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"THEORY OF THE ELECTRONIC AND STRUCTURAL PROPERTIES
OF SOLID STATE OXIDES"

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A. SUMMARY OF RESEARCH

This report covers the period of the grant from the initiation date of July 1, 1989 to May 1, 1990.

During this period we have concentrated on oxides which are relevant for electronic materials: oxides of silicon. We have initiated our work with emphasis on this material for several reasons. Silicon is a very well understood material and we have considerable experience with both silicon and silicon dioxide. Oxides of silicon are very important electronic materials used for the passivation of silicon based devices and are of considerable geological interest. Moreover, owing to the small energy differences between polytypes, the structural properties are complex and present formidable challenges to any structural theories.

We have considered several approaches to the structural properties of silicon oxides. One approach is to consider the construction of accurate interatomic potentials. At present, fully quantum mechanical calculations are simply too computationally intensive to be applied to non-crystalline or complex crystalline materials. To begin our study, we developed interatomic potentials for silicon and tested some existing interatomic potentials for silicon dioxide. We hope that by examining the pure phase and then examining the oxide phase we will develop better insights than by starting with the oxide alone.

Silicon provides a good testing ground for the construction of interatomic potentials. A good data base exists from theoretical work on the crystalline phases and small clusters. We have developed a new approach to this problem. Traditionally, interatomic potentials for silicon have been based on geometric perturbations around the ground state structure of diamond. We have chosen a novel approach which focuses on the "chemical" differences between silicon in a metallic phase and a covalent phase. And, we have developed "classical" potentials which mimic the role of dangling bonds by strengthening the back bonds of under-coordinated silicon atoms. With this approach we have been able to handle diverse silicon systems more accurately and faster than any other approach. For example, our work on the silicon clusters has led to the prediction that Si_n with $10 < n < 30$ exhibits an icosahedral growth pattern. This discovery has recently been verified experimentally.

For silicon dioxide, we have examined a new interatomic potential. This potential proposed by a Japanese group (Phys. Rev. Lett. **61**, 869 (1988)) yields dynamically stable phases of silica. We believed on the basis of our silicon work that this potential would not be satisfactory for describing the details of silica polytypes and, specifically, that it would fail to describe the pressure behavior of silica. Indeed, this is the case. We found strong departures from experiment for this interatomic potential. Moreover, we found if we modified the potential to agree with the structural details from experiment, then the compressibility was poorly reproduced.

We are also using a fully quantum mechanical approach to examine oxides of silicon. This approach is based on *ab initio* pseudopotentials and a total energy methods. This approach will allow us to predict the properties of silicon dioxide with no adjustable parameters. We are in the processes of developing new computer codes which will allow us to examine much larger systems more accurately and rapidly than in the past. Our first application of these methods would be to the total energy of silica phases. Moreover, we have developed a new oxygen pseudopotential which we are incorporating into total energy calculations for silica. This potential is more accurate and amenable to plane wave bases than previous work.

Most of the material in this report has been published and can be found in the following papers:

"Chemical Reactivity and Covalent/Metallic Bonding of Si_n^+ ($n=11-25$) Clusters,"
J.R. Chelikowsky and J.C. Phillips, Phys. Rev. Lett. **63**, 1653 (1989).

"Surface and Thermodynamic Interatomic Force Fields for Silicon Clusters and Bulk Phases," J.R. Chelikowsky, and J.C. Phillips, Phys. Rev. **B41**, 5735 (1990).

"Interatomic Potentials and the Structural Properties of Silicon Dioxide Under Pressure," J.R. Chelikowsky, H.E. King Jr., and J. Glinnemann, Phys. Rev. **B41**, xxx (1990).

B. INTERATOMIC POTENTIALS AND THE STRUCTURAL PROPERTIES OF SILICON DIOXIDE

First-principles interatomic potentials based on *ab initio* Hartree Fock self-consistent field calculations have recently been proposed for silicon dioxide. These pairwise potentials yield accurate ambient pressure internal structure parameters and dynamically stable polymorphs for several known forms of silica. We use these potentials to analyze crystallographic data for α -quartz under pressure. We find the potentials do not describe the changes in the internal parameters of α -quartz under pressure. Specifically, the potentials do not give the correct trends for the O-Si-O angles or the c/a ratio. We have included bond bending terms to modify the pairwise potentials. If the angles in question are fit to reproduce the experimental data, then the bulk modulus is in poor agreement with experiment. Our findings reinforce the need for a "covalent" term in the interatomic potential which is not based on quadratic expansions of bond bending and stretching forces.

I. INTRODUCTION

Recently, Tsuneyuki, Tsukada, Aoki and Matsui¹ (TTAM) proposed a new interatomic potential for silica. They used Hartree-Fock self-consistent-field calculations to examine clusters of SiO_2 . From these calculations, they fit *pairwise* interatomic

potentials to the structural energies of large silicon oxide clusters. These potentials were in turn used to examine known polymorphs of silica: α -quartz, α -cristobalite, coesite and stishovite. Using molecular dynamic simulations, TTAM found stable structures at normal pressures and temperatures. This was true despite large differences in the topologies and the densities of the structures considered. Moreover, they could reproduce the equilibrium structural parameters of the silica polymorphs. Earlier studies^{2,3} of silicon dioxide clusters had suggested that interatomic potentials would describe qualitatively, and sometimes quantitatively, the Si-O bond in the solid state. Nonetheless, the TTAM work showed for the first time that dynamic stability in silica polymorphs could be achieved on the basis of simple pairwise potentials.

The use of accurate *pairwise* forces would greatly enhance our ability to use molecular dynamics simulations to describe melting and glass formation of the silica polymorphs.^{4,5} Moreover, there are some recent proposals for high pressure forms of silica which could be examined by accurate pairwise forces⁶. However, SiO_2 has traditionally been viewed as a covalent material.⁷ Tetrahedral units of SiO_4 dominate the structural properties for those structures containing four-fold coordinated silicon, e.g. α -quartz, α -cristobalite and coesite. Therefore, the use of pairwise potentials would not be expected to reproduce angular forces present in SiO_2 , especially the relatively open structures such as found in α -quartz and α -cristobalite. Indeed, other workers^{2,3} have found it necessary to include three body forces in their description of silicas to replicate the ground state structural parameters. Unfortunately, the use of three body forces can greatly complicate the simulations for melting or crystal stability. Hence, the creation of an accurate pairwise potential would be quite useful and have widespread applications.

To explore this issue more thoroughly, we have extended the results of TTAM to the pressure behavior of α -quartz. Specifically, we use their interatomic potential to optimize the structure of α -quartz as a function of pressure and compare the results to recent experiments. Also, we examine possible modifications of their potential which include explicit three-body interactions.

II. INTERATOMIC POTENTIALS

An interatomic potential for silicon dioxide is often based on an ionic model. For such a model, the potential for two interacting species (ij) is given by

$$U_{ij}(R) = q_i q_j / R + g_0 (b_i + b_j) \exp[(a_i + a_j - R)/(b_i + b_j)] - c_i c_j / R^6 \quad (1)$$

where R is the interatomic distance between species (ij), q_i is the charge on the i th species. This is the form used by TTAM (and others). The parameters (a_i , b_i , g_0 , and c_i) may be found in Ref.1. Eq. (1) assumes ionic forces dominate the interatomic interactions. Such a form necessitates the evaluation of Madelung sums, which can increase the computational complexity of the problem.

We will use (1) to examine recent experimental data for the α -quartz structure. For this structure, the crystal energy varies with six structural parameters. If we fix the unit cell volume, then we are left with five parameters to optimize the crystal energy. We chose to vary the parameters: a , u , x , y , and z , as defined by Wyckoff.⁸ The c parameter is then fixed by the unit cell volume. We used a simplex program to vary the parameters and

minimize the crystal energy.

Our results for the equation of state for α -quartz agree very well with TTAM. We consider a Murnaghan equation of state⁹:

$$E(V) - E(V_0) = \frac{B_0 V}{B_0' (B_0' - 1)} \left[B_0' \left(1 - \frac{V_0}{V} \right) - \left(\frac{V_0}{V} \right)^{B_0'} - 1 \right] \quad (2)$$

where $E(V_0)$ is the crystal energy, B_0 is the bulk modulus, B_0' is the pressure derivative of the bulk modulus and V_0 is the volume, all taken at equilibrium. In Table I, we compare our results to the previous work. Generally, the equation of state parameters agree quite well. The equilibrium volume is larger than experiment¹⁰ by about 6%. The bulk modulus is nearly in exact agreement with experiment. The crystal energy is the energy to separate the crystal into the separate ions. (This presents some conceptual issues for O^{2-} which is unbound in free space.) We have considered a variety of initial conditions for our structural parameters and are confident that our structure is a global and not a local minimum.

