

Application of the Wolf damped Coulomb method to simulations of SiC

Y. Ma and S. H. Garofalini

Interfacial Molecular Science Laboratory, Department of Materials Science and Engineering, Rutgers University, Piscataway, New Jersey 08854

(Received 22 November 2004; accepted 21 December 2004; published online 2 March 2005)

A multibody interatomic potential is developed for bulk SiC using a modification of the Wolf *et al.* summation technique [D. Wolf, P. Keblinski, S. R. Phillpot, and J. Eggebrecht, *J. Chem. Phys.* **110**, 8254 (1999)] for the electrostatic interaction. The technique is modified to account for the short-range nonpoint charge effect. The nonelectrostatic interaction is modeled by a simple Morse-stretch term. This potential is then applied to β -SiC to calculate various bulk properties using molecular dynamics simulations. The simulated x-ray diffraction pattern, radial distribution functions, lattice constant, elastic constants, and defect energy agree well with experimental data. © 2005 American Institute of Physics. [DOI: 10.1063/1.1858860]

I. INTRODUCTION

Silicon carbide has long been a subject of intense research because of its great technological importance in semiconducting devices and structural ceramics.^{1,2} To understand its properties at microscopic level, atomistic simulation techniques have been widely used. Different computational models have been developed to describe bulk, surface, and defect properties of silicon carbide, including the most computationally expensive *ab initio* calculations.³ Recently, Zhao and Bagayoko calculated the electronic structure and charge transfer in both 3C and 4H SiC under the framework of local density functional theory.⁴ Rulis, Ching, and Kohyama studied the grain boundary in β -SiC.⁵ Although their results are generally very close to experimental observation (depending on basis set), one obvious drawback of such calculations is the high computational cost.

Classical simulations, on the other hand, are simpler, much less computationally demanding and yet still a powerful tool to study atomistic behavior with reasonable force fields. In this method, an empirical potential is used to describe the interactions between atoms. By appropriate parametrization of the potential function, one would be able to calculate and predict various properties of the model system with reasonable accuracy.⁶ One of those empirical potentials which is suitable for describing SiC is due to Tersoff,⁷ who constructed a multibody potential based on the concept of bond order, which has proved quite useful. The Tersoff potential and its later modification by Tang and Yip⁸ have proved to be able to describe some of the thermal and mechanical properties of SiC accurately.^{2,7-9} One of the drawbacks of Tersoff potential is that it is only suitable for highly covalent systems such as Si, C, SiC, and so on, so the transferability of this model is limited. On the other hand, even in a highly covalent system like SiC, the Si-C bond is still partially ionic. Recent *ab initio* calculations suggest that electrons are transferred from C atom to Si atom, although the magnitude of charge transfer in the different calculations ranges from $0.9e$ per atom to $1.4e$ per atom.^{4,5} Thus the system is subjected to an electrostatic field, which is missing

in Tersoff potential. The purpose of this paper is to present a simple multibody potential and its application to β -SiC. The major difference between ours and the Tersoff potential is that our potential takes into account the electrostatic field by introducing partial charge to Si and C atoms. This potential form can also be transferred to highly ionic systems without any difficulty. Our selection of partial charges on atoms falls within the range observed in the *ab initio* calculations.^{4,5} The details of this potential will be described in the following section. Then the results of model calculation on β -SiC will be presented in Sec. III. All the results are obtained by molecular dynamics simulations, although under different ensembles depending on the specific property considered. We used a $6 \times 6 \times 6$ cubic simulation cell with 1728 atoms in it. Periodic boundary conditions are applied to model a bulk environment. All the calculations are run for 30 000 steps with a time step of 1 fs except for elastic constants calculations, which are run for 100 000 steps. The radial distribution function, lattice constants, elastic constants, expansion, and defect energies were calculated and agree well with experimental values.

