Ideal crystal stability and pressure-induced phase transition in silicon

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The structural response of diamond-cubic silicon under hydrostatic compression is analyzed using both an empirical interatomic potential proposed by Tersoff and *ab initio* total-energy calculations. The stability analysis based on elastic stiffness coefficients (which are generalized elastic constants at finite strain) gives a critical pressure of 64 GPa at which the ideal lattice becomes unstable against homogeneous tetragonal shear deformation. This prediction is explicitly verified by direct molecular-dynamics simulation, which shows that the instability causes the lattice to transform to the β-Sn structure. It is demonstrated that the large value of the transition pressure implies an intrinsic activation barrier, for which the Tersoff potential results agree well with *ab initio* calculations. This barrier exists for a transformation involving ideal crystal lattices that, while uniformly deformed from the equilibrium diamond-cubic structure, do not contain any point or extended defects. We suggest that, due to the neglect of lattice defects, the critical pressure corresponding to this transformation represents the upper bound on the limit of stability. A lower bound, corresponding to the barrierless transition, is obtained by equating free energies of different phases. Lower bounds calculated with the Tersoff potential and present *ab initio* results are 12.7 and 7.8 GPa, respectively, close to the range of experimental values for the diamond-cubic to β-Sn transition under compression. To support our conjecture on the role of defects we invoke certain analogies between the studied structural transitions in crystalline solids and melting.

I. INTRODUCTION

It is well known experimentally that silicon under compression transforms from the diamond-cubic structure at low pressure to a high-pressure phase with tetragonal β-Sn structure.[1,2] Theoretical analyses of this transition have been mostly concerned with energy-volume calculations and the thermodynamic criterion of equal free energies.[3,4] More recently, similar treatments based on free-energy considerations have been reported for *metastable* phases of Si such as ST12 and BC8, which lie between the diamond cubic and the β-Sn structures.[5] However, little is known about the mechanical behavior aspects of the experimentally observed diamond-to-β-Sn transition. In particular, the question of whether one can regard the transition as triggered by an elastic instability has not been addressed. From elasticity considerations one may hope to obtain some understanding of how hydrostatic stress can bring about a symmetry change from cubic to tetragonal.

Recently, it has been shown that the analysis of the unstable structural response of a deformed lattice requires the use of elastic stiffness coefficients[6] which are the generalization of elastic constants to finite strain.[7,8] The validity of the derived stability criteria was tested for the cases of hydrostatic tension, uniaxial tension, and lattice expansion by isobaric heating. In each case, direct observation of lattice instability by molecular-dynamics simulation showed that the critical strain for the triggering instability could be predicted; moreover, simulations have revealed that instabilities can occur in sequence.

The purpose of this study is twofold: (i) to analyze the stability under compression of the silicon lattice in the diamond-cubic structure and (ii) to test the prediction of instability by molecular-dynamics simulation which also gives the final state of the system. Our description of lattice energy change with deformation will be based on two approaches: The first is an empirical interatomic potential function developed by Tersoff;[9] the second is an *ab initio* total-energy calculation based on density-functional theory.[10] For the analysis of mechanical behavior of the lattice under compression the Tersoff potential function is used consistently, both in the determination of elastic constants at finite strain and in the direct simulation of unstable structural response.

We will show first that on the basis of the newly formulated stability criteria, diamond-cubic Si under hydrostatic loading should fail at a critical pressure of 64 GPa at zero temperature and at a slightly lower value at 300 K, the predicted instability mode being the vanishing of the modulus against tetragonal shear which should occur with symmetry breaking. Then, from a simulation performed on a perfect lattice, we observe an abrupt transition from the diamond-cubic to the tetragonal structure at a pressure of 64 GPa at 300 K, with corresponding volume and energy reductions. Thus, the stability analysis and simulation results are in complete accord; moreover,

the simulation has shown that after the transition the atomic configuration has the expected β-Sn structure.

The above results, pleasing as they are for internal self-consistency, stand in contrast with the well-known experimental observation of a diamond-cubic to β-Sn structural transition in the pressure range of 8.8 to 12.5 GPa,[1,2] and with the theoretical results based on electronic structure calculations that give a transition pressure also in this range.[3,4] We show that this apparent conflict stems from the existence of an activation barrier which is taken into account in the stability analysis and in the simulation, but *not* in the thermodynamic requirement of equality of free energies. We also suggest that the apparent absence of a barrier in the experiments is possibly due to defects. To demonstrate our contention, we present *ab initio* calculations that show that the Tersoff potential results are qualitatively valid, not only in describing the energy-volume variation, but also in determining the activation energy of 0.3 eV/atom at pressures in the range of experimental observations for the transition.

