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Phonon dispersions of silicon and germanium from first-principles calculations

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We present the calculation of the full phonon spectrum for silicon and germanium with the pseudopotential method and the local-density approximation without using linear-response theory. The interplanar-force constants for three high-symmetry orientations [(100), (110), and (111)] are evaluated by supercell calculations using the Hellmann-Feynman theorem. By considering the symmetry of the crystal, three-dimensional interatomic-force-constant matrices are determined by a least-squares fit. Interactions up to the eighth nearest neighbors are included. The dynamical matrix, which is the Fourier transform of the force constant matrix, is hence constructed and diagonalized for any arbitrary wave vector in the Brillouin zone, yielding the phonon dispersion. In this paper we will present the calculation details and discuss various aspects of convergence. Phonon dispersions of Si and Ge calculated are in excellent agreement with experiments.

I. INTRODUCTION

The phonon spectrum of a solid is important in evaluating physical quantities such as specific heat, thermal expansion coefficient, and electron-phonon interactions.[1] Many empirical methods were developed[2,3] before first-principles calculations became feasible. Different kinds of interaction parameters were proposed; all had to be fitted to known experimental results, most commonly dispersion curves. These empirical methods provided insight into experimental observation, but lacked predictive power. With the advent of computational techniques, calculating phonon frequencies within the local-density approximation (LDA) became possible.[4-7] The approach can be divided into two categories: the supercell method[4,5] and the linear-response method.[6,7]

In the supercell method, total energy or forces are calculated within the frozen-phonon approximations as atoms in the supercell are displaced from their equilibrium positions. It is conceptually simple and computationally straightforward, but limited by the size of supercell that can be handled. Only phonons at high-symmetry points and along high-symmetry directions[4,5] have been studied by this method. On the other hand, the latest linear-response method calculates the electron-density response to a specific lattice distortion either by evaluating the potential change self-consistently[6] or by solving an integral equation in connection with the density change in the absence of electron-electron interaction.[7] The first-order change in electron density gives the second-order change in energy. Thus the phonon dispersion was calculated for several semiconductors[6] and aluminum.[7]

In this paper, we will demonstrate that it is indeed possible to obtain full phonon dispersion from a few simple supercell calculations. It is based on the observation that one-dimensional force constants between high-symmetry atomic planes (which can be evaluated easily by the supercell method) are linear combinations of three-dimensional interatomic-force constants. Therefore, if one knows the interplanar-force constants (longitudinal and transverse) for a few directions, interatomic-force constants can be found by solving a set of linear equations. Since crystal symmetry reduces the number of independent elements in the force-constant matrices, one may end up with more equations than needed for a given cutoff of interaction range. Therefore, solutions can be determined from a least-squares fit. A dynamical matrix for any wave vector can be calculated once interatomic-force constants are known. This approach needs only the normal LDA codes and can in principle provide information about nonlinear forces. We will use the diamond structure as an example and calculate the phonon dispersion for silicon and germanium within the harmonic approximation. The preliminary results for silicon with a smaller plane-wave energy cutoff was previously reported.[8]

The paper is organized as follows: the calculational method is presented in Sec. II and the results for Si and Ge in Sec. III. Discussions of convergence of force constants and other related topics are given in Sec. IV and the conclusion in Sec. V.

II. CALCULATIONAL METHODS

The method we present is based on the supercell approach[4,5] where forces on each atom in the supercell are calculated using the Hellmann-Feynman theorem.[9] Under the harmonic approximation, the total-energy change due to the displacements of atoms is written as[10]

$$U_{\text{harm}}=\frac{1}{2}\sum_{\mathbf{R},\mathbf{R}',\alpha,\beta}\mathbf{u}^{\alpha}(\mathbf{R})\cdot\mathbf{D}^{\alpha\beta}(\mathbf{R}-\mathbf{R}')\cdot\mathbf{u}^{\beta}(\mathbf{R}') , \qquad (1)$$

where $\mathbf{u}^{\alpha}(\mathbf{R})$ is the displacement from equilibrium of atom α in the unit cell associated with lattice vector $\mathbf{R}$, $\mathbf{D}^{\alpha\beta}(\mathbf{R}-\mathbf{R}')$ is the interatomic-force-constant matrix connecting atom α in unit cell $\mathbf{R}$ and atom β in unit cell $\mathbf{R}'$, and α and β are indices of atoms in the basis. We will limit our discussion to the diamond structure where two