II. THEORY AND MODEL

The most critical part in a molecular dynamics (MD) calculation is the interatomic potential, which determines the quality of the simulation. In this work, the interatomic potential consists of a two-body and three-body term and can be written as

$$E^{\text{total}} = E^{(2)} + E^{(3)}. \quad (1)$$

The pair term consists of a partial charge electrostatic interaction and a Morse-stretch term to describe nonelectrostatic interactions such as short-range repulsion, covalent interactions, and so on,

$$E^{(2)} = E^{\text{M-S}} + E^{\text{ele}}, \quad (2)$$

$$E^{\text{M-S}} = \sum_i \sum_{j<i} D_0 \{ \exp[\gamma_0(1 - r_{ij}/R_0)] - 2 \exp[\gamma_0/2(1 - r_{ij}/R_0)] \}, \quad (3)$$

$$E^{\text{ele}} = \sum_i \sum_{j<i} \frac{q_i q_j}{r_{ij}}. \quad (4)$$

The electrostatic summation in Eq. (4) should be treated with great care. Because of the slow convergence of the r^{-1} summation, evaluation of the total electrostatic energy has been a major challenge in condensed matter simulations. The standard Ewald sum technique is the most used to overcome this challenge although its applicability to disordered system has been questioned.^{10,11} Recently, Wolf *et al.* proposed a spherically truncated, pairwise r^{-1} summation and tested it for a few model systems¹⁰ as did others.^{11,12} This method, although mathematically much simpler and computationally more economic, preserves the high accuracy of Ewald sum and can be extended to disordered systems. In this work, the so called Wolf summation will be used to evaluate the electrostatic interaction. After Wolf, the total electrostatic energy can be written as

$$E^{\text{ele}} = \sum_{i=1}^N \sum_{j<i} \left(\frac{q_i q_j \operatorname{erfc}(r_{ij}/\beta)}{r_{ij}} - \lim_{r_{ij} \rightarrow R_c} \left\{ \frac{q_i q_j \operatorname{erfc}(r_{ij}/\beta)}{r_{ij}} \right\} - \left(\frac{\operatorname{erfc}(R_c/\beta)}{2R_c} + \frac{1}{\beta\pi^{1/2}} \right) \sum_{i=1}^N q_i^2 \right). \quad (5)$$

In the above equation, R_c is the cutoff distance and β is a parameter that determines the speed of the convergence of the summation. For detailed discussion on how to choose β and R_c , see Refs. 10–12.

A problem with Wolf summation one should note is that the use of r^{-1} summation is questionable. For long range interaction where the point charge assumption is valid, the interaction can certainly be described by Eq. (4). However, when dealing with interactions between atoms at or less than bonding distance, the r^{-1} summation is no longer valid because of the diffuse distribution of charges on atoms, where point the charge approximation is obviously invalid. One way to calculate this short-range electrostatic interaction is to evaluate the overlap integral between two atoms. It is rather cumbersome except for simple Slater orbitals. A simpler, empirical functional form also exists in literature to mimic the overlap integral.¹³ In this method, the short-range r^{-1} interaction is substituted by an empirical function as shown in Eq. (6), where γ is a parameter to be determined. We refer to this as “effective R ” hereafter in this paper:

$$\frac{q_i q_j}{r_{ij}} \rightarrow \frac{q_i q_j}{\left[r_{ij}^3 + \left(\frac{1}{\gamma_{ij}} \right)^3 \right]^{1/3}} = \frac{q_i q_j}{r_{\text{eff}}}. \quad (6)$$

For long interatomic distance, effective R summation approaches the normal r^{-1} summation. Thus for computational

simplicity, r^{-1} is substituted back into the summation at long interatomic distance. We use the same cutoff distance as in Eq. (5) to distinguish the short and long range coulombic summation. Thus Eq. (4) is now

$$E^{\text{ele}} = \sum_i \sum_{j<i} \frac{q_i q_j}{r_{\text{eff}}} + \sum_i \sum_{j<i} \frac{q_i q_j}{r_{ij}}. \quad (7)$$