The paper is organized as follows: In Sec. II we give some details of the Tersoff potential and the *ab initio* method of total-energy calculations. The thermodynamic criterion of structural transition, the equality of free energies, is examined in Sec. III where it is shown that the transition pressures determined in this way lie in the experimental range, as has already been established.[3,4] Section IV presents the elastic stability analysis valid at finite compression. It is shown that on the basis of stability criteria formulated in terms of the conventional elastic constants, even when evaluated at finite strain, *no* instability would occur in the lattice at arbitrary compression. On the other hand, the formulation based on elastic stiffness coefficients shows an instability in tetragonal shear. Predictions of the transition pressure obtained using the Tersoff potential are made at 0 K and 300 K. In Sec. V, molecular-dynamics (MD) results are described showing the volume and energy response to pressure, as well as temporal behavior for the onset of the instability. In Sec. VI, the determination of the activation barrier is discussed, and results are presented both for the Tersoff potential and for the *ab initio* calculation. In Sec. VII, we examine the variation of the transverse acoustic modes with pressure which complement the stability analysis. Finally, in Sec. VIII, we note that the thermodynamic and mechanical (stability) criteria for the present structural transition give lower and upper bounds, respectively, on the transition pressure, and draw an analogy with the melting transition, where, in the absence of defects or imperfections, the crystal can superheat to a point of mechanical stability.

II. TOTAL-ENERGY CALCULATIONS

The empirical potential function adopted for this work, among the many candidates that now exist in the literature,[11] is the one proposed by Tersoff.[9] This potential is chosen because it is one of a few, according to energy-volume considerations, capable of describing the diamond-cubic to β-Sn transition in Si under pressure. Furthermore, because its parameter values were determined by fitting the elastic constants, the potential is more likely to be applicable for the analysis of deformation behavior.

Since empirical potentials are optimized for a particular local environment of atomic configurations, they are generally not designed for conditions where the number of interacting neighbors can change abruptly. The Tersoff potential, being a nearest-neighbor model, can be expected to become unphysical in the high-pressure regime when the second neighbors come within the range of what was defined to be the first-neighbor range. The onset of this behavior is discernible in the energy-vs-volume results, it becomes more pronounced in the energy-vs-pressure results, and is even more serious in the calculation of elastic constants.

The fact that the Tersoff potential is applicable over a relatively wide range of pressures is due to its short cutoff range. When compared with other potentials with longer range cutoff, this may be viewed as an advantage. In the present study we find that the undesirable second-neighbor effects can be avoided in two ways: One way is to use a fixed-neighbor list which contains only the nearest neighbors; a second approach is to scale the cutoff with the cubic root of the system volume. By using these procedures, we have made sure that the finite range of the potential does not affect the physics of the problem.

The *ab initio* calculations are based on density-functional theory in the local density approximation,[10] with the exchange and correlation energy functional developed by Ceperley and Alder.[12] We use nonlocal norm-conserving pseudopotentials to model the atomic cores from Bachelet *et al.*[13] Plane waves with kinetic energy up to 16 Ry were included in the basis. The body-centered-tetragonal lattice was adopted for all calculations, with a uniform mesh of reciprocal space points corresponding to 78 points in the irreducible Brillouin zone.

III. THERMODYNAMIC TRANSITION

According to thermodynamics, the diamond-cubic phase of Si will coexist with the β-Sn phase at a pressure where the Gibbs free energies, $G = E + PV - TS$, of the two structures are equal. At zero temperature, the only information needed to determine the transition pressure is the energy variation with volume, since the pressure is given by the identity $P = -\partial E/\partial V$. Figure 1 shows $E(V)$ curves for the two structures given by the Tersoff potential and the present *ab initio* calculations. It can be seen that the Tersoff potential description is qualitatively similar to the *ab initio* results over the entire range of volumes examined. To determine the critical pressure for the transition P_c we apply the common tangent construction to obtain $P = 12.7$ GPa and $P = 7.8$ GPa for the Tersoff and the present *ab initio* results, respectively. These may be compared to corresponding values of 12.7 GPa, quoted recently,[11] and 9.9 GPa, the first known *ab initio* result.[3] For experimental values, the range of transition pressures observed is 8.8–12.5 GPa.[1,2] For the