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atoms are present in each unit cell. It can easily be generalized to other structures. Following conventional notation, the two atoms in the primitive cell will be referred to as a and c. The vector connecting their equilibrium positions is $\tau_{ac}=(a/4,a/4,a/4)$, where a is the lattice constant. The phonon frequencies of wave vector $\mathbf{k}$ are the eigenvalues of the dynamical matrix, $\Phi(\mathbf{k})$, which is simply the Fourier transform of the real-space interatomic-force constants,

$$\Phi(\mathbf{k})=\sum_{\mathbf{R}} e^{-i\mathbf{k}\cdot\mathbf{R}} \begin{bmatrix} \mathbf{D}^{cc}(\mathbf{R}) & \mathbf{D}^{ca}(\mathbf{R}) \\ \mathbf{D}^{ac}(\mathbf{R}) & \mathbf{D}^{aa}(\mathbf{R}) \end{bmatrix} . \tag{2}$$

Therefore, once interatomic-force constants are known, the phonon dispersion can be easily obtained.

In principle, force constants can be calculated within the LDA by using the Hellmann-Feynman theorem[9] and a supercell modeling of the atomic displacement, but since the size of the supercell can become alarmingly large using the conventional approach, this has never been achieved. On the other hand, the one-dimensional interplanar-force constants can be easily calculated using a long and slim cell along certain high-symmetry directions.[4,5] In these calculations, instead of one single atom being displaced, the whole layer of atoms are displaced. We have

$$-\mathbf{F}^{\alpha}(n)=\sum_{m,\beta}\lambda^{\alpha\beta}(n-m)\mathbf{u}^{\beta}(m) , \tag{3}$$

where $\mathbf{F}^{\alpha}(n)$ is the force on atom α in the nth layer, $\mathbf{u}^{\beta}(m)$ is the collective displacement of atom β in the mth layer, and $\lambda^{\alpha\beta}(n)$ is the interplanar-force-constant matrix for the chosen direction.

Note that the interplanar forces on each atomic layer are in fact superpositions of the interatomic forces:

$$\lambda^{\alpha\beta}(n)=\sum_{\mathbf{R},\hat{e}\cdot(\mathbf{R}+\tau_{\alpha\beta})=d_n}\mathbf{D}^{\alpha\beta}(\mathbf{R}) , \tag{4}$$

where $\hat{e}$ is the unit vector normal to the atomic layer and $\tau_{\alpha\beta}=\tau_{\alpha}-\tau_{\beta}$ is the vector connecting atoms α and β in the basis. An example is shown in Fig. 1 for the (100) planes, where open circles are atomic equilibrium positions and solid circles indicate the atomic plane displaced longitudinally. The dotted lines indicate interatomic forces included in the summation in Eq. (4) for the force on the adjacent plane. The solid box is the typical long and slim supercell containing 12 atoms if the interaction is truncated at the eighth nearest neighbor. For more details on the interplanar-force-constant calculation, see Ref. 5. Following Eq. (4), one linear equation can be found for the force on every plane in the unit cell and for two different kinds of displacements, longitudinal (L) and transversal (T) (three in the cases where the two transversal modes are nondegenerate).