The first term in Eq. (7) is a finite summation within the cutoff distance and can be evaluated explicitly; the second term is an infinite summation and in order to utilize the Wolf summation, we first add and then subtract a same term in Eq. (7):

$$E^{\text{ele}} = \sum_i \sum_{j<i} \frac{q_i q_j}{r_{\text{eff}}} + \sum_i \sum_{j<i} \frac{q_i q_j}{r_{ij}} + \sum_i \sum_{j<i} \frac{q_i q_j}{r_{ij}} - \sum_i \sum_{j<i} \frac{q_i q_j}{r_{ij}}. \quad (8)$$

Obviously, the first and last term in the above summation can be evaluated explicitly; the second and third term can be combined to use the Wolf summation given in Eq. (5). Also note that to avoid any discontinuities in the energy and its derivatives at the cutoff distance, we shifted Eq. (8) the same way as described in Ref. 10. The total electrostatic energy for a system with effective R can be written as

$$E^{\text{ele}} = \frac{1}{2} \sum_{i=1}^N \sum_{j \neq i} \left(\frac{q_i q_j}{r_{\text{eff}}} - \frac{q_i q_j}{r_{ij}} - \lim_{r_{ij} \rightarrow R_c} \left\{ \frac{q_i q_j}{r_{\text{eff}}} - \frac{q_i q_j}{r_{ij}} \right\} \right) + \frac{1}{2} \sum_{i=1}^N \sum_{j \neq i} \left(\frac{q_i q_j \operatorname{erfc}(r_{ij}/\beta)}{r_{ij}} - \lim_{r_{ij} \rightarrow R_c} \left\{ \frac{q_i q_j \operatorname{erfc}(r_{ij}/\beta)}{r_{ij}} \right\} \right) - \left(\frac{\operatorname{erfc}(R_c/\beta)}{2R_c} + \frac{1}{2R_{\text{effc}}} - \frac{1}{2R_c} + \frac{1}{\beta\pi^{1/2}} \right) \sum_{i=1}^N q_i^2. \quad (9)$$

The forces between any two atoms can then be written as

$$f_{ij} = \sum_{j \neq i} \left[q_i q_j \left(\frac{r_{ij}^2}{r_{\text{eff}}^4} - \frac{1}{r_{ij}^2} + \frac{\operatorname{erfc}(r_{ij}/\beta)}{r_{ij}^2} + \frac{2}{\beta\pi^{1/2}} \frac{\exp(-r_{ij}^2/\beta^2)}{r_{ij}} \right) - \left(\frac{R_c^2}{r_{\text{effc}}^4} - \frac{1}{R_c^2} + \frac{\operatorname{erfc}(R_c/\beta)}{R_c^2} + \frac{2}{\beta\pi^{1/2}} \frac{\exp(-R_c^2/\beta^2)}{R_c} \right) \right], \quad (10)$$

where r_{effc} refers to the limit of r_{eff} when r_{ij} approaches R_c .

The energy and force in Eqs. (9) and (10) are not quite consistent with each other since the energy is not the correct integral of the force. Thus a system governed by them does not conserve total energy.¹⁰ Although energy conservation is

TABLE I. Parameters for two-body interaction. $R_c=12.0 \times 10^{-8}$ cm, $q_{\text{Si}}=1.0$, $q_{\text{C}}=-1.0$.

	D_0 ($\times 10^{-12}$ ergs)	γ_0	R_0 ($\times 10^{-8}$ cm)	β ($\times 10^{-8}$ cm)	γ_{ij} ($\times 10^8$ cm $^{-1}$)
Si-Si	0.025	11.2	4.16	4.8	0.5282
Si-C	3.72	6.85	1.865	4.8	0.4879
C-C	0.023	11.2	4.16	4.8	0.4508

broken, by choosing a large enough R_c , we could be able to make the forces arbitrarily close to “true” Coulombic forces.¹⁰ In practice, we found that the energy is conserved fairly well. For MD runs under the microcanonical ensemble (N - V - E), we observed a small downward energy drift less than 0.0001 eV/molecule/ps, which is acceptable in MD simulations. Other runs were done using N - p - T simulations.