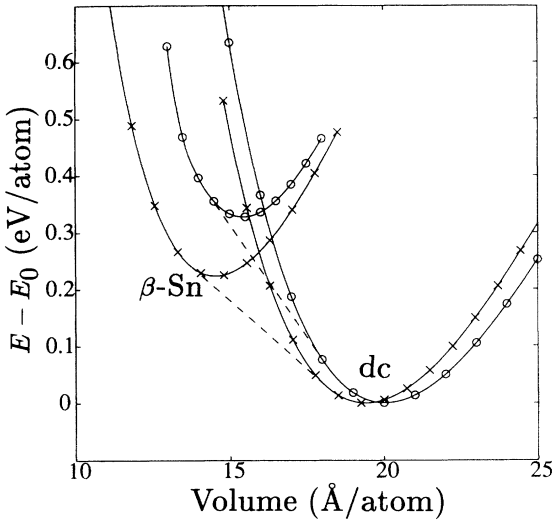

FIG. 1. Energy-vs-volume relations for Si in the diamond-cubic (dc) and β-Sn structures as calculated using the Tersoff potential (open circles) and by the present *ab initio* calculations (crosses).

Tersoff potential we obtain a c/a ratio of 0.524 for the β-Sn structure having the lowest energy; this agrees with the value given in Ref. 11.

IV. ELASTIC STABILITY CRITERIA

A different approach to the analysis of a structural phase transition is to consider the mechanical stability of the stressed lattice. By expressing the elastic energy of a crystal lattice in a quadratic form in the atomic displacements, the well-known stability conditions for a cubic crystal can be obtained as[14]

$$B_T = (C_{11} + 2C_{12})/3 > 0, \tag{1}$$

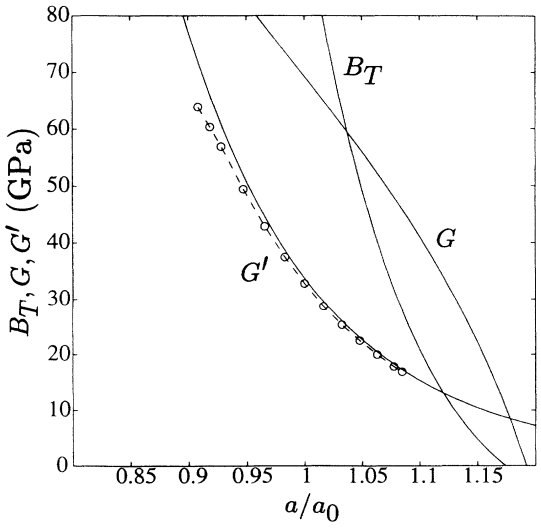

FIG. 2. Lattice stability criteria based on the C analysis, Eqs. (1)–(3), results obtained using the Tersoff potential at 0 K (curves) and 300 K (open circles).

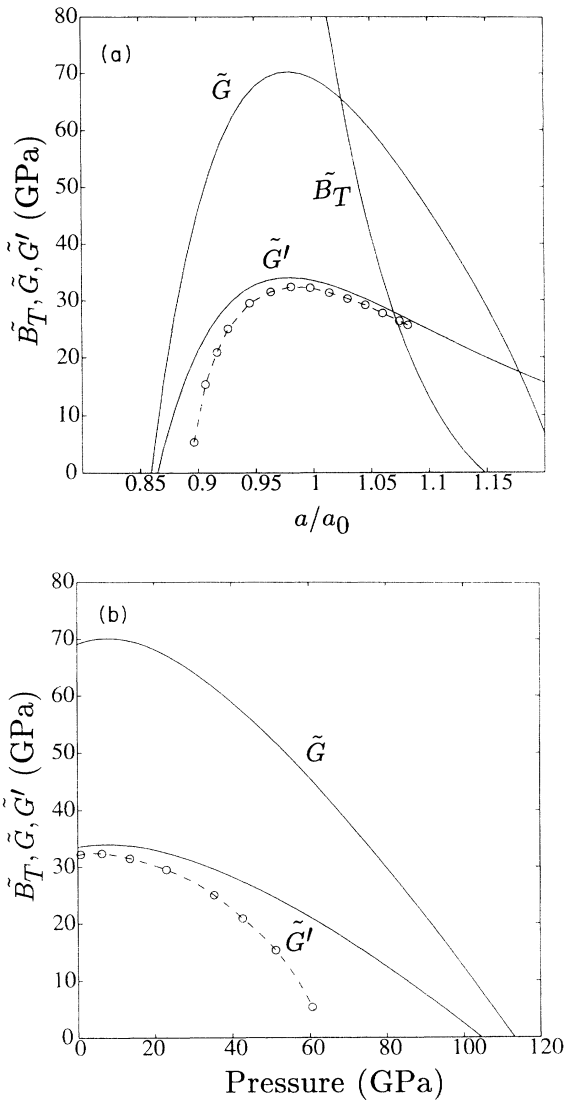

FIG. 3. Elastic stability criteria based on the B analysis, Eq. (5)–(7), results obtained using the Tersoff potential at 0 K (curves) and 300 K (open circles): (a) variation with lattice parameter (a_0 is the zero pressure lattice constant), (b) variation with pressure.

$$G = C_{44} > 0, \tag{2}$$

$$G' = (C_{11} - C_{12})/2 > 0, \tag{3}$$

where C_{ij} are the conventional elastic constants (in Voigt notation). B_T and G are bulk and shear moduli, respectively, and G' is a modulus against tetragonal shear. These conditions can be referred to as spinodal, shear, and Born criteria, respectively.