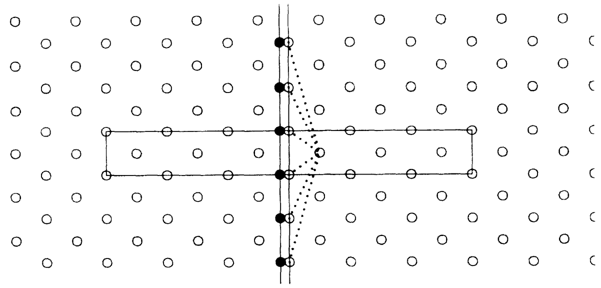

FIG. 1. Supercell for (100) planes. Empty circles are the equilibrium atomic positions and solid circles are the layer of atoms displaced longitudinally. The solid box is the long, slim unit cell containing 12 atoms. Dotted lines show the pairs of the interatomic forces, indicating that the planar force is written as the sum of interatomic forces as expressed in Eq. (4).

It turns out that knowing the interplanar forces for three plane orientations [(100, (110), and (111)] is sufficient to determine the interatomic-force constants in the diamond structure (when the cutoff is at the eighth nearest neighbor), since crystal symmetry greatly reduces the number of independent matrix elements. For the diamond structure, the inversion symmetry gives

$$\begin{aligned} &\mathbf{D}^{ac}(\mathbf{R})=\mathbf{D}^{ca}(-\mathbf{R}) , \\ &\mathbf{D}^{aa}(\mathbf{R})=D^{cc}(-\mathbf{R}) . \end{aligned} \tag{5}$$

Therefore, only two of the above four 3×3 matrices are independent. From the definition of the force constant in Eq. (1) as the second derivative of the energy, we have

$$\begin{aligned} &\mathbf{D}^{ca}(\mathbf{R})=\mathbf{D}^{ac}(-\mathbf{R})^{T} , \\ &\mathbf{D}^{cc}(\mathbf{R})=D^{cc}(-\mathbf{R})^{T} , \\ &\mathbf{D}^{aa}(\mathbf{R})=\mathbf{D}^{aa}(-\mathbf{R})^{T} . \end{aligned} \tag{6}$$

Additionally, the force-constant matrix transforms as a second-rank tensor

$$\mathbf{D}^{\alpha\beta}(\mathbf{R}')=S\cdot\mathbf{D}^{\alpha\beta}(\mathbf{R})\cdot S^{-1} , \tag{7}$$

where S is any point-group operation that maps $\mathbf{R}+\tau_{\alpha\beta}$ to $\mathbf{R}'+\tau_{\alpha\beta}$. This further reduces the number of independent elements in the 3×3 force-constant matrices.

In the calculation, we keep up to the eighth nearest neighbors in the summation of Eq. (2). The real-space convergence will be discussed later. With this cutoff, supercells for the (100), (111),and (110) planes include 8–16 atoms with the eighth nearest neighbors at the boundary. Two kinds of displacement (L and T) are considered for (100) and (111), and three kinds of displacement (L, T, and T_2) for the (110) calculation. The calculation is done within the local-density approximation using the soft pseudopotential[11] and the plane-wave basis. The Ceperley-Alder exchange-correlation[12] parameterized by Perdew-Zunger[13] is used.

III. RESULTS FOR Si AND Ge

We first checked the convergence of the calculated Hellmann-Feynman forces with respect to the energy cutoff of the plane waves. For a 10% displacement of the bond length along the [111] direction, the force and energy change as a function of plane-wave cutoff are shown in Figs. 2 and 3 for Si and Ge, respectively. The forces are accurate to within 1 mRy/a.u. with an energy cutoff of 18 Ry for Si and 20 Ry for Ge. These are the energy cutoffs used in this calculation. The difference in the