We have also checked the TTAM potential results against two other structures: the calcium fluorite and the rutile structures. We find that α -quartz is lower in energy by about 50 kcal per molecular unit than the calcium fluorite structure. This is a surprising result as one might have expected the calcium fluorite structure to be favored by pairwise forces. We suspect that the anion-anion repulsion term is so large as to favor the α -quartz structure over the fluorite structure. However, the total energy of the optimized rutile structure is within ~ 1 kcal of the α -quartz structure. Within computational uncertainty it is indistinguishable from quartz. Our results are in agreement with TTAM who point out

their potential may not describe crystal energies between different polymorphs. We speculate that the differences may worsen as a function of pressure since the structural properties were fixed at ambient pressures.

III. α -QUARTZ UNDER PRESSURE

Pressure measurements can provide a stringent test for interatomic potentials. For example, charge transfer between Si and O may occur with pressure. Moreover, we expect changes in the bonding hybridization between Si and O. Such bonding changes are difficult to reproduce with a classical potential. For example, only recently has it been possible to reproduce accurately the pressure behavior of elemental silicon¹¹. It was necessary for Si to include explicitly the coordination dependence of the silicon potential and to use an angular dependent interaction term which is modeled on the "covalent->metallic" transition in silicon.

One advantage we have in this study is an accurate description of structural changes as a function of pressure. Previous pressure work on SiO₂ has been carried by Levien *et al.* and Hazen *et al.*¹⁰. However, their results were limited in pressure range and accuracy. We compare to the recent work of Glinnemann *et al.*¹² who made measurements to 10.2 GPa. The measurements of Glinnemann *et al.* were made on a small single crystal sample enclosed in a diamond anvil cell. The cell design and equi-inclination X-ray scattering geometry allowed higher pressures while maintaining high precision. The conventional crystallographic quality factors (R's) obtained from the least squares structural refinements were approximately 2.5%. Consequently, the bond angles and distances are well

determined.

IV. COMPARISON BETWEEN EXPERIMENT AND THEORY

Using the the TTAM potential, we attempted to reproduce the Glinneimann *et al.* data.

To illustrate the behavior of α -quartz under pressure, we have considered four fiducial structural features: the c/a ratio, the average bond length of Si-O, the Si-O-Si bond angle and the O-Si-O bond angles. There are four distinct O-Si-O angles near the tetrahedral angle of 109.5° . Intuitively, the O-Si-O angle is expected to be "stiff" compared to the Si-O-Si angle. This condition would account for most polytypes of silica being based on the tetrahedral unit of SiO_4 .

In Figure 1, we show the c/a ratio as measured and as predicted by the TTAM potential. The experimental trend appears linear over the entire pressure range considered. The TTAM potential predicted a strongly quadratic behavior. In Figure 2, we examine the average Si-O bond length. Again, the TTAM potential yields the correct trend, but not the quantitative features. The bulk modulus change is reproduced accurately, but not the bond lengths. Therefore, we expect the angular features to be poorly reproduced. This is not the case for the Si-O-Si angle. The angle is too large at zero pressure compared to experiment, but the change with pressure is well replicated by the theory. This is shown in Figure 3.

In Figure 4, we display the O-Si-O bond angles as measured and predicted as a

function of pressure. The pressure behavior of these angles will provide a strong challenge to any pairwise force. The spread from the largest to smallest angle is semi-quantitatively reproduced by the TTAM potential, but the details are poorly reproduced. While it is true that the variation in angle is small, it is also true that subtle variations play a crucial role in differentiating the various polytypes of silica.¹³

To examine this feature in more detail, we considered the inclusion of non-pairwise forces, i.e. bond bending forces. These forces in their simplest form can be written as

$$E_{\text{bond-bending}} = \alpha \sum_{\text{Si-O-Si}} (\theta_{\text{Si-O-Si}} - \theta_{\text{Si-O-Si}}^0)^2 + \beta \sum_{\text{O-Si-O}} (\theta_{\text{O-Si-O}} - \theta_{\text{O-Si-O}}^0)^2 \quad (3)$$

where $\theta_{\text{Si-O-Si}}$ and $\theta_{\text{O-Si-O}}$ correspond to the equilibrium Si-O-Si and O-Si-O bonds. We take the equilibrium angles for the constant angles in (3) as $\theta_{\text{Si-O-Si}}^0 = 144^\circ$ and $\theta_{\text{O-Si-O}}^0 = 109.5^\circ$. Lasaga and Gibbs² have used this type of bond-bending interaction where (α, β) are fit to quantum chemistry calculations. Since the TTAM potential is not identical to the Lasaga-Gibbs potential, we have adjusted (α, β) to fit the pressure data.

We find that it is possible to adjust the two parameters (α, β) to reproduce qualitatively the experimental results for the complex O-Si-O bonding angles. This is shown in Figure 5 where we illustrate the O-Si-O angles as a function of *volume*. The values we find for (α, β) are larger than those suggested by Lasaga and Gibbs, i.e. $\alpha \approx 0.02$ Kcal/mole/deg² and $\beta \approx 0.08$ Kcal/mole/deg². This results in a "stiffer" lattice.

We find that the first term in Eq. (3) will improve the agreement at the equilibrium volume. Specifically, the TTAM potential yields angles for the O-Si-O angles which

deviate noticeably from the ideal tetrahedral angle. The first term in (3) reduces such deviations. The second term in (3) improves the angular dispersion with pressure. This suggests that the key term in controlling the pressure behavior is the "stiffness" of the Si-O-Si bond. However, this procedure has a serious flaw. Namely, the terms in (3) can only "stiffen" the crystal as they are positive definite terms. After adjusting (α, β) to reproduce the angular terms, we find that the bulk modulus is nearly 1.9 Mbar or about a factor of 4 to 5 too large compared to experiment.

It is likely that the key issue here involves a subtle interplay involving the O-O repulsive interaction, i.e. the $q_i q_j / R$ term where (i, j) refer to the oxygen ion. This term is important in stabilizing the α -quartz structure versus the CaF_2 structure and in controlling the compressibility of silica. By reducing this term, the bulk modulus could be lowered. Conceivably, one could lower the charge on the Si and O ions to lower the bulk modulus and using (3) get an accurate angle dependence. However, in such a situation the relative stability of α -quartz structure versus the CaF_2 structure might suffer.

V. CONCLUSIONS

In summary, it is very significant that the TTAM potential results in dynamically stable structures for known polytypes of silica. As the authors note, the strong Si-O bond is no doubt responsible for this. However, as we have shown, pairwise interactions cannot fully reproduce the properties of silica. Specifically, the details of the internal structural parameters are not well reproduced. This result can be attributed to "covalent forces" which affect the angular interactions.

The TTAM potentials and similar ones have been used to describe structural features of silica polytypes. Given the results of our study it is unclear whether these potentials are accurate enough to provide detailed structural information, especially in comparing one polytype with another. From our work with angular forces, it might appear that one could achieve greater accuracy with the inclusion of simple "bond bending" forces. At present, we feel this is not the best way to proceed. We feel potentials for silica should be made via the route for silicon interatomic potentials¹¹. If we had detailed quantum mechanical calculations for crystalline polymorphs of silicon dioxide, we could then test whether a particular interatomic potential would yield the correct equation of state for a large number of structures.

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TABLE CAPTIONS

Table I. Equation of state and structural parameters for SiO_2 in the α -quartz structure. The theoretical values are from the interatomic potential of Tsuneyuki *et al.*¹ The experimental values are from Levien *et al.*¹⁰ and Glinnemann *et al.*¹². The crystal energy is the energy required to separate the crystal into the constituent charged ions as defined by Eq. (1).

TABLE I.