Recently it has been demonstrated that Eqs. (1)–(3) do not correctly describe the stability limits of crystals at finite strain.[7,8] The proper stress-strain relations for this purpose were shown to be the elastic stiffness tensor, defined as $B_{ijkl}(\mathbf{X}) \equiv [\partial\sigma_{ij}(\mathbf{x})/\partial\eta_{kl}]_{\mathbf{x}}$,[6] where σ_{ij} and η_{kl} are the applied stress and Lagrangian strain tensors, $\mathbf{X}$ and $\mathbf{x}$ are the coordinates before and after the

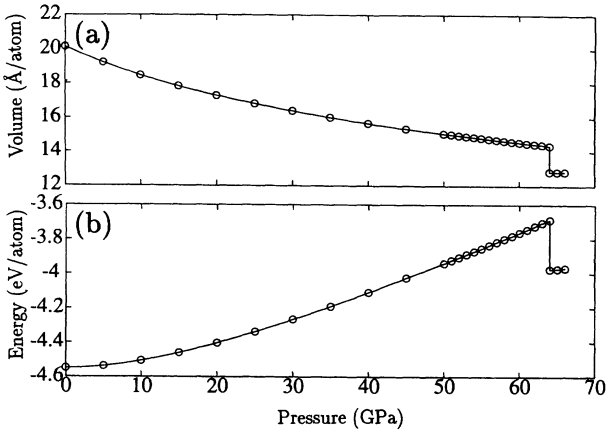

FIG. 4. System response of Si (dc) lattice at 300 K to hydrostatic compression as simulated by MD using the Tersoff potential: (a) volume behavior, (b) energy behavior.

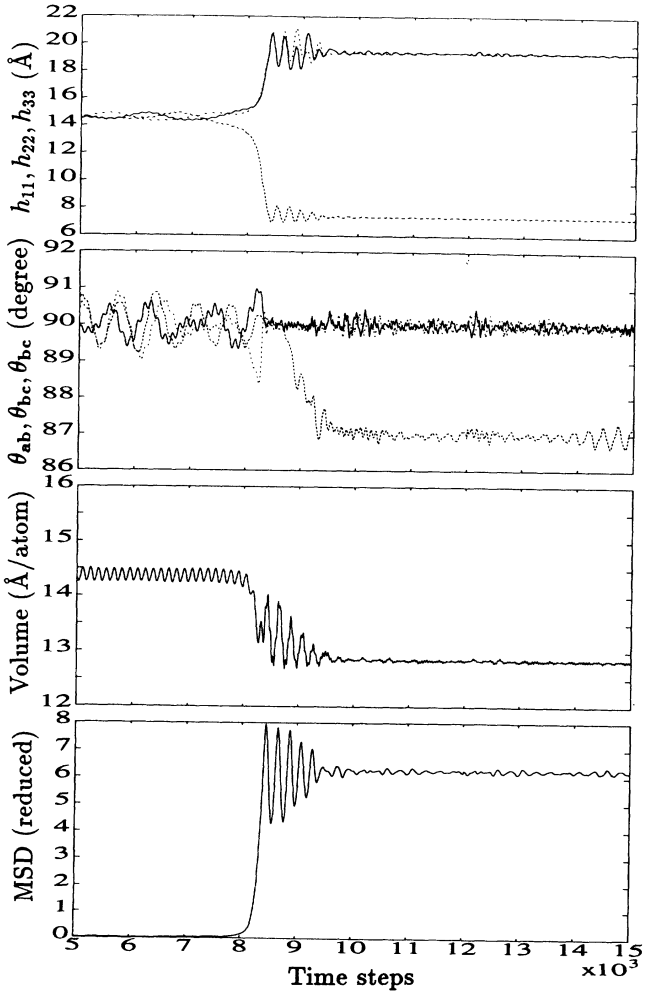

FIG. 5. Temporal behavior during simulation at 300 K and critical pressure of 64 GPa showing the onset of the Born instability followed by a shear instability.