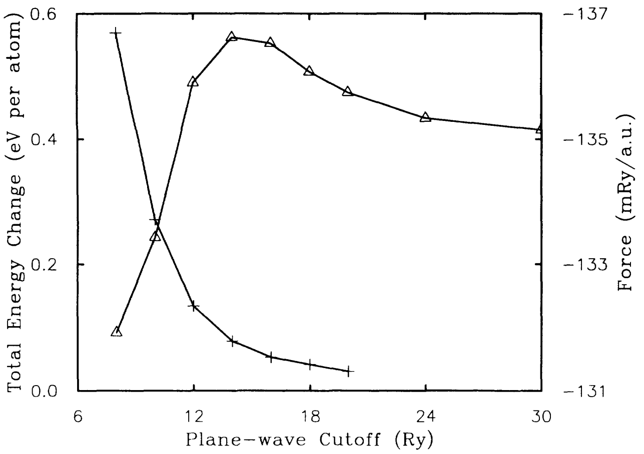

FIG. 2. Total-energy change and forces (triangles) as a function of the plane-wave energy cutoff for Si. Ten special k points for the two-atom primitive cell (and its equivalent) are used in both calculations. The force is for a bond length reduction of 10%.

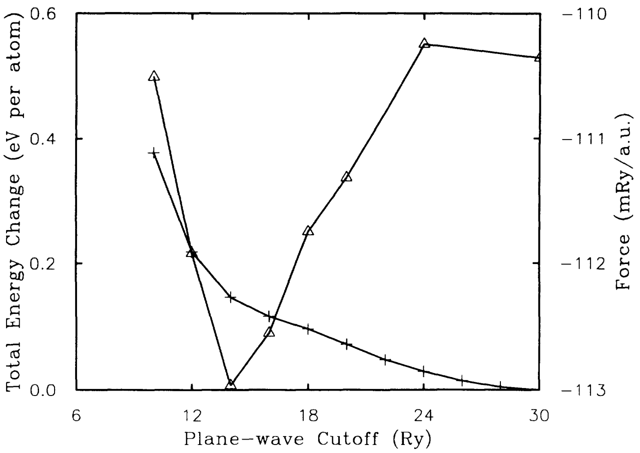

FIG. 3. Total-energy change and forces (triangles) as a function of the plane-wave energy cutoff for Ge. Ten special k points for the two atom primitive cell (and its equivalent) are used in both calculations. The force is for a bond length reduction of 10%.

frozen-phonon results for TA(X) in Si using the cutoffs of 12 and 18 Ry is about 5%.[8] Therefore, these results correspond to more converged values than those reported earlier.[8]

In calculating interplanar forces, three different supercells are chosen for the (100), (111), and (110) orientations. They are different in size (number of atoms), shape, and symmetry. The same accuracy for the calculated interplanar-force constants along different directions has to be maintained in order to reduce the error in the final results of the interatomic-force constants. Therefore, a consistent k-space representation is necessary. The k points used in each case are equivalent to the ten special k points for the primitive cell of the diamond structure. This set is chosen according to previous convergence studies.[14] Usually, the limited k-point sample does not introduce a serious error in total-energy calculations for semiconductors.[14] However, it is important to keep the sampling consistent when the forces are concerned, especially when examining various supercells, because the error induced is more significant in the force than in the energy. The calculation is performed using the theoretical equilibrium lattice constant.

As a test, five displacements $(0,\pm u,\pm 2u)$ are included in each planar force calculation for Si at the energy cutoff of 12 Ry to get a better description of the harmonic term. The size of u is typical at 1% of the lattice constant. The zero displacement calculation is important because it checks the accuracy of the calculated forces. Theoretically, the force should be exactly zero, but due to the limited number of k points and plane waves, a very small value may occur (less than 0.1 mRy/a.u., much less than the convergence error). The force constants obtained from the five-point fit [error $\sim O(u^5)$] do not differ significantly from those obtained from the three-point $(0,\pm u)$ fit. The difference is less than 2%, which is comparable to errors introduced by the limited number of plane waves. Most of the results presented below are obtained from the three-point fit.

The interatomic interactions up to the eighth nearest

TABLE I. Planar-force constants of Si (10^5 dyn/cm). Supercells contain 8 and 12 atoms for the [100] direction, 8 atoms for the [111] direction, and 16 atoms for the [110] direction, respectively. The sum excludes the values from the first row.

