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Interpretation of cluster structures in terms of covalent bonding

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We show that a pair-potential model [Phys. Rev. B **40**, 10 351 (1989)] for covalent bonding can be used to describe microcluster configurations in semiconductors. The model regards bonding as due to electrons in covalent bonds. In its original form, there was no bond-bond term (or bond-charge term) to account for interaction between electrons in different bonds, and it took the form of a pair potential truncated after the fourth bond. In this paper, we introduce a bond-bond force in the form of another pair potential acting between bonds. The relative strength of this force distinguishes between the different cluster configurations observed in carbon and silicon. The configurations of various silicon clusters found with this model are related neither to the close-packed metallic microclusters nor to the open diamond structure of bulk silicon. This is in good agreement with electronic-structure calculations but differs from results obtained previously with empirical potentials derived from bulk structures. The additional term does not affect the excellent reproduction of the stability of various bulk lattices found previously, and the potential is therefore transferable between the two regimes.

I. INTRODUCTION

The development of interatomic potentials for silicon modeling is a subject of intense recent interest.[1-10] The transferability of such models between various applications, especially from bulk structures to small clusters, has proved a major obstacle.[11] Recent work in small silicon clusters has shown their structure to be extremely varied, and completely different to the structures adopted by other elements. We show that a simple model can explain, in a qualitative way, the structures of silicon and carbon clusters, and that their difference is related to the relative ease with which multiple bonds can form in carbon relative to silicon.

In a recent paper, Carlsson[12] placed all interatomic potential schemes into four groups of ascending complexity: pair potentials, pair functionals, cluster potentials, and cluster functionals. In most previous work on semiconductors, one of these levels has been selected from physical arguments, and then some function of the interatomic distances and angles has been chosen. As the level of complexity increases, the number of free parameters tends to rise and the number of constraints imposed on the system by the initial assumptions is reduced. It is generally accepted that the range of parameters used to fit the potential, the better it is likely to perform when applied to unfitted phenomena. The drawback to this approach is that the increasingly complex functions which it introduces are increasingly less easy to interpret physically. An alternate approach is to study the constraints introduced at each level of complexity, so as to determine which physical properties can be understood at which level of approximation. Here we adopt the latter approach. We show that, with certain physically intuitive modifications, the pair potential level (which has the advantage of being the fastest for computational purposes) is adequate for describing bulk and cluster configurations.

A recent paper has shown that it requires only a simple (i.e., nonoscillatory) pair potential to stabilize the diamond structure in silicon, provided that each pairwise bond is associated with an occupied electronic orbital and, hence, the number of such bonds is limited by the number of available electrons. Although this is the simplest model yet proposed for silicon, its prediction of the stability of various structural polytypes is in closer agreement with electronic structure prediction than any other model not fitted explicitly to such data. Not only does the model order the various high-pressure phases correctly, but this ordering is constraint imposed by the approximations made in setting up the model, and cannot be altered by judicious fitting. This strongly suggests that the original assumptions were sound, and demonstrates that three-atom forces are not essential to stabilize the diamond lattice, as has previously been suggested.[12] It is perhaps not surprising, in view of the traditional picture of a covalent bond, that the dominant contribution to the energy should come from two-atom interactions.

There has been renewed recent interest in the structure of small semiconductor microclusters, stimulated by a desire to study growth processes. While cluster problems are tractable by local-density-functional (LDF) calculations, full simulation of growth is not, and for such studies it is desirable to develop an empirical potential scheme which is transferable from cluster to bulk energetics. In this paper we present a suitable framework for such a scheme.

The structure of silicon clusters has been shown to be related neither to the close-packed structure of metals nor to the open structure of diamond lattice fragments. Characterizing these clusters is rather difficult because they tend to be significantly distorted from the geometric shapes which are commonly used to describe them, often allowing more than one such geometric (or topological) description. One suggestion applied recently is to compare average coordination number and bond length of empirical clusters to the same properties derived from local-density approximation (LDA) calculations. This allows general trends to be studied, which provide greater insight than the exact morphology of individual clusters, especially since the energy differences between possible clusters can be lower than typical room-temperature thermal energies. A drawback is that these comparisons between models are sensitive to the arbitrary choice of cutoff distance for what is described as a bond. In view of the difficulties involved in describing the structures, and the small difference in energy between them, we regard the most important test of a potential to be the correct description of the general features common to such clusters (in silicon and germanium this means three-dimensional, approximately fourfold coordinated, cagelike structures; in carbon it means one-dimensional chains, either linear or rings). In terms of energy, it is also important that the difference between the stable and metastable states is of the right magnitude, since these metastable states may well be important in growth phenomena.