deformation. The stiffness tensor is rather simply related to the elastic constant tensor C_{ijkl}, their difference being a linear function of the stress,

$$B_{ijkl} = C_{ijkl} + \tfrac{1}{2}[\sigma_{il}(\mathbf{X})\delta_{jk} + \sigma_{jl}(\mathbf{X})\delta_{ik} + \sigma_{ik}(\mathbf{X})\delta_{jl} + \sigma_{jk}(\mathbf{X})\delta_{il} - 2\sigma_{ij}(\mathbf{X})\delta_{kl}]. \quad (4)$$

By writing the elastic energy of deformation in terms of the Lagrangian strain one obtains[7,8] new stability criteria for cubic crystals under hydrostatic compression in a form analogous to Eqs. (1)–(3),

$$\tilde{B_T} = (B_{11} + 2B_{12})/3 > 0, \quad (5)$$

$$\tilde{G} = B_{44} > 0, \quad (6)$$

$$\tilde{G'} = (B_{11} - B_{12})/2 > 0, \quad (7)$$

where we define[8]

$$B_{11} = (C_{11} - P), \quad (8)$$

$$B_{12} = (C_{12} + P), \quad (9)$$

$$B_{44} = (C_{44} - P). \quad (10)$$

Henceforth, we will refer to Eqs. (1)–(3) and (5)–(7) as the C and B analysis, respectively.

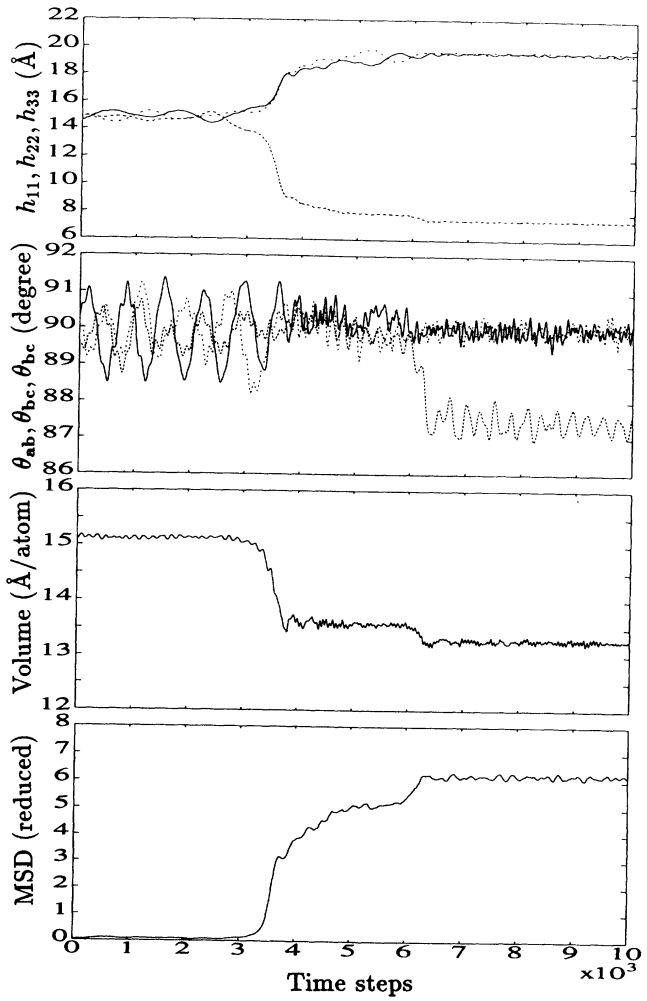

FIG. 6. Same as Fig. 5, at 1000 K and pressure of 49 GPa.

To determine which instability dominates, we compute the elastic constants C_{11}, C_{12}, and C_{44} at zero temperature and 300 K and at various states of compression through fluctuation formulas;[15] these calculations require averaging over long MD simulation trajectories, particularly in the case of C_{44}. Because the fluctuation formula cannot be used to obtain C_{44} at zero temperature, we also performed a stress-strain calculation while allowing for atomic relaxation within each unit cell.[16]

Figure 2 shows the behavior of the three moduli with uniform compression and dilatation on the basis of C analysis, Eqs. (1)–(3). It can be seen that none of the stability conditions are violated when the diamond-cubic lattice is compressed; consequently, no pressure-induced transition is predicted by the conventional stability criteria. Figure 3 shows the corresponding results of the B analysis, Eqs. (5)–(7). By converting the lattice parameter change to pressure, one sees clearly that the Born stability criterion is violated at a compression of 64 GPa (300 K) and 105 GPa (0 K). It is also known from analysis of the eigenmode of deformation that this instability is characterized by symmetry breaking.[7,8] As an aside, we note that the B and C analyses give reasonably similar results for the structural response to hydrostatic tension. Both Figs. 2 and 3 show that under pure dilatation the spinodal condition is first violated at values of a/a_0 not too different for the two formulations.