	[100]		[111]		[110]					
n	Longitudinal	Transversal	Longitudinal	Transversal	n		T_2	LL	TT	LT
0	+2.527	+2.085	+2.437	+2.182	0	cc	+2.084	+2.174	+2.413	+0.000
+1	−1.130	−1.874	−1.244	−0.138		ca	−1.858	−0.276	−1.134	+0.000
−1	−1.130	−0.270	−0.977	−2.078	1	cc	+0.074	+0.064	−0.149	+0.046
±2	−0.151	+0.063	−0.093	+0.026		ca	−0.143	−0.973	−0.538	−0.524
+3	+0.012	−0.000	+0.007	−0.040	2	cc	+0.002	−0.029	+0.061	−0.015
−3	+0.012	−0.081	−0.034	−0.001		ca	−0.036	−0.005	+0.014	+0.009
±4	−0.005	+0.014	−0.002	+0.006	3	cc	+0.002	+0.002	−0.022	+0.003
+5		−0.008				ca	−0.005	−0.010	−0.022	+0.014
−5		−0.019			4	cc	−0.005	−0.003	+0.007	+0.000
						ca	+0.000	+0.000	+0.000	+0.000
Sum	−2.543	−2.098	−2.438	−2.193	Sum		−2.082	−2.184	−2.432	+0.000

TABLE II. Planar force constants of Ge (10^5 dyn/cm). Supercells contain 8 and 12 atoms for the [100] direction, 8 atoms for the [111] direction, and 16 atoms for the [110] direction, respectively. The sum excludes the values from the first row.

	[100]		[111]				[110]			
n	Longitudinal	Transversal	Longitudinal	Transversal	*n*		T_2	*LL*	*TT*	*LT*
0	+2.203	+1.800	+2.145	+1.924	0	*cc*	+1.813	+1.882	+2.068	+0.000
+1	−0.975	−1.595	−1.061	−0.129		*ca*	−1.610	−0.232	−1.007	+0.000
−1	−0.975	−0.265	−0.879	−1.814	1	*cc*	+0.057	+0.058	−0.113	+0.040
±2	−0.130	+0.063	−0.093	+0.022		*ca*	−0.124	−0.836	−0.456	−0.450
+3	+0.005	+0.001	+0.015	−0.038	2	*cc*	+0.008	−0.021	+0.057	−0.014
−3	+0.005	−0.076	−0.033	−0.012		*ca*	−0.039	−0.009	+0.012	+0.014
±4	−0.001	+0.013	−0.001	+0.006	3	*cc*	+0.003	−0.002	−0.018	−0.003
+5		−0.005				*ca*	−0.005	−0.014	−0.029	+0.013
−5		−0.022			4	*cc*	+0.000	−0.002	+0.010	+0.000
						ca	+0.001	+0.001	+0.007	+0.000
Sum	−2.202	−1.810	−2.142	−1.937	Sum		−1.808	−1.882	−2.067	+0.000

neighbors are included in the calculations. This corresponds to a total of 31 independent matrix elements. The number of atoms in the unit cell is 12 for (100), 8 for (111), and 16 for the (110) orientations, respectively. For the (100) longitudinal mode, the force decays very fast, so that an eight-atom cell is sufficiently converged. Tables I and II list the calculated interplanar-force constants for Si and Ge, showing that the sum rule is well satisfied.

From these results, we have 61 equations to solve for 31 independent parameters. A least-squares fit is employed to determine these matrix elements. Note that the low frequencies of the TA modes are determined by the small difference of two large numbers. In order to get the low-frequency TA modes correct, the difference of certain force constants has to be very accurate. This is included in the fitting. In addition, more weighting is included for low-lying TA branches. The results of interatomic-force constants are listed in Table III, in which coordinates are in units of $a/4$ and notations for the force constants follow Herman's work.[15]