Property	Theory	Experiment
<u>Equation of state</u>		
Crystal energy (kcal/mole)	-1236.7	-
Cell volume ($\text{\AA}^3$)	121.38	113.59
Bulk Modulus (Mbar)	0.37	0.38(3)
$(\partial B/\partial P)_{P=0}$	3.20	6(2)
<u>Structural Parameters</u>		
c ($\text{\AA}$)	5.56	5.42
a ($\text{\AA}$)	5.02	4.92
u	0.4602	0.4698
x	0.4259	0.4151
y	0.2771	0.2675
z	0.1213	0.1194

FIGURE CAPTIONS

Figure 1. The c/a ratio for α -quartz as a function of pressure from experiment¹² and as predicted by the interatomic potential of Tsuneyuki *et al.*¹

Figure 2. The average bond length for Si-O in α -quartz as a function of pressure from experiment¹² and as predicted by the interatomic potential of Tsuneyuki *et al.*¹

Figure 3. The Si-O-Si angle in α -quartz as a function of pressure from experiment¹² and as predicted by the interatomic potential of Tsuneyuki *et al.*¹

Figure 4. a). The O-Si-O angles in α -quartz as a function of pressure from experiment.¹² There are four distinct O-Si-O angles in α -quartz. An illustration of these angles may be found in Ref. 10.

b). The O-Si-O angles in α -quartz as a function of pressure as predicted by the interatomic potential of Tsuneyuki *et al.*¹ The agreement with experiment is poor.

Figure 5. The O-Si-O angles as a function of *volume*. The angles are from the interatomic potential of Tsuneyuki *et al*¹ as modified by the bond bending forces as indicated in Eq. (3). While the behavior of the angles as a function of pressure is in qualitative agreement with experiment (Fig. 4a), the detailed behavior is not correct. The pressure versus volume curve for this potential yields a bulk modulus for α -quartz which is about 4-5 times larger than experiment.

Fig. 1

Fig. 2

O-Si-O Angle (degrees)

Pressure (GPa)

0-Si-0 Angles (degrees)

C. CHEMICAL REACTIVITY AND BONDING OF SILICON CLUSTERS

Interatomic force fields have been developed to the the equations of state of bulk silicon phases, e.g. diamond, white tin, face centered cubic structures of silicon, and the average coordination number of small silicon clusters. In this work, we applied these potentials to medium size silicon clusters, i.e. Si_n where $n = 11 - 25$. We find the very surprising result that beginning at $n=7$, near $n=13$ and near $n=19$, these clusters follow a pentagonal growth pattern (icosahedral plus associated face capping). Our results are fully consistent with "magic numbers" found in the reaction rates for the addition of C_2H_4 molecules to Si_n^+ clusters. This result is also consistent with recent work for the reaction of H_2O and O_2 to silicon clusters.

Vapor phase clusters of Si_n^+ have been prepared and analyzed for trends in relative abundance¹ and chemical reactivity² for $3 \leq n \leq 60$ or 24, respectively. Magic numbers (extrema) for these properties are observed which presumably reflect differences in cluster structures. Here we show how these magic numbers can be understood based on structures predicted by a thermodynamic classical force field³ developed by us to fit the equations of state of bulk phases⁴ and coordination numbers^{5,6} of small clusters of Si. As we anticipated,³ our classical method becomes quite accurate for $n > 10$. First-principles quantum-mechanical calculations^{5,6} have successfully predicted the structures and properties of Si_n^+ clusters for $n \leq 10$.

Covalent-metallic phase transitions are the key to the functional form used to construct our force field. The analytic details of the force field are the same as those described previously,³ and the values of the parameters have not been changed. The primary reason for the stability of our theory, as compared to the kaleidoscopic variations in analytic detail and parametric values which have characterized almost all other work,⁷⁻¹⁵ is that our treatment of bond-bending forces is physically consistent. We use a novel angular cutoff which means that bond-bending forces are strong only for smaller bond angles, in parallel with the usual radial cutoff, which makes radial forces strong only for nearer neighbors. Moreover, our bond bending angular function is $\cos 3\theta$, not $\cos \theta$, because the former provides the rapid angular variation needed to describe the "phase transition" between metallic ($\theta = 60^\circ$) and covalent ($\theta = 110^\circ$) bonding.

In Fig. 1 we show our results for the bulk phases⁴ of Si. In our previous work³ we fitted our parameters for the bulk energy to the equations of state for the covalent diamond and metallic simple, body-centered and face-centered cubic phases. In this Figure we show in addition the results for the metallic hexagonal close packed and semimetallic β -Sn phases with both our functions and our parameters *unchanged*. The sign and magnitude of the very small fcc-hcp difference agrees very well with the calculation of Chang and Cohen,⁴ also shown in the Figure. This confirms the accuracy of our cutoff functions. Of greater importance to our central theme, the metal-semiconductor transition, is the excellence of the unadjusted fit to the equation of state for β -Sn.

We now turn to the structure of Si_n clusters for $10 \leq n \leq 25$. These were determined by a combination of Monte Carlo and molecular dynamics techniques.^{16,17} The latter has been partially optimized and is now essentially as effective as such simulations^{12,13} using much simpler potentials,⁷ so that our practical upper limit for n is much larger than 25. However, the structures of the clusters with $3 \leq n \leq 23$ already show striking properties which have immediate application to chemical reactivities.

First we show in Fig. 2 the smaller bond-angle distribution for all clusters in the range $3 \leq n \leq 20$. While previous potentials based on $\cos\theta$ were always *designed* to favor tetrahedral angles θ_t (usually trivially through a term in the energy proportional to $(\cos\theta - \cos\theta_t)^2$), there is no such bias in our functions.³ Instead what we see in Fig. 2 is that the smaller bond angles are all concentrated near $\theta = \pi/3$ (close-packing) or near θ_t (tetrahedral packing).

This is what one would have expected from a bond-bending energy dependent on $\cos 3\theta$, but the virtual absence of bond angles near $\pi/2$ reflects, in addition, certain geometrical constraints which one might not have anticipated. These packing constraints in effect amplify the significance of the covalent/metallic distinction.

For $n > 10$ the cluster geometries turn out to be very different from what one might have expected based on the bulk phase diagram, Fig. 1. At $n = 13$ the structure is that of an atom-centered icosahedron. This structure, which can be described as composed of 1-5-1-5-1 layers, is the second element of a pentagonal growth sequence¹⁹ which began with $n=7$ (the bicapped 1-5-1 pentagon) and which leads to the double icosahedron 1-5-1-5-1-5-1 at $n = 19$. Several clusters from this sequence are shown in Fig. 3. Note the regular addition of capping atoms¹⁹ at $n = 14, 15$ or 20 , etc.

The icosahedral-pentagonal growth sequence is well known for two-body central forces¹⁹ appropriate to inert gases, and indeed magic numbers $n = 13, 19$ (23 or 25), ..., 55, etc. have been observed for Xe and other inert gas clusters.¹⁸ However, to generate the phase diagram of Fig. 1, large three-body forces are required as well. Our calculations show that back-bonding forces³ in small clusters can cause a remarkable re-appearance of these simple geometrical structures.

Our model also shows for a wide range of parameters that at $n = 11, 12, 16, 17$ and 18 the clusters do *not* belong to the pentagonal growth sequence but

may instead have layered character similar to that of one of the $n = 10$ isomers⁶ which has a 3-3-3-1 trigonal prismatic structure. For instance, we find $n = 16$ corresponds to 1-6-1-6-2.

We now turn to recent experimental data which apparently vindicate the main features of our results. The size dependence² of the rate constant for the addition of the first C_2H_4 molecule on to Si_n^+ is shown in Fig. 4. Note the non-reactive minima at $n = 13, 19$ and 23 . These correspond to the icosahedron, the face-capped or double icosahedron, and edge-sharing two-face-capped icosahedron. It is clear that uncapped or completely capped icosahedra containing only five-fold coordinated atoms have minimal reactivities, whereas the C_2H_4 molecules will react when there are at least two nearest-neighbor four-fold coordinated ad atoms. Denoting these ad atoms by Si^* , the reactive configuration is apparently the bridge $Si^*-H-CH=CH-H-Si^*$. The C_2H_4 reactivity with one Si^* ad atom is little more than with none.