V. MOLECULAR-DYNAMICS SIMULATION OF COMPRESSION

Direct MD simulation is the most straightforward way of testing the predictions of the stability analysis. For our study a simulation cell is employed which contains 216 atoms on a perfect diamond-cubic lattice with periodic boundary conditions. The lattice parameter is initially set at the equilibrium value appropriate to 300 K, and constant temperature is maintained by velocity rescaling. Stress is imposed following the method of Parrinello and Rahman.[17] The system is first equilibrated at zero pressure, then pressure is incrementally increased with an equilibration period of at least 15000 time steps (each step is 0.26 fs).

Figure 4 shows the system volume and energy at various stages of hydrostatic compression. An abrupt volume decrease is seen at 64 GPa, along with a corresponding energy reduction. This pressure is in close agreement with that predicted in Fig. 3. Figure 5 shows the temporal evolution at 64 GPa of the three diagonal elements of the simulation cell matrix h_{ij} (Ref. 17) and the angles between the basis vectors **a**, **b**, and **c** of the cell. Here, a structural transformation is clearly observed at about time step 8000. The symmetry change from cubic to tetragonal is compatible with the nature of the Born instability. Notice also that at about time step 8500 a second response, having the character of a shear deformation, apparently sets in. In general, stability criteria such as Eqs. (5)–(7) are intended to predict only the first instability mode. Nevertheless, Fig. 3 indicates that the next possible instability under compression is the vanishing of the shear modulus. Thus, for compression loading the overall correspondence between the predictions of the B analysis and the simulation results is remarkably close. In a previous study of tension-induced transitions, equally good agreement between predictions and simulations, as well as the occurrence of a sequence of instabilities, were obtained for a close-packed lattice.[7,8] In Fig. 6, we show corresponding results obtained at T = 1000 K, where the critical pressure has decreased as a

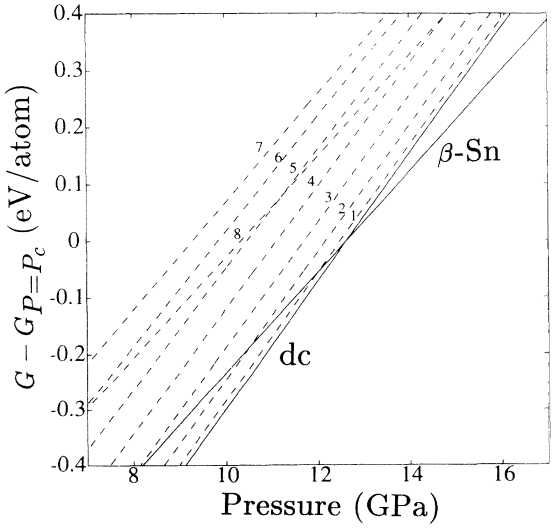

FIG. 7. Variation of free energy at 0 K with compression for intermediate structures with various c/a ratios between diamond-cubic and β-Sn; results obtained using the Tersoff potential. The labels denote c/a ratios: $1 \rightarrow 1.4, 2 \rightarrow 1.3, 3 \rightarrow 1.2, 4 \rightarrow 1.1, 5 \rightarrow 0.9, 6 \rightarrow 0.8, 7 \rightarrow 0.7$, $8 \rightarrow 0.6$.

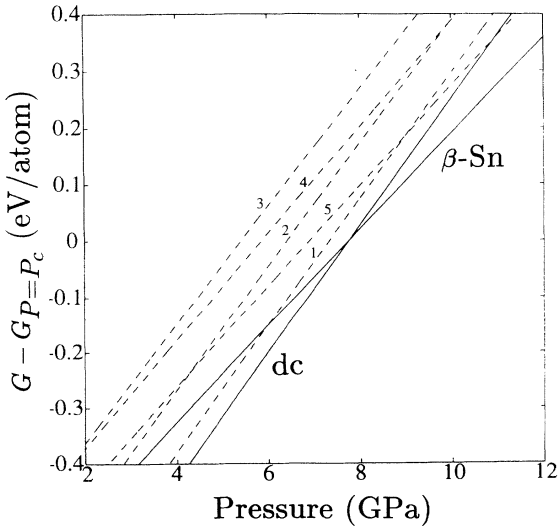

FIG. 8. Same as Fig. 7, obtained by *ab initio* calculation. Labels denote c/a ratios: $1 \rightarrow 1.2, 2 \rightarrow 1.1$, $3 \rightarrow 0.90, 4 \rightarrow 0.72, 5 \rightarrow 0.64$.