Using these interatomic-force constants, the calculated phonon dispersions for Si and Ge are shown in Figs. 4 and 5, respectively. Solid lines are calculated results, while experimental data are denoted by circles and stars.[16] The black squares are from the direct frozen-phonon calculations for zone-boundary modes using suitable supercells. As a whole, the calculated results compare very well with experiment. Small discrepancies exist at very low frequencies, which correspond to very small eigenvalues of the dynamical matrix ($m\omega^2$). As an example, $m\omega^2$ equals to 0.311 and 0.165 (10^5 dyn/cm^2) for TA(X) and TA(L) in Si, respectively. Even a small error in the force constants can create a visible effect in phonon dispersion curves in the very-low-frequency region. The phonon density of states is also shown in the figures. Comparing phonon frequencies calculated from the interplanar-force constants with those from the final interatomic-force constants for the [100], [111], and [110] directions, one finds an error of 2%, resulting from the 0.3% error in the least-squares fit.

TABLE III. Coordinates of neighbors and corresponding force-constant matrix elements for Si and Ge. Coordinates are expressed in units of $a/4$ with a being a cubic lattice constant. The force constant matrix elements are in conventional notations (Ref. 15) (10^5 dyn/cm).

NN	Coordinate	Si				Ge			
0 *cc*	(0,0,0)	$a_0=$	2.237			$a_0=$	1.952		
1 *ca*	(1,1,1)	$\alpha_1=$	−0.547	$\beta_1=$	−0.388	$\alpha_1=$	−0.478	$\beta_1=$	−0.330
2 *cc*	(2,2,0)	$\mu_2=$	−0.035	$\nu_2=$	−0.029	$\mu_2=$	−0.025	$\nu_2=$	−0.027
		$\gamma_2=$	0.017	$\delta_2=$	0.068	$\gamma_2=$	0.013	$\delta_2=$	0.056
3 *ca*	$(\bar{1},\bar{2},\bar{3})$	$\mu_3=$	0.007	$\nu_3=$	−0.010	$\mu_3=$	0.011	$\nu_3=$	−0.007
		$\gamma_3=$	0.008	$\delta_3=$	0.001	$\gamma_3=$	0.004	$\delta_3=$	0.000
4 *cc*	(0,0,4)	$\mu_4=$	−0.013	$\delta_4=$	0.018	$\mu_4=$	−0.015	$\delta_4=$	0.001
5 *ca*	(3,3,1)	$\mu_5=$	−0.002	$\nu_5=$	−0.001	$\mu_5=$	−0.003	$\nu_5=$	0.002
		$\gamma_5=$	0.004	$\delta_5=$	−0.030	$\gamma_5=$	0.003	$\delta_5=$	−0.029
6 *cc*	(2,2,4)	$\mu_6=$	−0.002	$\nu_6=$	0.006	$\mu_6=$	−0.003	$\nu_6=$	0.006
		$\gamma_6=$	−0.000	$\delta_6=$	0.001	$\gamma_6=$	−0.002	$\delta_6=$	0.004
		$\epsilon_6=$	0.002			$\epsilon_6=$	0.000		
7 *ca*	(1,1,5)	$\mu_7=$	0.000	$\nu_7=$	0.004	$\mu_7=$	−0.000	$\nu_7=$	0.003
		$\gamma_7=$	0.002	$\delta_7=$	0.004	$\gamma_7=$	0.002	$\delta_7=$	0.001
7′ *ca*	$(\bar{3},\bar{3},\bar{3})$	$\alpha_7=$	0.004	$\beta_7=$	−0.002	$\alpha_7=$	0.000	$\beta_7=$	−0.006
8 *cc*	(4,4,0)	$\mu_8=$	−0.002	$\nu_i=$	−-.002	$\mu_8=$	−0.003	$\nu_8=$	−0.006
		$\gamma_i=$	−0.008	$\delta_8=$	0.012	$\gamma_8=$	−0.001	$\delta_i=$	0.021