Our results indicate that in the range $n = 10-20$, the Si_n cluster structures oscillate between metallic pentagonal growth structures and covalent molecular structures. In effect, in this range Si_n clusters are vicinal to a covalent-metallic "phase transition". It may well be that in the addition reaction the covalent molecule C_2H_4 remains intact and reacts strongly only with fully covalent Si_n structures ($n = 10$ and 16) and much more weakly with metallic structures ($n = 13$ and 19). This appears to be a case of 'like prefers like', which often occurs in covalent network structures. This preference originates from the presistence of the covalent energy gap, accompanied by phase-matched occupied

valence orbitals, from the rings of Si_n into interlocking rings including C_2H_4 segments. In earlier days this phenomenon was sometimes described as resonating valence bonds, in which case large capture cross sections near $n = 16$ could also be described as resonant addition.

Our model also yields relative cluster energies and it predicts that $n = 13$ will be especially stable. However, careful studies²⁰ of the effect of ionizing laser energy and intensity on beam distributions have revealed many effects (including cluster fragmentation, which is likely to be especially strong for "metallic" clusters) which preclude inference of relative cluster energies from beam distribution intensities in cases where the ionization energies (here known²⁰ to be ≥ 7 eV) are large. This makes the data shown in Fig. 4 relatively more informative, because the addition reaction is non-destructive.

Until first-principles calculations of medium-size clusters become available, it is difficult to say how accurate our model is in calculating small energy differences between covalent and metallic structures for a given n . We have, however, varied the magnitude of our back-bonding parameters over as much as a factor of 2 and have found that our qualitative conclusions remain unchanged. Thus while our model cannot yet treat these small energy differences, it has achieved the goal expected of a classical model, that is, it generates plausible candidate structures suitable for first-principles calculations. At present (and for the foreseeable future) it appears that the first-principle methods themselves^{5,6} encounter formidable difficulties at just this point. Thus our classical method complements the more fundamental atomic orbital⁵ and

pseudopotential⁶ quantum calculations.

In conclusion we have shown that without any adjustments whatsoever our previously published force field³ gives an excellent fit to the equations of state of two additional crystalline phases. It also predicts very surprising pentagonal growth structures for clusters in the range $n = 13-25$. These structures partially explain magic numbers recently observed experimentally² in the addition reaction of C_2H_4 with Si_n^+ . We believe that these successes demonstrate that we have constructed the first satisfactory classical model for interatomic forces for any element which is not an inert gas.

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FIGURE CAPTIONS

- Fig. 1 We compare our result (below) for the equations of state for crystalline phases of Si with those calculated (above) by first principles methods (ref. 4).
- Fig. 2. Distribution of smaller bond angles in Si_n clusters ($n = 3-20$), as calculated by our method. Note that almost all the bond angles lie either at the metallic ($\theta = 60^\circ$) or covalent ($\theta \geq \theta_c = 110^\circ$) limits.
- Fig. 3. Pentagonal growth clusters for several values of n , as obtained from our model. For $n=15$ the atoms denoted in the text by Si^* are shaded.
- Fig. 4. Rate constants for the addition of the first C_2H_4 to Si_n^+ , as reported in ref. 2 and reproduced here for the reader's convenience.

Fig. 3

D. SURFACE AND THERMODYNAMIC INTERATOMIC FORCE FIELDS FOR SILICON

Interatomic force fields are used to describe the phase stability of crystalline silicon and small clusters of silicon. We show that when three body forces are adjusted to describe covalent versus metallic phase transitions instead of small amplitude atomic vibrations, a simple and accurate force field is obtained. This force field can be easily modified to describe energies and structures of Si_n vapor clusters. A key aspect of the cluster problem is the transfer of bond strength from dangling bonds to back bonds. We expect this potential to have widespread applications to the formation and activation energies for diffusion in crystalline Si and to the structural properties of amorphous and liquid silicon.

I. INTRODUCTION

The determination of the structure of extended nonperiodic systems such as clusters, liquids and amorphous solids is one of the difficult problems in condensed matter physics. For these systems, experimental probes cannot yield complete structural information. Probes for surface structure now exist, e.g. the scanning tunneling microscope, but not for bulk nonperiodic structures or clusters. Current *ab initio* quantum methods have proved to be very useful for predicting the structure of small clusters. However, they are still too cumbersome to handle systems of sufficient size to make useful predictions for amorphous solids or liquids.

It would seem that for large numbers of atoms it should be possible to replace the complete quantum mechanical description by a simpler classical interatomic force field model. Calculations with such a model can be carried out several orders of magnitude more rapidly than is possible with *ab initio* methods. However, at the atomic level our understanding of the quantum-mechanical forces is still in its infancy. While we easily understand the tetrahedral coordination of crystalline Si in terms of hybridized sp^3 orbitals, how can a classical model describe the metallic high-pressure phases of Si, or the Jahn-Teller reconstructions of Si surfaces? Indeed, what can we reasonably expect from classical forces? These questions have recently attracted much interest and have been answered in several ways. Here we present a new approach. We make detailed comparisons of our results both with the best available first-principle calculations and with the results obtained with other classical models. We believe that the present classical method is the only one which has yielded accurate results for both the bulk phase diagram and cluster structural trends.

Before the coming of effective methods to compute the total energy of solids, one had to rely exclusively on an experimental data base of elastic constants and vibrational spectra for silicon in the diamond structure. However, this limited data base has changed dramatically in the last several years. Particularly, the theoretical work of Yin and Cohen on the high pressure phases of silicon¹ has allowed one to have access to accurate information on more general configurations of crystalline silicon. Also, highly sophisticated molecular orbital calculations² exist on Si_n for $n \leq 10$. On the experimental side, measurements on the vapor

phases of Si_n^+ and Ge_n^+ clusters have been reported³ for $2 \leq n \leq 60$. These developments have produced a new battery of data on silicon which encompasses the range from small clusters to many crystalline phases.

The process of transcribing quantum mechanical forces into classical ones is not automatic or routine. It will no doubt be based on intuition instead of an analytic process. Also, considering that quantum forces are nonlinear and nonlocal, we might expect some "non-intuitive" classical forces, e.g. larger three body terms than two body terms.

Several attempts have been made to model the new data bases.⁴⁻¹² However, these models have met with only limited success. For example, when emphasis was placed on bulk phases, the resulting morphology for clusters was not consistent with the quantum chemistry results. Conversely, when emphasis was placed on fitting structural information for silicon clusters, equations of state for the resulting bulk phases were poorly reproduced. These contradictions are easily understood. If "over-coordinated" silicon structures are fit by classical potentials, there is no reason to suppose that "under-coordinated" cluster structures will be accurately reproduced, and vice versa. Most of the early work in this area concentrated in fitting bulk silicon polytypes such as the high pressure phases, e.g. fcc, hcp structures. A fit to such structures may reproduce twelve-fold coordinated silicon, but not two-fold coordinated silicon structures. Generally, when a particular data base is fit, the resulting classical forces seldom prove accurate for regimes not included in the fit.

To ensure that our model has physical content, we demand that it provide accurate descriptions of two extreme systems: small clusters and various crystalline phases. Clusters contain many dangling bonds. We expect large reconstruction energies in the clusters owing to incomplete coordination.² Such reconstructions will be absent in the crystalline systems. These systems primarily are high pressure phases where silicon is over-coordinated.¹ By incorporating both limits in our force field description, we hope to enhance our capacity to describe systems which reside between these regimes. These intermediate cases would include structural defects, liquids and amorphous solids.

II. CRYSTALLINE PHASES OF SILICON: THERMODYNAMIC INTER-ATOMIC FORCE FIELD

A. Defining a Bulk Phase Force Field

Bond-stretching and bond-bending classical force fields (CFF) usually depend on the interatomic vector, $\mathbf{R}_{ij}$, between atoms i and j . These interactions are respectively functions of the magnitude of this vector and the dot product $\mathbf{R}_{ij} \cdot \mathbf{R}_{jk}$. A term involving $\cos(\theta_{ijk})$ commonly appears, where θ_{ijk} is the angle between $\mathbf{R}_{ij}$ and $\mathbf{R}_{jk}$. The key difference between our approach and that of previous CFFs is that we choose our angular function in a physical, rather than a geometrical way. Our function is designed to simulate the free energy change at a metal-semiconductor transition. This transition is expected to be first order. The discontinuous transition involves large changes in the coordination and the conductivity of the silicon phases. For example, a relevant transition may involve converting the open, covalent four-fold diamond structure to a metallic, compact, twelve-fold face centered cubic structure. An energy function which is discontinuous in a macroscopic sense is "S-shaped" on an atomic scale.¹³ The smallest bonding angle θ_{ijk} , in the phases we consider varies from $\pi/3$ in a close packed structure to $2\pi/3$ in graphite. If we use $\cos\theta_{ijk}$ to describe angular forces,⁴⁻¹² we are using a function which is nearly linear in the range of interest. However, if we instead use $\cos 3\theta_{ijk}$, then this function varies rapidly near $\theta_{ijk} = \pi/2$, corresponding to the metal-semiconductor transition, and slowly near $\theta_{ijk} = \pi/3$ (metallic phases) or near $\theta_{ijk} = 2\pi/3$ (semiconducting phases).