result of contributions from thermal stress. One sees that generally the same behavior is observed, albeit at lower pressure. The final structure obtained after equilibration is the β-Sn structure with c/a ratio 0.54. This is fairly close to the optimal value obtained from the present *ab initio* calculations (0.55) and other reported values.[2,3]

VI. ACTIVATION BARRIER AGAINST HOMOGENEOUS DEFORMATION

The fact that a compression-induced transition of the diamond-cubic structure requires considerable pressure implies the existence of an activation barrier along the reaction path of homogeneous deformation. We have determined this barrier using the following method. We prepare a series of intermediate lattice structures which have c/a ratios between the limiting values of $\sqrt{2}$ (diamond-cubic) and 0.524 (β-Sn). (Notice that at equilibrium the β-Sn structure obtained using the Tersoff potential has a c/a ratio of 0.524, while experiments as well as *ab initio* calculations give 0.55.) For each of these lattices we calculate the energy and pressure at several values of atomic volume using the Tersoff potential. The family of energy-pressure relations thus generated are shown in Fig. 7. It can be seen that as c/a decreases from the diamond-cubic value, the energy-pressure curves shift upward in energy, for values up to $c/a = 0.7$, and as c/a decreases beyond that value, the curves shift downward in energy. At $c/a = 0.524$ a crossing occurs with the curve for the diamond-cubic structure at a pressure of about 12.7 GPa. Qualitatively, the same behavior is obtained from the *ab initio* calculations as can be seen in Fig. 8. The pressure at which crossing takes place is about 7.8 GPa. The activation barrier in the sense of homogeneous deformation along a reaction coordinate identified with the c/a ratio can be displayed explicitly by converting the results of Fig. 7 to energy variations with c/a ratio at fixed pressures. This is shown in Figs. 9 and 10. The barrier height, 0.6 (Tersoff) and 0.35 (*ab initio*) eV/atom at zero pressure, is seen to decrease with increasing pressure and vanishes at around 80 (Tersoff) and 60 (*ab initio*) GPa. Recall from Sec. IV that the transition pressure given by elastic stability criteria at zero temperature is 105 GPa (Tersoff). The activation energies at the critical pressures obtained according to thermodynamics are about 0.3 (Tersoff) and 0.2 (*ab initio*) eV/atom.

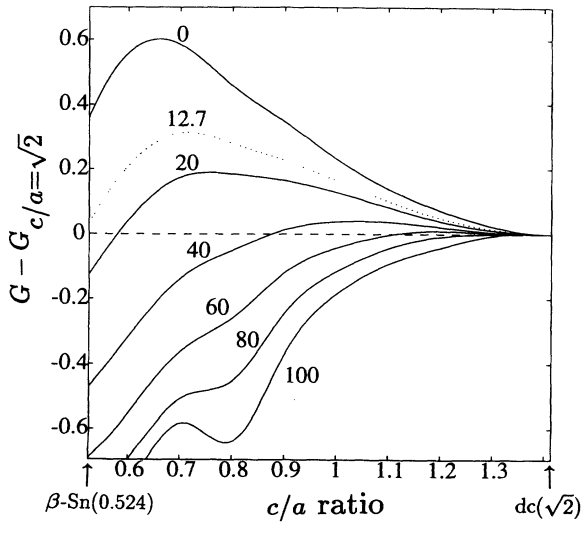

FIG. 9. Curves of free energy at 0 K along a reaction path of homogeneous deformation based on the results of Fig. 7. Numbers denote pressures in GPa.

VII. GRUNEISEN RELATIONS

In addition to the stability analysis, Gruneisen relations were examined at zero temperature by using the Tersoff potential. Figure 11 shows the variations of phonon frequencies at 0 K. It is observed that only the transverse acoustic mode softens under pressure while others stiffen. This demonstrates that the transverse acoustic mode is a pressure-sensitive soft phonon mode, most likely associated with the phase transition from the diamond-cubic structure to the β-Sn structure. The frequency of the transverse acoustic mode vanishes at a pressure of 102 GPa. This pressure limit of vibrational stability is almost the same as that obtained by the B analysis.