The intention of this paper is to show that the potential scheme used necessarily leads to chainlike or open, cagelike structures depending largely on the strength of the double bonds and the bond-bond repulsion. It turns out that these qualitative features are almost independent of the parametrization—neither close-packed nor diamond fragment clusters can be obtained. This, we believe, is the most important result of the paper. At this stage we do not attempt to present a definitive parametrization for a given material nor to fit exactly the cluster configurations found by *ab initio* calculations. We note that, while other empirical potentials have been applied to cluster phenomena, in each case they have had to undergo extensive reparametrization before giving correct results. We believe that it is preferable to adopt a model in which the cluster configurations follow naturally from the physics which motivates the model's formulation, rather than one in which these features arise from careful parametrization.

II. PAIR POTENTIALS

Recently, it has been shown that an empirical representation of cohesion in silicon in terms of quasiclassical electrons in two-center bonding states leads to a good description of structural energies and reconstructions.[1] In this model, each atom contributes four electrons to covalent bonding orbitals, and the exclusion principle prevents more than eight electrons (four antispin pairs) from sharing the same atom as one of the foci of their orbitals. The important innovation of this model lies in the approximation that electronic states are highly localized, so that the cohesion per atom can be associated with four covalent bonds.

In this paper we use a parametrized version of the model, in which the energy is written as a pair potential:

$$E=\tfrac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}Ae^{-\alpha r_{ij}}-\tfrac{1}{2}\sum_{i=1}^{N}\sum_{k=1}^{4}Br_{ik}e^{-\beta r_{ik}}\ . \qquad (1)$$

Values for the parameters A, B, α, and β are given in the original paper.[1] The i and j summations run over all atoms in the crystal, while the k summation is over the four bonded neighbors associated with atom i.

Methods for choosing which neighbors are regarded as "bonded" have been discussed previously.[1] For cluster simulations, it is generally easiest to set up the bonding map at the beginning of the simulation and leave it unchanged during the minimization. This increases the number of metastable states found, but the large barriers to rebonding means that standard minimization procedures find it difficult to go between bonding arrangements. As with all such calculations, the minimizations were done using many different starting configurations, where the configuration specifies both atomic positions and where the bonds are.

For studies of clusters, we expect that electrons in different bonds will be forced closer together than in the bulk structure. Thus, it will be more important to consider interactions between them. To model this, we add a bond-bond term in the form of a repulsion between the bonds. The functional form of this term is chosen by analogy with the three-body term of Stillinger and Weber;[2] but, in keeping with our interpretation of bonds being occupied covalent states, the term only exists between pairs of bonds rather than between all sets of three atoms (hence, the sums over m and n). Moreover, since we regard every bond as being occupied by exactly two electrons, the strength of the bond-bond interaction depends only on the distance between bond centers and not explicitly on the lengths of the bonds. It is thus similar to the "bond-charge" and "effective-particle" approaches.[13-16] Important differences relate to the fact that bonds and double bonds are included explicitly and the bond-bond repulsion occurs only between bonds associated with the same atom. This is in keeping with the origin of this repulsion lying in the orthogonality constraints on neighboring orbitals. Although formally written as a repulsion between bond centers, the major contribution to this repulsion comes from regions near the common atom where the overlap between orbitals is largest.

The bond-bond term has only one free parameter, C, which represents the strength of the bond-bond repulsion. The parameter w is adjusted such that the minimum of the function falls at the tetrahedral bond angle in the diamond structure for silicon. This has the advantage that it affects neither the bulk silicon lattice parameter nor binding energy, both of which were fitted previously:

$$F_{\text{bond-bond}}=\sum_{i}\sum_{n=1}^{3}\sum_{m=n+1}^{4}C[\cos(wR_{k_m k_n})+\tfrac{1}{3}]^2\ . \qquad (2)$$

Notice that the term is effectively *another pair potential;* it is independent of the position of the central atom. The central atom i serves only to determine between which atoms the pair potential acts.