The three-body potential is adopted from the Stillinger-Weber¹⁴ potential which was originally designed for Si, but which was used by Feuston and Garofalini to describe the interactions in the more ionic vitreous silica.¹⁵ Since the tetrahedral angle in SiC is the same as that in silica, this potential is also suitable to study the SiC system. In short, it can be written as

$$E^{(3)}(r_{ij}, r_{ik}, r_{jk}) = \left[\lambda_{ijk} \exp\left(\frac{\gamma_{ij}}{r_{ij} - r_i^c} + \frac{\gamma_{ik}}{r_{ik} - r_i^c}\right) \times \left(\cos \theta_{jik} + \frac{1}{3}\right)^2 \right], \quad (11)$$

where i is the central atom with nearest neighbors j and k , and θ_{jik} is the angle between r_{ij} and r_{ik} with the vertex at i .

The two-body potential parameters are listed in Table I, while all three-body potential parameters are listed in Table II.

III. RESULTS AND DISCUSSION

A. Structure of β -SiC at 300 K

The x-ray diffraction pattern of a N - p - T zero pressure β -SiC crystal at 300 K was calculated and is shown in Fig. 1, along with that of a perfect crystal. There is no discernible change in the peak positions from that of a perfect crystal, as our calculated lattice constant at 300 K (4.346 Å) is only slightly smaller than the experimental value [4.3596 Å (Ref. 16)]. Also, Fig. 2 shows the radial distribution function at 300 K which gives a first neighbor Si-C distance of 1.88 Å, in close agreement with experimental value 1.887 Å.

B. Elastic constants

The stability of a crystal under no external stress is governed by its elastic constants. The calculation of elastic constants provided a good test of the interatomic potential. Sev-

eral methods exist in the literature to calculate the elastic constants for a crystal at finite temperature.^{17,18} In this paper, we use the so called fluctuation formula¹⁸ to calculate elastic constants of β -SiC. We have derived the fluctuation formulas for our potential and calculated the zero stress isothermal elastic constants of β -SiC up to 1500 K. For these calculations, molecular dynamics simulations were performed for 100 000 steps (100 ps). The reason why we run for such a long time is due to the poor convergence behavior of C44. As mentioned in the literature, the internal strain relaxation between Si and C sublattices is responsible for the large fluctuations in C44 while it does not affect C11 and C12 by symmetry.² In our simulation, the fluctuation term of C11 and C12 are much smaller than that of C44. Thus we would be able to get the desired convergence in less than 30 000 steps (30 ps) for C11 and C12. For C44, even though we run for 100 000 steps, the fluctuation is still very high compared to that of C11 and C12. The comparison of fluctuation terms of C11, C12, and C44 for a calculation at 300 K is shown in Fig. 3. Note that we could have stopped our simulation around 50 ps to get a result with similar accuracy.

To ensure that the crystal is under zero stress, we start our simulation based on the structure obtained by constant pressure runs described above. During the simulation, the atom velocities are rescaled to generate the canonical ensemble at the desired temperature. By this method, the elastic constants of β -SiC from 100 to 1500 K were calculated. Although the experimental elastic constants at high temperature are not available, our calculation showed that at 300 K, the calculated results agree well with experimental values. The results at 300 K are summarized in Table III, along with experimental values and those calculated by a modified Tersoff Potential.⁸ The temperature dependence of the elastic constants is shown in Fig. 4. For the temperature range in our study, we observed the expected thermal softening behavior of the elastic constants. Also note that C11 and C44 decrease

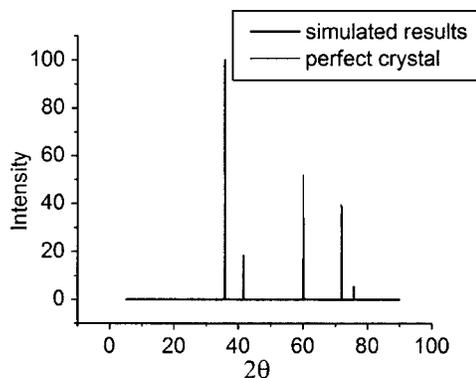


FIG. 1. XRD pattern of simulated and perfect crystal.