VIII. DISCUSSION AND CONCLUSIONS

In this work, we have studied the structural response of diamond-cubic Si to hydrostatic compression from the standpoint of stability analysis and direct MD simulation. These two approaches give consistent results which show that a pressure considerably higher than that predicted by the thermodynamic criterion is required to induce the transition from diamond-cubic to β-Sn structure in defect-free crystals. This apparent conflict can be explained by noting the difference between a transition proceeding along a specific reaction path (in the present

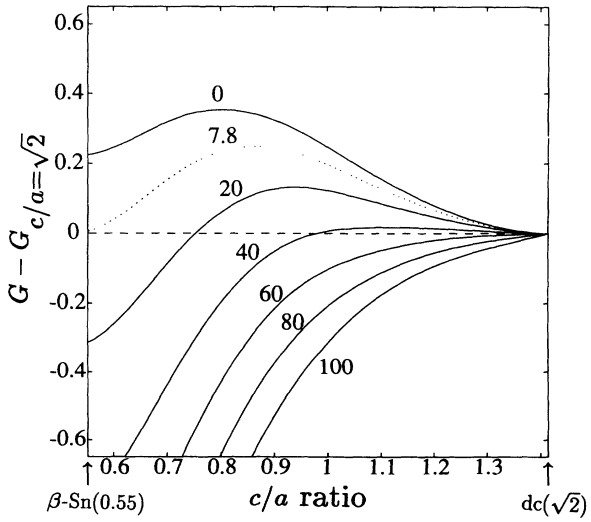

FIG. 10. Same as Fig. 9, obtained by *ab initio* calculation.

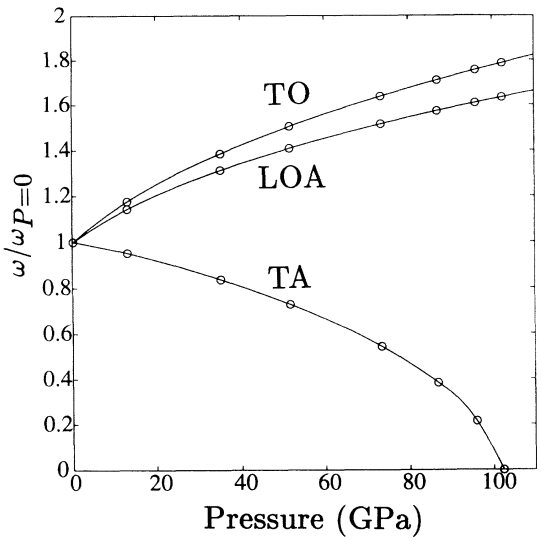

FIG. 11. Variations of phonon modes with pressure as calculated using Tersoff potential at zero temperature.

context a homogeneous deformation), and a transition based on equality of free energies without specification of reaction path. Indeed, one may interpret the free-energy criterion as the statement that the two structures may coexist at the transition pressure where the thermodynamic driving force vanishes. Given this distinction, it follows that the path of homogeneous deformation should give the *upper limit* of the transition pressure because what is violated is the ideal or intrinsic lattice stability. In contrast, the thermodynamic prediction should represent the *lower limit* because no kinetic constraints of any kind are taken into account. Concerning the experimental observations[1,2] we believe the presence of any lattice defect will generally promote the transition by local symmetry breaking and stress concentration. Thus, the experimentally observed pressure should be close to the estimated lower limit.

In order to provide concrete evidence for the above conjecture, extensive simulations that include a variety of point or extended defects are necessary. In light of the fact that very little is known about the atomistic nature of the transformation, the effect of every possible defect must, in principle, be analyzed. Simulations of this nature are prohibitively time consuming and are not a viable alternative at present. In their place we offer a plausibility argument, based on the observation that the present contrast between the thermodynamic and mechanical basis of the structural transition is analogous to crystal melting where a similar distinction has been established. Molecular-dynamics simulations[18,19] of isobaric heating (at zero pressure) of diamond-cubic Si have shown that a perfect single crystal with periodic boundary conditions could be superheated well past the melting point T_m, predicted for the potential model employed on the basis of free-energy calculations.[20] The lattice finally collapsed in a homogeneous manner at a temperature T_s. In contrast, when an interface was introduced, such as a free surface or a grain boundary, melting would nucleate at the interface at temperatures between T_m and T_s, and the melt-crystal interface would propagate into the bulk region. By measuring several such propagation velocities and extrapolating to zero velocity one obtained a temperature close in value to T_m.[18] These results demonstrate that there exist two kinds of melting transitions: One is a thermodynamic process, based on equality of free energies, which is heterogeneous and, therefore, can be suppressed in the absence of a nucleation site; the other is a homogenous mechanical process that is brought about by an elastic instability, thus defining the limit of metastability.[7,21]

Finally, we note that our results have revealed a striking qualitative difference between the recently formulated stability analysis based on elastic stiffness coefficients, the B analysis in Sec. IV, and the conventional approach based on elastic constants.[14] In the case of hydrostatic compression, the former has provided an explanation of the transition that is directly observed by simulation, whereas the latter would predict no instability at any compression.

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