While there are obvious advantages to using the physically significant function $\cos 3\theta_{ijk}$ instead of the geometrical function $\cos\theta_{ijk}$, there are disadvantages as well.¹³ The geometrical function is single-valued, but $\cos 3\theta_{ijk}$ is multiple-valued. Thus while $\cos 3\theta_{ijk}$ has the correct qualitative behavior when θ_{ijk} is the smallest bond-angle, if we were to use this function for all bond angles, there would be substantial cancellation of bond-bending energies between bond pairs with larger and smaller bond angles. This unwanted cancellation can be avoided¹³ by imposing an angular cutoff which effectively retains only bond-bending energies for smaller bond angles.

The angular cutoff effectively erases the long-range phase coherence which is characteristic of quantum-mechanical wave functions in favor of short-range interaction energies.

Because we are using a classical force field, we feel that this is logically the only correct procedure. All other attempts⁴⁻¹² to model interatomic forces in Si have used $\cos\theta_{ijk}$ summed over all bond angles (small and large) without an angular cutoff. While on geometrical grounds this approach seems safe enough, as well shall see our quite different approach yields dramatic improvements in the fit to the bulk phase diagram. We believe that the original of this success lies primarily in the fact that our model incorporates the basic physics of the metal-semiconductor transition in an internally self-consistent way. We also believe that this is not possible with $\cos\theta_{ijk}$ because this geometrical factor does not recognize the quantum-mechanical content of the metal-semiconductor transition which occurs between small and large values of the smallest bond angle. Our view is supported by the failure of *many* workers who used $\cos\theta$ to achieve good fits to the bulk phase diagram in spite of the fact that all of them used at least as many (often more) adjustable parameters than we have used.

The explicit expression for our thermodynamic interatomic force fields (TIFF) in the crystalline state is

$$E[\{\mathbf{R}\}] = \sum_{i,j \text{ } i \neq j} [A \exp(-\beta_1 R_{ij}^2)/R_{ij}^2 - g_{ij} \exp(-\beta_2 R_{ij}^2)/R_{ij}] \quad (1)$$

where R_{ij} is the interatomic distance between (i,j) and the many body forces are contained within the factor g_{ij} . We wish g_{ij} to be large for covalent systems with large bond angles resulting in a shorter bond length R_{ij} as compare to metallic systems with small bond angles.

We define g_{ij} as

$$g_{ij} = g_0 + g_1 S_{ij} S_{ji} \quad (2)$$

where

$$S_{ij} = 1 + \langle \cos(3\theta_{ijk}) \rangle$$

$$\langle f(\theta_{ijk}) \rangle = [f]/[1]$$

$$[f(\theta_{ijk})] = \sum_{k, k \neq ij} f(\theta_{ijk}) \exp(-\lambda_1 \theta_{ijk}^4) \exp(-\lambda_2 R_{ijk}^4)$$

with $R_{ijk} = (R_{ij} + R_{ik})/2$. This form for f represents a very short range function which has sharp angular and radial cutoffs. The parameters (λ_1, λ_2) are fixed to be $(\lambda_1)^{-1} = (\pi/2)^4$

and $(\lambda_2)^{-1} = R_0^4$ where R_0 is the nearest neighbor distance in the diamond structure. The factor S_{ij} ranges from 0 for metallic systems to 2 for covalent systems. Also, for $\theta_{ijk} < \pi/3$ ($> 2\pi/3$) we saturate $\cos(3\theta_{ijk})$ so that $\cos(3\theta_{ijk}) = -1(+1)$.

The parameters A , β_1 , β_2 , g_0 , and g_1 are determined by fitting the equation of state at $T=0K$ for diamond, simple cubic, body centered cubic and face centered cubic Si structures as calculated by Yin and Cohen.¹ These structures have coordination numbers of 4, 6, 8, and 12, respectively. The equations of state for these structures can be accurately reproduced by the Murnaghan form:¹⁴

$$E(V) = \frac{B_0 V}{B'_0(B'_0 - 1)} \left[B'_0 \left(1 - \frac{V_0}{V} \right) - \left(\left(\frac{V_0}{V} \right)^{B'_0} - 1 \right) \right] + E(V_0) \quad (3)$$

This form requires knowing the equilibrium energy, $E(V_0)$, volume, V_0 , bulk modulus, B_0 , and pressure derivative of the bulk modulus, B'_0 . The data base from Yin and Cohen provides roughly twice the number of points to be fit as parameters. The resulting parameters for our interatomic potential are given in Table I.

B. Bulk Phases of Silicon

Our TIFF results for the equations of state are compared in Figure 1 to Biswas and Hamann's CFF work⁵ and to the Yin-Cohen quantum mechanical calculations.¹ Our TIFF potential does a better job of replicating the quantum mechanical results than does the CFF work. This is true even though the Biswas-Hamann potential requires more parameters, and is more successful in fitting the bulk phase diagram than any of the other $\cos\theta$ models. Specifically, the equilibrium volume and placement of the bcc and fcc phases are reproduced better in our work. We also obtain the correct ordering in energy of the bcc and fcc phases, although the energy difference between these phases is quite small.

In Figure 2, we compare our work to the equations of state calculated by Chang and Cohen.¹⁵ Their work is an extension of the work of Yin and Cohen.¹ In this figure, we have included two additional structures: the white tin structure (β -Sn) and the hexagonal close packed (hcp) structure. We did not fit our potential parameters explicitly to either structure. Nonetheless, the agreement with Chang and Cohen is quite good. In Table II, we summarize the calculated equation of state data and compare to other theories and

systems where $\theta_{ij} \sim 2\pi/3$ we expect large reconstructions. For metallic systems where $\theta_{ij} \sim \pi/2$ we expect much less reconstruction. We describe the back bonding strengthening by the factor:

$$Q_{ij} = 1 + zD_1 \sin[\alpha(\theta_{ij} - \pi/3)] \quad (5)$$

For metallic surfaces where $\theta_{ij} \approx \pi/2$, $Q_{ij} \approx 1$. For crystals,⁵ $Q_{ij} = 1$ as $D_1 = |D_1|$ is zero. D_1 is small in clusters, except for surface atoms. By making clusters more compact, back bonding reduces covalent interactions and increases metallic interactions. To minimize the number of parameters, we assume that for each interaction ij :

$$\Delta g_0/g_0 = -\Delta g_1/g_1 = \mu(Q_{ij}Q_{ij} - 1) \quad (6)$$

The change in (g_0, g_1) vanishes for crystals. We need to determine four back-bonding parameters: z , α , μ , and λ_3 . We used the molecular orbital studies of Raghavachari and Rohlfing² for structural properties and energies of Si_n clusters with $n \leq 10$ to fix our four parameters. The parameters are given in Table IV.

One complication of this procedure is that the quantum chemistry clusters may exhibit Jahn-Teller distortions. Especially for small clusters, these effects may be significant and will break symmetry. We expect the nature of the symmetry breaking to depend on valence electron filling of specific molecular orbitals. Such effects cannot be included in our classical model. However, with increasing cluster size we expect that steric hindrance will reduce Jahn-Teller effects. The structures obtained from our potential should become much more reliable for $n > 10$.

B. Determining Minimum Energy Structures

For elemental crystalline matter, usually only a few lattice parameters are necessary to determine the structure. One can vary these lattice parameters to determine the lowest energy structure. The problem is considerably more complex for clusters. For small clusters, it is possible to construct an inventory of structures and explore each topologically distinct case.² However, the number of possible structures grows so rapidly that this approach becomes impractical for more than about ten atoms.