TABLE II. Parameters for three-body interaction.

	r_i^c ($\times 10^{-8}$ cm)	λ ($\times 10^{-10}$ ergs)	γ ($\times 10^{-8}$ cm)
C-Si-C	2.85	5.5	2.3
Si-C-Si	2.85	5.5	2.3

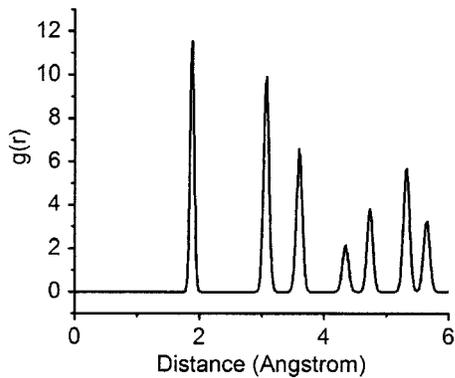


FIG. 2. Simulated radial distribution function.

with temperature at much higher rate than C12, which is consistent with the calculation by Tang and Yip.⁸

C. Thermal expansion

The lattice constant of β -SiC up to 1500 K at zero pressure was also calculated. A constant pressure molecular dynamics simulation is carried out at each temperature to de-

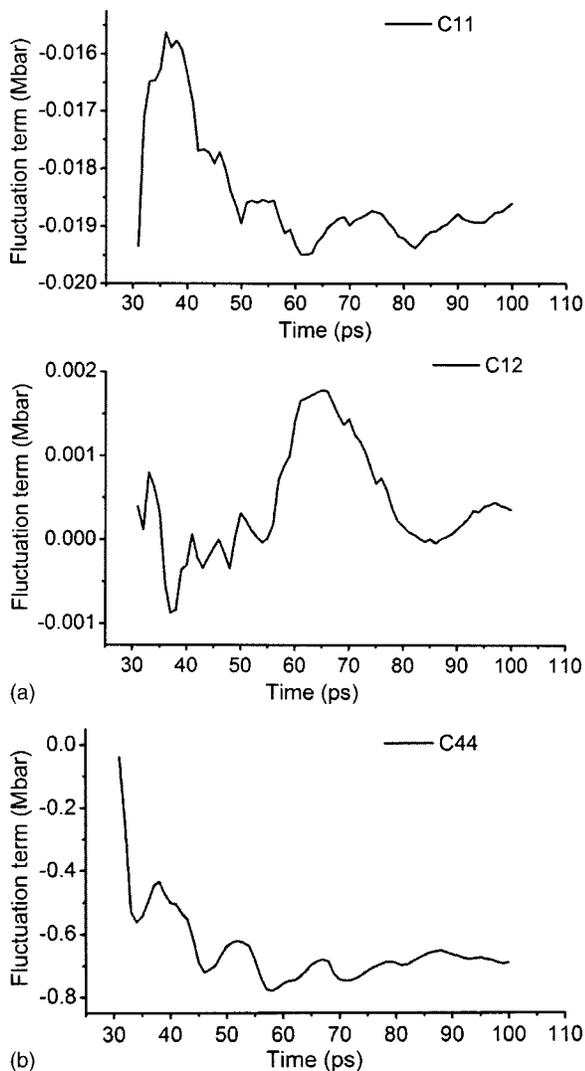


FIG. 3. Comparison of fluctuation term of C11, C12, and C44. Notice that a much larger scale for fluctuation term was used in C44.

TABLE III. Comparison of elastic constants calculated in this work, modified Tersoff potential (Ref. 8), and experimental values.

