ and X with experiment. The first row gives values calculated in the *ab initio* force constant (FC) approach using a plane-wave expansion with a kinetic energy cutoff (E_{pw}) of 6 Ry. The second and third rows are obtained in the frozen phonon (FP) approach with $E_{pw} = 6$ and 10 Ry, respectively. The experimental values are given in the fourth row.

	LO(Γ)	TO(Γ)	LOA(X)	TA(X)	TO(X)
FC (6 Ry)	14.32	14.25	11.79	4.82	12.73
FP (6 Ry)	14.33	14.33	11.73	5.02	12.75
FP (10 Ry)[a]	15.16	15.16	12.16	4.45	13.48
Expt.[b]	15.53	15.53	12.32	4.49	13.90

[a]See Ref. 1.

[b]See Ref. 3.

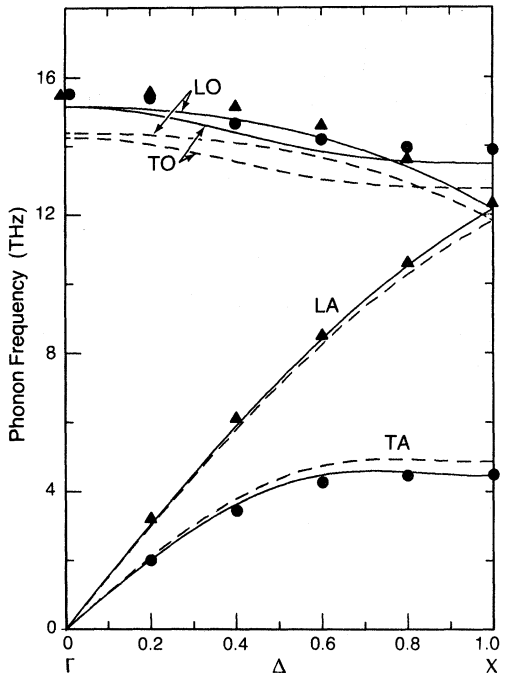


FIG. 2. Phonon frequencies from Γ to X in the [001] direction. The dashed lines are calculated from the *ab initio* force constants with $E_{pw}=6$ Ry (see text). The solid lines are calculated using the *ab initio* third-nearest-layer force constants ($E_{pw}=6$ Ry) and the frozen-phonon results at Γ and X ($E_{pw}=10$ Ry). The experimental points (Ref. 3) are denoted by dots (transverse) and triangles (longitudinal).

inant experimental features[3]: The TA modes are low lying and flat near the zone boundary, and the TO and LO modes cross each other. The calculated frequencies agree with experimental values to within 10%. A major source of errors comes from the limited number of plane waves in the basis set ($E_{pw}=6$ Ry). This is confirmed by frozen-phonon calculations at Γ and X. When the kinetic energy cutoff (E_{pw}) is increased from 6 to 10 Ry, the calculated frequencies at Γ and X in the frozen-phonon approach change by 5% and become in better agreement with experiment (Table I). Without actually carrying out *ab initio* force constant calculations $E_{pw}=10$ Ry, which involves diagonalization of rather large matrices (850×850), we may instead make a good estimate of these force constants in the following way. Because the third-nearest-layer force constants do not change appreciably when E_{pw} is increased, the values for $E_{pw}=6$ Ry can be used. The other force constants are adjusted such that the frozen-phonon results at Γ and X for $E_{pw}=10$ Ry are reproduced since it is expected that both the force-constant approach and the frozen-phonon approach yield practically the same results for $E_{pw}=10$ Ry as is the case for $E_{pw}=6$ Ry (see Table I). The resultant phonon dispersion curves, as indicated by solid lines in Fig. 2, are considered to be better converged with respect to E_{pw}.[15] They are in excellent agreement with experiment.[3] Here we emphasize that the only input information in the present calculations is the atomic number, mass, and the diamond crystal structure.

The peculiar features of the TA dispersion curves merit some more detailed discussion. The small values of the TA modes are mainly due to the large differences in the transverse first-nearest-layer force constants (k_1 and $k_{\bar{1}}$). This is consistent with the physical picture that the bond-bending forces are quite small compared to the bond-stretching forces. The flatness of the TA modes can be attributed to the non-negligible value of $k_{\bar{3}}$, which is important for TA modes near Γ but has little effect on TA modes near X. The fact that $k_{\bar{3}}$ is not negligible also demonstrates the long-range nature of the interatomic interactions.[13]

In summary, we demonstrate that the phonon dispersion curves of Si along the [001] direction can be calculated from first principles using *ab initio* interlayer force constants. The excellent agreement with experiment suggests that both the pseudopotential and the local-density-functional formalisms can be used to obtain accurate information about lattice dynamical properties. The approach of *ab initio* interlayer force constants can be applied to various symmetry directions in the Brillouin zone or to different materials[16] and is expected to facilitate important microscopic interpretations of lattice vibrations of solids.

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[1]M. T. Yin and M. L. Cohen, Phys. Rev. Lett. 45, 1004 (1980).

[2]P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964); W. Kohn and L. J. Sham, *ibid.* 140, A1133 (1965).

[3]G. Dolling, *Inelastic Scattering of Neutrons in Solids and Liquids* (IAEA, Vienna, 1963), Vol. II, p. 37; G. Nilson and G. Nelin, Phys. Rev. B 6, 3777 (1972); for a review on phonons in semiconductors, see S. K. Sinha, CRC Crit. Rev. Solid State Sci. 4, 273 (1973).

[4]F. Herman, J. Phys. Chem. Solids 8, 405 (1959). The

study was done for Ge.
[5]A. W. Solbrig, J. Phys. Chem. Solids 32, 1761 (1971); R. Tubino, L. Piseri, and G. Zerbi, J. Chem. Phys. 56, 1022 (1972).
[6]W. Weber, Phys. Rev. Lett. 33, 371 (1974); Phys. Rev. 15, 4789 (1976).
[7]P. E. Van Camp, V. E. Van Doren, and J. T. Devreese, Phys. Rev. Lett. 42, 1224 (1974).
[8]L. J. Sham, Phys. Rev. 188, 1431 (1969); R. M. Pick, M. H. Cohen, and R. M. Martin, Phys. Rev. B 1, 910 (1970).
[9]D. R. Hamann, M. Schlüter, and C. Chiang, Phys. Rev. Lett. 43, 1494 (1979).
[10]We have performed total energy calculations for bulk Si with the same kinetic energy cutoff ($E_{pw}=6$ Ry). The calculated equilibrium lattice constant is 0.7% smaller than the experimental value of 5.43 Å.
[11]J. Ihm, A. Zunger, and M. L. Cohen, J. Phys. C 12, 4409 (1979); 13, 3095E (1980); J. Ihm, M. T. Yin, and M. L. Cohen, Solid State Commun. 37, 491 (1981).
[12]E. Wigner, Phys. Rev. 46, 1002 (1934).
[13]The fifth-nearest-neighbor interatomic interaction has already been included in this assumption.
[14]M. Born and K. Huang, *Dynamic Theory of Crystal Lattices* (Oxford University Press, London, 1954), p. 221.
[15]We estimate the convergent errors are within 0.3 THz for phonon frequencies calculated using $E_{pw}=10$ Ry.
[16]We have learned that a method similar to what we propose here has been recently applied to GaAs by K. Kunc and R. M. Martin (unpublished).