It should be emphasized that the choice of this functional form is purely arbitrary and does not follow from the physical interpretation of the model. Since we hope to study general trends, the choice of a specific functional form must be treated with caution. To this end, other functions were also tried: these led to similar results and, in keeping with the principle of demonstrating the consequences of using pair potentials, no attempt was made to obtain an optimized form. Furthermore, the weakening of double bond (which was previously added explicitly[1]) follows naturally from the repulsion between two overlapping bonds: $32C/9$. A triple bond is weakened even more (by $32C/3$) since it includes three pairs of bond-bond repulsions.

The repulsive interbond force favors coplanarity of the bonds to an atom which has a double bond. Moreover, since bonds which do not share an atom do not interact, there is no unphysical tendency for these planes (at either end of a double bond) to be perpendicular (as in effective particle approaches[16]). The tendency for atoms surrounding a double bond to be coplanar may be an important effect in determining cluster geometries.

For various strengths of bond repulsion, we calculate energies of various defect structures and small clusters. The choice of the Stillinger-Weber form means that the cohesive energy and lattice parameter of silicon in the diamond structure is unchanged from the original fitting. The relative stability of various crystal structures, which were particularly well described in the original model, are largely unaltered by the bond-bond term (the diamond stability is enhanced somewhat). This consistency follows directly from the form of the three-body interaction. The only departure comes at very low values of C, for which the strength of the double bond is increased. For the unphysical case of $C=0$, where the quadruple bond is four times as strong as the single bond, the stable bulk structure is zero-dimensional, consisting of separated dimers. As C increases, stability goes through the one- and two-dimensional phases (chain and degenerate graphitic layer, the latter corresponding to bonding in carbon. We discuss the implications of degeneracy in choosing the double-bonded sites later). The stable three-dimensional diamond phase is reached for $C>0.25$.

While the original parametrization was for silicon, and we shall again deal mainly with that element here, the formalism appears to have a wider applicability in covalent materials. We will show how other elements (particularly carbon) can be described qualitatively using different values of the bond-bond parameter C.

III. CLUSTERS

We examined the lowest-energy configuration for clusters of small numbers of atoms using various values of bond-bond repulsion C. The energy minimization was carried out by first specifying the bonding arrangement, then relaxing the energy by molecular statics to find the equilibrium atomic positions. Once this minimization had been done, the cluster was heated and subjected to a simulated anneal and quench. This latter process was repeated several times for each of the lowest-energy configurations. This give us some assurance that the minimum-energy configurations found are global, rather the local, minima for the given bonding arrangement. For each cluster size, a wide variety of initial bonding arrangements were relaxed, including multiply bonded structures. Finally, the bonding arrangement itself was varied using a Monte Carlo technique to try to locate any configurations that had been missed by previous methods. For an increasing number of atoms in a cluster, the energy per atom in the most stable structure is shown in Fig. 1.

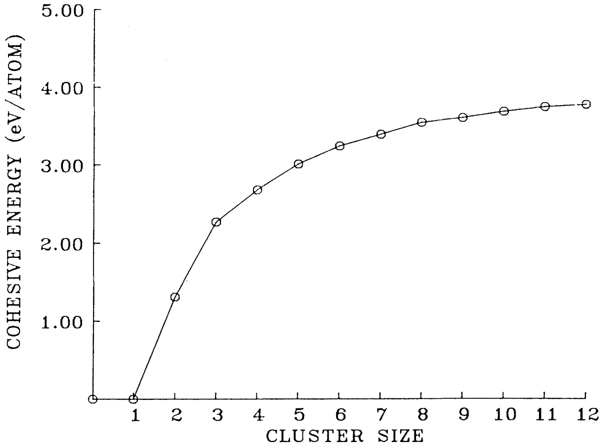

FIG. 1. Variation of cohesive energy per atom with the number of atoms in the cluster.