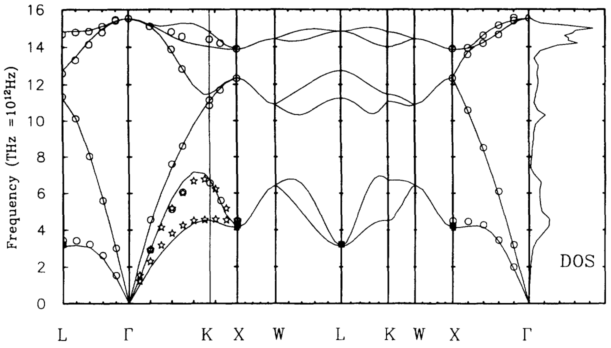

FIG. 4. Phonon dispersion and density of state for Si. The results are obtained with a plane-wave energy cutoff of 18 Ry. Solid lines are calculated results and experimental values are shown as circles (Dolling, Ref. 16) and stars (Nilsson and Nelin, Ref. 16). Solid squares are the frozen-phonon results.

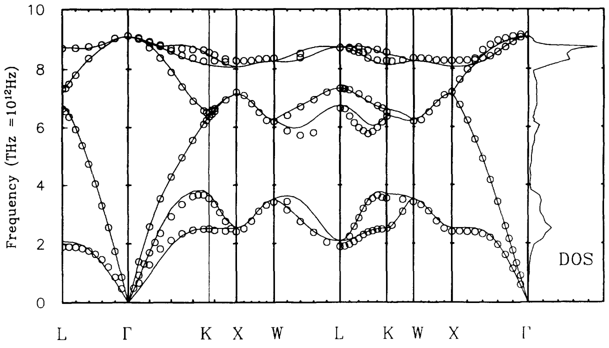

FIG. 5. Phonon dispersion and density of state for Ge. The results are obtained with a plane-wave energy cutoff of 20 Ry. Solid lines are calculated results and experimental values are shown as circles (Nilsson and Nelin, Ref. 16).

IV. DISCUSSIONS

A. Real-space convergence

In real calculations, the sum in Eq. (2) has to be truncated at some distance. It should reflect the range of the interatomic interactions in the material. The convergence in elemental semiconductors is well studied in the literature. It has long been realized that the flatness of the TA branch near the zone boundary comes from long-range interactions. As Herman[15] pointed out, the fifth nearest-neighbor interaction is vital for reproducing the flatness. Interactions between atoms farther apart are of minimal effect. This was again examined by Mazur and Pollmann[17] recently. They further speculated that the next important contribution after the fifth nearest neighbor will be the eighth nearest neighbor (the next atom in the zig-zag chain along the [110] direction), but they did not find that it caused any visible effect on phonon dispersion curves. In our study, we included all the force constants up to the eighth nearest neighbor in our calculation. The results do indicate that the eighth nearest neighbors are more important than the sixth and seventh nearest neighbors (Table III), but the increase in the number of neighbors included from the fifth to eighth nearest neighbors had little effect on the dispersion. If the notion that the force constant for atoms connected by the zig-zag chain along the [110] direction is important is correct, then the next atom along the chain will be the thirteenth nearest neighbor [coordinates $(5a/4,5a/4,a/4)$]. As the magnitude of force constants decays (Table I), the contribution will be negligible.

Another check of the convergence is the interplanar force (or force constants) for each layer. It has to decay fast enough. For example, for the (100) transverse force constants, we had to go up to the fifth layer before the force constants became small enough (1% of the nearest-neighbor value). The other thing to check is the sum rule, $\sum_n \lambda(n)=0$, for each direction and polarization. In our calculation (see Tables I and II) this is satisfied to within 1% of the zeroth layer force constants. One other check, usually neglected, is the agreement in the calculated optical-phonon frequencies at Γ from different directions and polarizations. This is important because it measures the quality (consistency) of the data obtained from different supercells and different polarizations. In our silicon calculation, the frequencies agree to within 0.5%.

In addition, real-space convergence can be checked by comparing the bulk modulus calculated from the equation of state and from interatomic-force constants. This should directly indicate whether all the important force constants are included in the calculation. Our test shows that we have an agreement to within 2% by including the eighth nearest neighbors.