There are several techniques to minimize a multi-parameter function. We have used both a Monte-Carlo (MC) simulated annealing algorithm and a molecular dynamics (MD)

III. SILICON CLUSTERS: SURFACE INTERATOMIC FORCE FIELD

A. Dangling Bond Corrections to the Bulk Force Field

If we apply our TFF potentials to small silicon clusters, we find the lowest energy structures to be rings for Si_n where $n < 8$. For $n \geq 8$, we find a three dimensional structure where the rings are capped-off. In Figure 3, we illustrate the lowest energy structures for $n \leq 10$. We note for $n=10$ that we obtain the adamantine cage. The adamantine cage can be considered to be a diamond structure fragment. It is noteworthy that we obtain this fragment as it strongly suggests that diamond is the true ground state structure for our bulk silicon potential. For structures larger than $n=10$, we continue to build up "bulk" like fragments of "diamond-like" silicon. In Figure 4, we illustrate typical structures for $n=13, 16$ and 19 . Si_{19} is interesting in that it resembles graphitic rings linked by five-fold rings. Such structural units are expected for covalent networks.

Our results based on the bulk silicon potential are at strong variance with the structures obtained from molecular orbital theory. The quantum chemistry study of silicon clusters by Raghavachari and Rohlfing² yields three dimensional structures for $n > 5$. Moreover, the average coordination of their structures may exceed four (especially for $n > 6$) which is indicative of a metallic structure. The quantum chemistry work is similar to that found by other theoretical methods.²¹ In contrast, the average coordination of the clusters in Figure 3 never exceeds 2.5.

This disagreement between the structures predicted from our bulk phase potential and those predicted by quantum chemistry is not surprising. Structural features which are associated with under-coordinated silicon atoms, i.e. dangling bond features, are not described by our bulk energy. To remedy this omission, we must modify our potentials for under-coordinated species.

Specifically, the transfer of dangling bond strength to back bonds can produce more compact or more metallic structures. This transfer will depend on the angle θ_{ij} between the dangling bond and back bond. Let us define a "dangling bond vector", $\mathbf{D}$, as follows:

$$\mathbf{D}_i = - \sum_{j, j \neq i} \mathbf{R}_{ij} \exp(-\lambda_3 R_{ij}^4) / \sum_{j, j \neq i} \exp(-\lambda_3 R_{ij}^4) \quad (4)$$

We expect that back bonding strengthening will vary with the angle θ_{ij} . For covalent

experiment. For the diamond structure, our calculated values for B_0 , $E(V_0)$ and V_0 are comparable to the best theoretical values.

We find that the hcp structure is $\sim 0.02\text{eV}$ lower than the fcc structure and that its equation of state is almost identical to the bcc equation of state. Chang and Cohen find a similar placement for the hcp structure relative to the fcc structure. They found a c/a ratio of 1.69 which is larger than the ideal ratio, but consistent with experimental values ranging from 1.64 to 1.70. Our potential yields an ideal c/a ratio of 1.63 to within $\sim 1\%$. Also, Chang and Cohen find a larger separation between bcc and hcp than we do. To within $\sim 5\text{meV}$, we find the same equilibrium energy for the bcc and hcp structures. Our accuracy in the fitting is probably $\sim 10\text{meV}$ so we cannot distinguish between bcc and hcp structures.

The β -Sn structure can be considered a "transition structure" from the covalent diamond structure to a metallic structure. The β -Sn coordination is rigorously four-fold, but the two next nearest neighbors are only $\sim 5\%$ more distant. Thus β -Sn can be considered to be six-fold coordinated, or a Jahn-Teller distorted octahedron. Our equilibrium volume for β -Sn is slightly larger than predicted by Chang and Cohen. Otherwise, the equations of state are similar. With respect to our c/a ratio, we find a value of about 0.62 as opposed to the quantum mechanical prediction and experimental¹⁶ value of 0.55. Our larger c/a ratio can be attributed to the angularly dependent energy factor in (3). A larger c/a ratio would produce larger angles, θ_{ijk} , which are closer to the tetrahedral angle. Perhaps a slightly weaker angular dependence would improve the c/a values.

We have examined the stability of the diamond structure versus the β -Sn structure as a function of pressure. We find that at $\sim 140\text{kbar}$ the diamond structure will transform to the β -Sn structure. This value is higher than experiment¹⁶⁻¹⁹ which ranges from 88 to 125 kbar and higher than the quantum mechanical predictions. The value of the transition volume for the diamond and β -Sn structures is quite good. Given that we have not adjusted our parameters to the pressure data, the agreement is surprisingly good and very much better than would be obtained by other currently available interatomic potentials based on $\cos\theta$. In Table III, we summarize our pressure calculations and compare to experiment and other theories.

approach. In the MC method, we begin by randomly placing Si atoms in a cube. Each atom is required to be at least 3.5 Å from its neighbor and from the walls. The cube is heated initially to about 5000 K. We displace each atom in random discrete steps and determine the change in energy, ΔE . If the energy of the cluster is lowered, then the step is accepted. If the energy is raised, the step is accepted with a probability given by $P = \exp(-\Delta E/kT)$. At high temperatures, steps which raise the energy are commonly accepted. As the temperature is lowered, eventually only steps which lower the energy are accepted. Provided the temperature is lowered slowly enough, and provided enough steps are taken, the resulting structure should be a global minimum in terms of the structural energy.

One method of determining the optimal step size is to adjust the step size to maintain a success rate of 50% in the steps taken. We have used an alternative procedure which produces similar results, yet is somewhat easier to implement. We scale the step size so that the maximum step size, $\delta R_{\max}$, is given by $\delta R_{\max}(T) = \delta R_{\max}(T_{\text{initial}})(T/T_{\text{initial}})^{1/2}$. This is the scaling one would expect in a Debye solid. As the cluster condenses into a stable state, one expects that a Taylor series of the energy would not contain terms linear in the atomic coordinates. In this regime, $\Delta E/kT \approx \text{constant}$ and $P \approx \text{constant}$. An acceptance rate of 50% can be maintained as temperature is lowered through a judicious choice of $\delta R_{\max}(T_{\text{initial}})$, which we find is about 0.5 Å. Our annealing scheme employed 100 temperature divisions between T_{initial} and T_{final} , (which was taken to be 100 K.) The temperature anneal schedule is such that for the N th division $T_N = \gamma T_{N-1}$ where $\gamma = 0.96$. For each temperature division, we took 500 steps per particle. The total number of steps was 50,000 per particle with an anneal rate of about 10 MC steps/atom-K. These parameters are similar to ones used in MC work on amorphous silicon.²²

To see whether this annealing process is adequate, we performed two tests. First, we constructed an inventory of all the structures of Si_n examined in molecular orbital calculations.² We then scaled the bond lengths in these structures until a minimum in the energy was achieved. This procedure resulted in an upper bound on the lowest energy structure. Then we used our MC algorithm to determine the structure. If the MC method did not yield a structure with a lower energy, we then annealed more slowly until we

atoms to be coordinated if the distance between atoms is less than a given distance, R_0 . Here we define R_0 to be 3 Å. (We have also defined coordination by a weighting function similar to that in Eq. (4) for D_1 . The results are quite similar.) We also compare to the quantum chemistry work of Raghavachari and Rohlfing.² Clearly, the presence of a back bonding term results in a much improved agreement in compactness between the quantum chemistry structures and those obtained from our interatomic potentials.

We obtain similarly coordinated structure as from the quantum chemistry calculations for silicon clusters for $n \leq 10$; however, the structures often differ in detail. For example, $n=8$ is a bicapped octahedron in both cases. Our interatomic potential yields a structure where adjacent faces are capped. For the quantum chemistry work, opposite faces are capped.

For silicon clusters with $n > 10$, the geometries are very different than one what might have expected based on the bulk phase diagram in Figures 1 and 2. The dominant structural feature in Figure 6 is the icosahedron. This is reflected in Figure 7, where we have an anomalously large average coordination at $n=13$ and $n=19$. These structures correspond to ideal icosahedral structures. For example, the $n=13$ structure is that of an atom-centered icosahedron. The $n=13$ structure can be considered to be composed of 1-5-1-5-1 layers. This is the second element of a pentagonal growth sequence²⁵ which began with $n=7$ (the bicapped pentagon with a 1-5-1 sequence). The continuation of this sequence leads to the $n=19$ structure which is the double icosahedron, i.e. a 1-5-1-5-1-5-1 sequence. We have preliminary results which suggest that the sequence continues with a stable $n=25$ triple icosahedron.