We examined possible configurations for Si_3 up to Si_{12}. At very low values of C (weakly interacting electrons), multiply bonded structures are favored. This can be regarded as the molecular limit. Triple bonds are unstable and the low-C configuration is a doubly bonded monatomic chain, typical of carbon clusters.[17] Although the model allows neither for delocalization of electrons, nor for dipole-dipole interactions, at low values of C the bulk diamond structure does become unstable with respect to a degenerate two-dimensional graphitic layer represented by alternating double and single bonds (as noted previously,[1] this degeneracy is indicative of a conducting phase). At increasing values of C, the number of double bonds is progressively reduced, but they are completely eliminated only for certain cluster numbers. This is not surprising, since it has been shown that large clusters and surfaces of bulk silicon reconstruct in a way which can be readily explained by double bonding.[1,18,19]

For dimers, the lowest-energy structure varies from quadruply bonded (no bond-bond repulsion) to singly bonded as the bond-bond repulsion is increased. The observed interatomic distance and binding energy for silicon ($R \approx 2.22$ Å, $E \approx 2.62$ eV) are found in the doubly bonded regime with a value of $C \approx 0.7$. As we shall see, this value of C also gives configurations and energies for larger clusters consistent with previous calculations for silicon.[20-22]

A. Trimers

From the results of *ab initio* calculations, the carbon trimer is believed to have a linear structure while the silicon trimer adopts an acute isosceles triangle structure[20,21] with an opening angle of about 80° (although this configuration is generally believed to be only slightly lower in energy than the equilateral triangle). Metallic trimers have the equilateral triangle structure. In all cases, the interatomic distances are rather smaller than in the bulk material.

The interpretation of these structures within the present scheme is very simple—the equilateral triangle consists of three double (or three single) bonds, the isosceles of two doubles and one single, and the linear structure of two doubles. We find that the controlling force behind the relative stability comes from the bond-bond repulsion, and that, at a certain critical value of C, a transformation occurs from one to the other. We also examined other possible structures and found that, for still higher bond-bond repulsion, two double bonds from the center atom, with no bonding between the outer atoms, becomes the favored configuration. The (obtuse) opening angle is then determined by the minimum in the bond-bond repulsion and so is very sensitive to the exact form chosen for $F_{\text{bond-bond}}$. For metallic clusters we expect the electronic structure to show fully delocalized electrons in three-center orbitals; the present model cannot describe this situation (one which leads to close packing). Thus, the isosceles triangle configuration of the silicon dimer is consistent only with a covalent bonding picture, while the equilateral triangle could result from either covalent or metallic bonding. This suggests that the onset of covalent bonding in silicon comes at a cluster size of only three atoms. The results for the trimer are shown in Fig. 2.

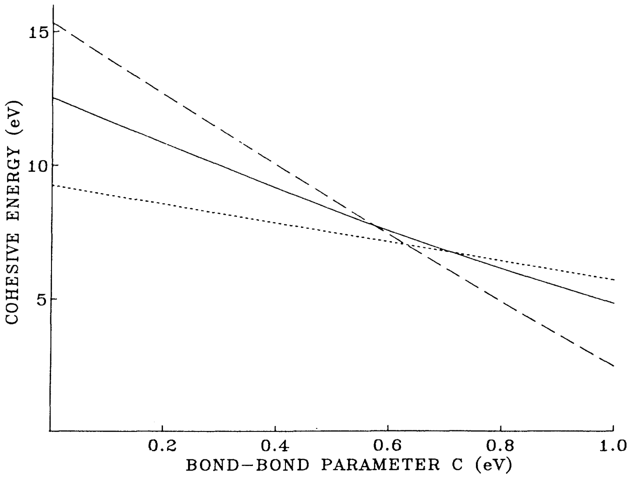

FIG. 2. Cohesive energy of various cluster configurations for $N=3$ (trimer), shown as a function of the bond-bond repulsion parameter C. The equilateral triangle is represented by the dashed line, the acute isoceles triangle by the solid line, and the obtuse isoceles triangle by the dotted line.