Table IV lists and compares results for the zone-boundary TA modes calculated by the direct frozen-phonon method, by the interplanar force, and by the three-dimensional atomic-force constants. These are low-frequency modes at high symmetry points. The direct frozen-phonon calculations for X and L include, in principle, an infinite range of interactions. Hence the results can be used to check the convergence of planar-force results. If up to the eighth nearest neighbors are in-

TABLE IV. Comparison of phonon frequencies of TA(X) and TA(L) modes in Si obtained by the dynamical matrix calculation (DM) and other methods.

	Frozen phonon		Planar force			DM	EXP (Ref. 16)
	energy	force	8 layer	12 layer	16 layer		
TA(X)	4.22	4.22		4.37	4.27	4.10	4.49
TA(L)	3.21	3.21	3.37			3.12	3.43

cluded [8 and 12 layers for the (111) and (100) supercells, respectively], the planar-force results have an error of a few percent. The final three-dimensional dynamic matrix results have an error of 2–3 %. The 16-layer calculation (for the [100] direction supercell) includes up to the sixteenth nearest neighbors. The results are very close to the frozen-phonon results. Hence, error induced from real-space truncation is insignificant considering error induced from the limited number of plane waves, as discussed in the previous section.

B. Determination of force constants

In order to uniquely determine all elements of interatomic-force-constant matrices for an arbitrary cutoff, one may need to know the interplanar force constant along some low-symmetry direction. In the case of the diamond structure, it can be understood by examining the symmetry relations expressed in Eqs. (5), (6), and (7). $\mathbf{D}^{ca}$ is always symmetric, hence it has no more than six independent elements, which can be uniquely determined from the interplanar-force constants of the (100), (111), and (110) orientations. The difficulty is with $\mathbf{D}^{cc}(\mathbf{R})$, which can have as many as nine independent elements for a certain $\mathbf{R}$. This first occurs at coordinates $(a/2,a,3a/2)$, corresponding to the fourteenth nearest neighbor. If an interaction of this range has to be included, it is then necessary to consider, for example, the (012) rather than the (110) planes. This corresponds to 20 atoms per cell instead of 16. For this low-symmetry plane, there are three independent displacements (one longitudinal and two transverse). The forces generated also each have three independent components. Therefore, we have nine linearly independent equations that are sufficient to solve for the nine matrix elements. For Si and Ge, the cutoff at the eighth nearest neighbor is well justified, so it is not necessary to perform the (012) supercell calculations. Instead, the (110) supercell calculation provides all the necessary information.

Although we studied only elemental semiconductors in the diamond structure, the same method can be applied to calculations of phonon spectra for other semiconductors in, for example, zinc-blende or wurtzite structures. The size of supercells will be similar given a similar interaction range. Because of the reduced symmetry, the number of independent force-constant matrix elements will increase. On the other hand, with a lower symmetry, there will be more inequivalent atomic displacements, thus producing more planar-force-constant data. In the end one still has enough linear equations to solve for force constants from three supercell calculations.

As in any other force-constant calculations (including the linear-response method), the number of modes to be considered increases with the complexity of the material being studied. However, for bulk materials with a given interaction range, the number of repeated units in a supercell used in planar-force calculations may decrease when the number of atoms per unit cell increases. This makes the application of this method to more complex materials possible, although one is limited by the size of supercells that can be easily handled by the present standard.

V. CONCLUSION

In conclusion, we have demonstrated that it is possible to obtain the phonon dispersion over the entire Brillouin zone through a direct calculation of forces within the local density approximation. The input needed is interplanar-force constants along several high-symmetry directions. Calculations for Si and Ge are presented and the agreement with experiment is excellent. We discussed truncation and unique determination of force constants. This method requires only the usual total-energy–force codes and the calculation is straightforward. Even though only the harmonic interaction is considered in this paper, the higher-order response can be obtained, in principle, with this method. Additionally, this method will not be restricted by the crystalline or electronic structure of the material being studied.

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