(Mbar)	This work	Modified Tersoff potential ^a	Expt. values
C11	4.32	4.2	3.90 ^b
C12	1.46	1.2	1.42 ^b
C44	2.44	2.55	2.56 ^b
B	2.41	2.2	2.50 ^c

^aReference 8.

^bReference 3.

^cReference 20.

termine the equilibrium lattice constant at zero pressure. The calculated results and experimental values are given in Fig. 5. Although our results are numerically close to the experimental data, our calculation failed to predict the temperature variance of linear thermal expansion coefficient. In the whole temperature regime, simulated lattice constants vary linearly with temperature. We fitted our data to a third-order polynomial function of temperature giving

$$a(\text{nm}) = 0.43347 + 3.31326 \times 10^{-6}T + 7.247 \times 10^{-10}T^2 - 1.7806 \times 10^{-13}T^3,$$

the linear thermal expansion coefficient is then given by

$$\begin{aligned} \text{Coefficient of thermal expansion} &= (1/a)(da/dT) \\ &= 7.6 \times 10^{-6} \text{ K}^{-1}. \end{aligned}$$

Experiments showed that the coefficient of thermal expansion starts at around $0.3 \times 10^{-6} \text{ K}^{-1}$ at 100 K and increases to $4.5 \times 10^{-6} \text{ K}^{-1}$ at around 500 K and finally reaches $5.5 \times 10^{-6} \text{ K}^{-1}$ at 1500 K.¹⁶

Although our data do not fit perfectly with experiments, especially for the temperature from 100 to 500 K, their accuracy is still noticeable considering that our parameters are fitted only for optimized elastic constants.

D. Defect energy

As a final test of this potential, the vacancy formation energy has been calculated. A pair of Si and C atoms has been eliminated from their equilibrium position and thus two vacancy sites are formed, while maintaining the charge neu-

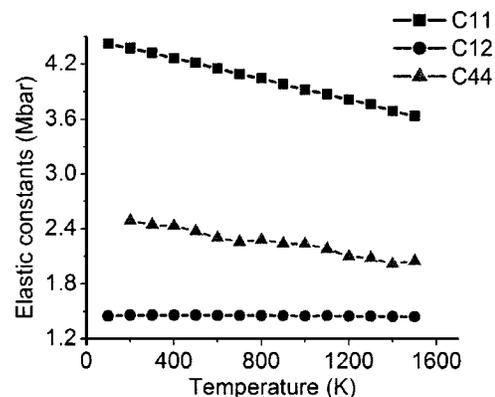


FIG. 4. Temperature variance of elastic constants.

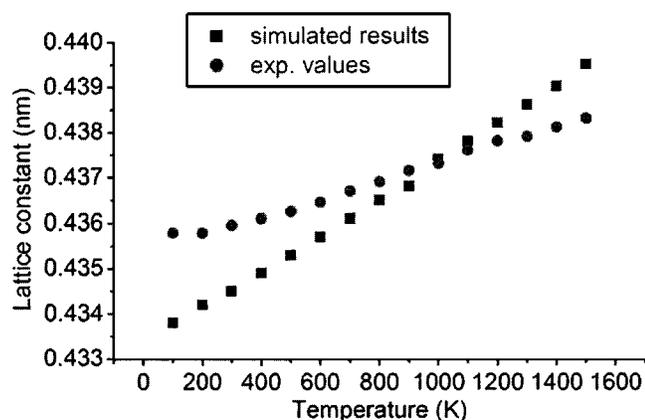


FIG. 5. Temperature variance of lattice constant.

trality of the system. Then the lattice is allowed to relax. The resulting energy is 14.22 eV, compared to 12.7 eV by local-density approximation calculation¹⁹ and 7.4 eV by original Tersoff potential.⁷

IV. CONCLUSION

In this paper, we present the application of the Wolf-Coulomb-summation method with a short-range overlap correction in molecular dynamics simulations of β -SiC using a simple many-body potential. The potential was developed using the structure and elastic constants of β -SiC, with the thermal expansion and defect energies being predicted. Our simulated results are generally very close to experimental data. Although a couple of other potentials exist for describing SiC, our potential is computationally easier to use, with little compromise on accuracy in bulk properties. Another benefit is that the same potential form has been used in simulations of more ionic systems, such as silica and silicates, enabling use of this potential in oxidation studies of SiC.