Such metallic-like structures may seem surprising for silicon clusters. Icosahedral pentagonal growth sequence structures have occurred previously for two-body central force potentials, e.g. metallic or inert gas clusters. Magic numbers with $n=13, 19, (23 \text{ or } 25), \dots, 55$, etc. have been observed for Xe and other inert gas clusters.²⁶ However, our structures result from potentials which possess strong angular character as evidenced by the bulk phases in Figures 1 and 2. Our calculations show that back-bonding forces in small clusters can cause a remarkable reappearance of these simple geometric structures.

Our model also shows for a wide range of parameters that at $n=11, 12, 16, 17$ and 18

obtained a lower energy structure. As a second test we did some MD simulations.

To set up the MD program, we embedded our cluster in a viscous heat bath. Random initial velocities and coordinates were assigned to each atom. The equation of motion for the X-component of the i th particle was given by

$$M\ddot{X}_i = -\partial E\{R_{ij}\}/\partial X_i - M\beta\dot{X}_i + G(T) \quad (7)$$

where M is the mass of the atom, $E\{R_{ij}\}$ is given by Eqs. 1, 2, 4-6, β is the viscosity parameter and G is a randomly fluctuating force. Quite generally β and G are related by the fluctuation-dissipation theorem,²³ i.e. the probability of a random force, G , is given by $P(G) = (2\pi\sigma)^{-1/2} \exp(-G^2/2\sigma^2)$ where $\sigma = (2\beta M k T h^{-1})^{1/2}$ and h is the time step used to integrate (7). We use the numerical integration described by Tully *et al.*²³

The MD approach to the structure was used to check the MC results. In the MD calculations, we started with a heat bath whose temperature was on the order of 3000 K. The temperature of the bath was slowly lowered to 100 K. The temperature anneal schedule is similar to that used for the Monte Carlo runs, i.e. for the N th division $T_N = \gamma T_{N-1}$ where $\gamma = 0.9$. Approximately 30 temperature divisions were used with about 300 integration steps per division. The viscosity parameter was similar to that proposed by Wang and Chen.²⁴ Specifically, for our time step we take $h=300$ a.u. ($1 \text{ a.u.} = 2.42 \times 10^{-17} \text{ sec}$) and for the viscosity $\beta = 0.001 \text{ a.u.}^{-1}$. Our total anneal time is $\sim 0.1 \text{ nsec}$. We did not repeat the MC work for each structure, but examined the Si_n clusters, with $n=10, 13, 16$ and 19 . We are reasonably confident that the lowest energy structures we present are global minimums. However, given the possibility of large kinetic barriers, one can never be "absolutely certain."

C. The Structure of Si_n for $n \leq 20$

In Figures 5 and 6 the minimum energy structures for Si_n for $n \leq 20$ are illustrated. We find a much higher average coordination unlike the structures with no back bonding corrections. This is expected with the increase in central force interactions at the expense of angular interactions (see Eq. (6)). In Figure 7, we present a quantitative comparison of the average coordination for the clusters with and without back bonding. We define two

that these clusters do not belong to simple pentagonal growth sequence. Instead we have a layered character similar to that of one of the $n=10$ isomers^{1,21} which has a 3-3-3-1 trigonal prismatic structure. We find that $n=16$ corresponds to 1-6-1-6-2 and $n=17$ corresponds to capping off a face on the $n=16$ structure. For $n=18$, we have a 1-5-6-5-1 stacking sequence. It is tempting to suppose that the icosehedral structures are related to the closed-packed bulk phases, while the other uniaxial structures are related to the β -Sn bulk phase.

In Figure 8, we present the cluster energies as a function of size and again compare the results to quantum chemistry calculations. The absolute values of the cluster energies from quantum chemistry calculations have been adjusted by rescaling of the correlation energy.² Owing to such difficulties in estimating the binding energies, we feel at this stage one should concentrate on the structural aspects. Nonetheless, the agreement is adequate, although some noticeable difference do occur. For example, the energy of Si_8 is lower per atom than the cluster energy of Si_7 in the quantum chemistry calculation whereas the opposite is observed in the interatomic potential work. Similar results have been observed using other interatomic potentials.²⁷ We also illustrate in Figure 8 a liquid drop model curve fit to the interatomic potential. We used a simple expression for $E(n)/n = E_b(1 - an^{-1/3} - bn^{-2/3})$ for this fit. If we fit (a,b) to our cluster energies for $n>6$, we obtain an estimate for the bulk binding energy, E_b , of about 4.9eV/atom.²⁸ This value is remarkably close to the diamond structure binding energy of 4.6eV/atom.

From Figure 8, we note that $n=6, 10, 13$ and 19 are especially stable. This stability has been confirmed by theory² and experiment²⁹ for $n=6$ and 10 ($n=7$ is also a stable cluster). For larger clusters, so far it has not been possible to determine which are most stable. Careful studies³⁰ of the effect of ionizing laser energy and intensity on beam distributions have revealed cluster fragmentation effects which are likely to be strong for "metallic" clusters. Such an effect precludes inference of relative cluster energies from beam distribution intensities in cases where the ionization energies, I_n , are large (in Si_n $I_n > 7\text{eV}$ for $n<10$).

In Figure 9, we present the radial distribution functions averaged over the clusters for $n\leq 20$. We obtain a distinct separation between first and second neighbors which allows us to make a satisfactory definition of coordination numbers. It is interesting that the

structures. We expect that uncapped or completely capped icosahedra containing only six-fold coordinated atoms have minimal reactivities whereas the C_2H_4 molecules will react when there are at least two nearest neighbor four-fold coordinated adatoms. Denoting these adatoms by Si^* , the reactive configuration could be the bridge $Si^*-H-CH=CH-H-Si^*$. If so, then the C_2H_4 reactivity with one Si^* adatom is little more than with none. In Figure 13, we illustrate the capping process for $n=13, 14$ and 15 .

Our results indicate that in the range of $10 \leq n \leq 20$, the Si_n cluster structures oscillate between metallic pentagonal growth structures and covalent molecular structures. In effect, in this range Si_n clusters border on a "covalent-metallic" phase transition. It may well be that in the addition reaction, the covalent molecule C_2H_4 remains intact and reacts strongly only with fully covalent Si_n structures, such as $n=10$, and 16 , and much more weakly with metallic structures, such as $n=13$ and 19 . Until first principles calculations of medium size clusters become available, it is difficult to say how accurate our model is in calculating small energy differences between covalent and metallic structures for a given n . However, we have varied the magnitude of our back bonding term by as much as factor of two, i.e. we have changed μ from 4 to 2, and find that our qualitative conclusions remain unchanged. While our model may not yet address such small energy changes, we feel it has achieved the goal expected for a classical model: it has generated plausible candidate structures suitable for first-principle calculations.

IV. CONCLUSIONS

We have presented in detail a new interatomic force field which describes accurately both the phase stability of crystalline silicon as well as, the structures of small and medium-size clusters of silicon. Our force field differs from previous work in two fundamental aspects. First, we show that when three body forces are adjusted to describe a "covalent $\rightarrow$ metallic" phase transition instead of small amplitude atomic vibrations, a simple and accurate force field is obtained. As the bond angle, θ , changes from metallic ($\theta = \pi/3$) to covalent ($\theta = 2\pi/3$) we expect to see a rapid transition in the bond character. Thus, our force field is based on an angular function which behaves as $\cos(3\theta)$ as opposed to $\cos(\theta)$. Using this form of the potential we are able to generate for the first

ratio of the nearest neighbor to the next nearest neighbor for our clusters is similar to that of the diamond structure. In Figure 10, we consider how the bond length varies with coordination. We find a somewhat complex behavior. For coordination numbers (CN) at CN=4 and CN=12, we find much smaller bond lengths than at other coordinations, e.g. a maximum occurs at CN~6-8. If we consider the bond strength to be related to a bond length, then we would expect strong bonds to be formed with CN=4 or 12 and weak bonds with CN=6-8. Again, this would reflect our covalent (CN=4) to metallic transition (CN=12). Note that for CN=12 triangles of nearest neighbors are formed, but not for CN=8. The decrease in bond length from CN=2 to CN=4 is not expected from quantum mechanical calculations and is probably a failing of our potential.