ACKNOWLEDGMENTS

The authors acknowledge support from the NSF, Award No. DMR-0010062 in collaboration with the NANOAM project of EU-CORDIS (Grant No. G5RD-CT-2001-00586).

¹*Silicon Carbide—1973*, edited by R. C. Marshall, J. W. J. Faust, and C. E. Ryan (University of South Carolina, Columbia, 1974); *Silicon Carbide, a High Temperature Semiconductor*, Proceedings of the Conference on Silicon Carbide, edited by J. R. O'Connor and J. Smiltens (Pergamon, New York, 1960).

²M. Tang, Ph.D. thesis, Massachusetts Institute of Technology, 1995.

³W. R. L. Lambrecht, B. Segall, M. Methfessel, and M. van Schilfgaarde, *Phys. Rev. B* **44**, 3685 (1991); V. Y. Aristov, P. Soukiassian, A. Catellani, R. Di Felice, and G. Galli, *ibid.* **69**, 245326 (2004); F. Gao, E. J. Bylaska, W. J. Weber, and L. Rene Corrales, *ibid.* **64**, 245208 (2001).

⁴G. L. Zhao and D. Bagayoko, *New J. Phys.* **2**, 16 (2000).

⁵P. Rulis, W.-Y. Ching, and M. Kohyama, *Acta Mater.* **52**, 3009 (2004).

⁶J. Lampinen, R. M. Nieminen, and K. Kaski, *Surf. Sci.* **200**, 101 (1988); E. Pearson, T. Takai, T. Halicioglu, and W. A. Tiller, *J. Cryst. Growth* **70**, 33 (1984).

⁷J. Tersoff, *Phys. Rev. B* **39**, 5566 (1989).

⁸M. Tang and S. Yip, *Phys. Rev. B* **52**, 15150 (1995).

⁹L. J. Porter, J. Li, and S. Yip, *J. Nucl. Mater.* **246**, 53 (1997).

¹⁰D. Wolf, P. Koblinski, S. R. Phillpot, and J. Eggebrecht, *J. Chem. Phys.* **110**, 8254 (1999).

¹¹P. Demontis, S. Spanu, and G. B. Suffritti, *J. Chem. Phys.* **114**, 7980 (2001).

¹²D. Zahn, B. Schilling, and S. M. Kast, *J. Phys. Chem. B* **106**, 10725 (2002).

¹³J. N. Louwen and E. T. C. Vogt, *J. Mol. Catal. A: Chem.* **134**, 63 (1998); K. S. Smirnov and B. van de Graaf, *J. Chem. Soc., Faraday Trans.* **92**, 2475 (1996).

¹⁴F. H. Stillinger and T. A. Weber, *Phys. Rev. B* **31**, 5262 (1985).

¹⁵B. P. Feuston and S. H. Garofalini, *J. Chem. Phys.* **89**, 5818 (1988).

¹⁶A. Taylor and R. M. Jones, in *Silicon Carbide—A high temperature semiconductor*, edited by J. R. O'Connor and J. Smiltens (Pergamon, London, 1960).

¹⁷M. Finnis, *Interatomic Forces in Condensed Matter* (Oxford University Press, New York, 2003); D. C. Wallace, *Thermodynamics of Crystals* (Wiley, New York, 1972).

¹⁸J. R. Ray, *Comput. Phys. Rep.* **8**, 109 (1988).

¹⁹J. Bernholc, A. Antonelli, C. Wang, and R. F. Davis, presented at the 15th International Conference on Defects in Semiconductors, Budapest, Hungary, 1988 (unpublished).

²⁰*Gmelins Handbuch der Anorganischen Chemie*, Silicium, Part B, 8th ed. (Verlag Chemie, Weinheim, 1959).