In Figure 11, we present the bond angle distribution. While previous potentials based on $\cos\theta$ were often designed to favor tetrahedral angles θ_t , (as through an energy term proportional to $(\cos\theta - \cos\theta_t)^2$), there is no such bias in our potential. We find that the bond angles are all concentrated near $\theta = \pi/3$ (close packing) or near θ_t (tetrahedral packing). Given our $\cos(3\theta)$ functional form, we might have expected this behavior. However, the virtual absence of bond angles near $\pi/2$ reflects certain geometrical constraints which one might not have anticipated. These packing constraints in effect amplify the significance of the covalent/metallic distinction.

Unlike the case of crystalline silicon the experimental and theoretical "data base" for clusters is quite sparse. For crystalline silicon we have structural information from rather complete pressure work, both experiment and theory, as evidenced in Figures 1 and 2, and Tables II and III. For clusters we must rely on more indirect comparisons to verify the predictions of cluster model.

Some recent experimental data do seem to support our predictions. The size dependence of the rate constant³¹ for the addition of the first C_2H_4 molecule on to Si_n^+ is shown in Figure 12. For $n \leq 12$ the rate constant, k_2 , is an erratic function of n as expected from the variety of cluster geometries calculated for $n \leq 10$ by quantum chemistry methods.² For $n \geq 13$ and $n \geq 19$ smooth rises in k_2 are observed. We interpret this behavior is indicative of a common core with a repeated building block, i.e. a geometric growth sequence. We suggest that the non-reactive minima at $n=13$, 19 and 23 correspond to our icosahedral

time equations of state for crystalline silicon which achieve an accuracy comparable to that obtained from quantum mechanical calculations. For example, we are able to predict the diamond-to-white tin transition pressure to within $\sim 20\text{--}30\%$.

The second aspect of our work which differs from previous efforts is the explicit inclusion of a term which transfer bond strength from dangling bonds to back bonds. With this term our bulk interatomic force field is simply modified to obtain energies and structures of Si_n vapor phase clusters. Small silicon clusters would have open polycyclic structures without this back bonding term. From highly accurate molecular orbital calculations, we know small silicon clusters actually assume close packed, or metallic-like, structures. Our back-bonding force is able to reproduce accurately the coordination trends obtained from the quantum chemistry work. Moreover, we predict surprising pentagonal growth structures for clusters in the range $n=13\text{--}25$. These structures partially explain magic numbers recently observed in the addition reaction of C_2H_4 with Si_n^+ .

We believe that the success of our interatomic force field for silicon for a wide variety of bonding configurations bodes well for widespread applications. For example, one might use such a force field to study the formation and activation energy for diffusion of intrinsic defects in crystalline silicon, or perhaps to the structural properties of amorphous and liquid silicon. This is the first time a classical force field has been successful in describing the condensed properties of any element which is not an inert gas.

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TABLE CAPTIONS

- Table I. Parameters for the bulk terms of our interatomic potential for silicon. See Eqs. (1,2) and the text for details.
- Table II. Equation of state parameters for silicon in various structures. See Eq. (3). Sources of experimental and pseudopotential values discussed in text.
- Table III. Transition pressures and volumes for the cubic diamond to β -Sn transition. The transition volumes (V_t) are normalized to the experimental equilibrium volume of the diamond structure ($20.01 \text{ \AA}^3/\text{atom}$). The pseudopotential work is from Chang and Cohen.¹⁵ Experimental data are from (a) Jamieson¹⁷ and (b) Hu and Spain.²⁰
- Table IV. Parameters for the dangling bond corrections to the bulk force field. See Eq. (4-6) and the text for details.

TABLE I

$A(\text{eV}) = 182.44$	$\beta_2(\text{\AA}^{-2}) = 0.151$
$\beta_1(\text{\AA}^{-2}) = 0.550$	$g_1(\text{eV}) = 2.644$
$g_0(\text{eV}) = 7.08$	$\lambda_1 = (2/\pi)^{-4}$
$\lambda_2(\text{\AA}^{-4}) = 0.1773$	

TABLE II

Structure	Cohesive Energy (eV)	Lattice Constants (Å)	Bulk Modulus (Mbar)	Derivative of Bulk Modulus with Pressure
Diamond				
Present work	4.62	5.36	1.01	5.00
Experiment	4.63	5.43	0.99	~
Pseudopotential	4.84	5.45	0.98	~
β -Sn	4.33	4.64(a) 2.89(c)	1.50	4.26
Simple cubic	4.21	2.47	1.47	5.37
Hexagonal close packed	4.13	2.71(a) 4.41(c)	1.81	5.05
Body centered cubic	4.13	3.03	1.90	6.07
Face centered cubic	4.11	3.81	1.80	4.94

TABLE III

		$V_t(\text{diam})$	$V_t(\beta - \text{Sn})$	Pressure (kbar)
Present work		0.87	0.72	140
Pseudopotential		0.93	0.72	93
Experiment	(a)	0.918	0.710	126
	(b)	0.911	0.706	113

TABLE IV

$$\lambda_3(\text{\AA}^{-4}) = 0.02379 \quad z(\text{\AA}^{-1}) = 0.0951$$

$$\mu = 4.0 \quad \alpha = 1.70$$

FIGURE CAPTIONS

Figure 1. Equation of state for silicon as a function of atomic volume. Shown are the body centered cubic (BCC), face centered cubic (FCC), simple cubic (S-CUBIC) and diamond structures. The volumes have been normalized to the experimental equilibrium volume of the diamond structure. We present results from (a) the interatomic potential of Biswas and Haman⁵, (b) the quantum mechanical results of Yin and Cohen¹ and (c) the present work.

Figure 2. Equation of state for silicon including the hexagonal close packed (hcp) and the white tin structure (β -Sn). The top panel is from the work of Chang and Cohen¹⁵; the bottom panel is from our interatomic field.

Figure 3. The structure of Si_n with $3 \leq n \leq 10$ without back bonding contributions. These structures disagree with those obtained from quantum chemistry calculations² as the effect of dangling bonds are not included.

Figure 4. Structures of Si_n for $n = 13, 16$ and 19 without back bonding contributions. Note how these structures resemble fragments of the diamond structure.

Figure 5. The structure of Si_n with $4 \leq n \leq 10$ with back bonding contributions. These structures resemble with those obtained from quantum chemistry calculations² as the effect of dangling bonds is included.

Figure 6. The structure of Si_n with $11 \leq n \leq 20$ with back bonding contributions. Note how these structures are close packed in contrast to Figure 4. The structure of these clusters is dominated by a pentagonal growth sequence.

Figure 7. The average coordination of Si_n . Shown are results from quantum chemistry calculations² ($-\Delta-\Delta-$), and our interatomic force field ($-\bullet-\bullet-$) without back bonding corrections for Si_n with $n \leq 10$. Also shown are results for our interatomic potential ($-o-o-$) with back bonding corrections for $n \leq 20$. Note the anomalously high coordination for $n = 13$ and $n = 19$ which correspond to icosahedral structures.

Figure 8. The binding energy of Si_n . Shown are results from quantum chemistry calculations² ($-\bullet-\bullet-$), from our interatomic force field ($-o-o-$) and from liquid drop model ($-$).

Figure 9. Radial distribution function for Si_n averaged over $n \leq 20$.

Figure 10. Bond length as a function of coordination for Si_n . Note the minima at coordination numbers corresponding to the covalent case ($\text{CN}=4$) and the metallic case ($\text{CN}=12$).

Figure 11. Angular distribution function for Si_n averaged over $n \leq 20$. Note that almost all the bond angles lie either at the metallic ($\theta = 60^\circ$) or covalent ($\theta = 109.5^\circ$) limits.

Figure 12. Rate constants for the addition of the first C_2H_4 to Si_n^+ as measured by Jarrold, *et al.*³¹.

Figure 13. Pentagonal growth clusters for Si_n as obtained from our interatomic force field for $n = 13-15, 19$. For $n = 15$ the atoms denoted by Si^* in the text are shaded.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 3

Figure 6

Figure 7

Figure 8

Figure 9

Figure 11

Figure 12

Figure 13

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