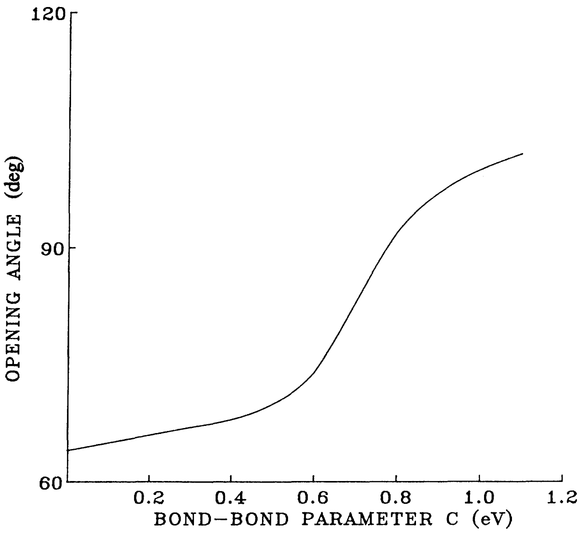

FIG. 3. Variation of the opening angle of the isoceles triangle trimer structure with bond-bond repulsion parameter (C).

For the acute isoceles triangle configuration, the variation of the opening angle with C is shown in Fig. 3. While we refer to this angle as acute, to differentiate the configuration from the two-double-bond-only configuration, it does, in fact, become greater than 90° for large C. The rapid variation of the opening angle around $C \approx 0.7$ is consistent with the observation[20,21] that the bond-angle restoring forces are rather small.

The only previous empirical potential to obtain the isoceles triangle was the revised version of the modified Biswas and Hamman potential[4] (BH). There is a distinct difference in the cause of the departure from equilateral—in the present case it arises from the bond order, while in BH it is caused by selecting a three-body interaction with negative curvature at 60°.

B. Four to seven atoms: Apparent close packing

Other configurations of clusters involving four, five, and six atoms were also examined. It was found that the stable structure was slightly more dependent on the arbitrary functional form chosen for the bond-bond term than in the trimer. This is because of the wider variety of bond lengths and angles present in each structure. Using the $F_{\text{bond-bond}}$ function from Eq. (2) on various four-atom clusters, we found the structures shown in Fig. 4 to be the most stable. They are tetrahedron with single bonds only (four dangling bonds), and doubly bonded square, parallelogram with nonadjacent double bonds (two dangling bonds). As with the trimer, we find a trend with increasing C of progressively fewer double bonds and eventually a prototype close-packed structure (tetrahedron). From the observed configurations of the dimer and trimer, we deduce that, for Si, the appropriate value of C is about 0.7. This leads to a prediction of a flat parallelogram as

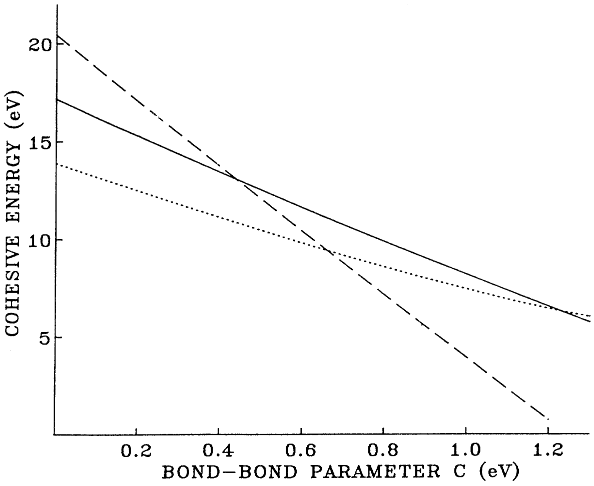

FIG. 4. Cohesive energy of various cluster configurations for $N=4$, shown as a function of the bond-bond repulsion parameter C. The dashed line represents the double-bonded square, the solid line the tetrahedron, and the dotted line the parallelogram.

the equilibrium structure of the Si quadrumer. This is again consistent with more complex LDA (Ref. 22) and tight-binding calculations.[20,21]

For the five-atom clusters, we examined the doubly bonded chain (linear and ring), the square pyramid with two nonadjacent double bonds in its base, and various triangular bipyramids. Once again, the doubly bonded ring structure is the most stable at low C, then the more open pyramid structure with two double bonds, and finally the prototype close-packing configuration (the triangular bipyramid), although we found this to be somewhat distorted due to double-bond formation for $C<0.7$.

For six-atom clusters, the same trend holds: doubly bonded ring at low C giving way to a capped trigonal bipyramid and then an octahedral configuration at $C>0.6$. There is a departure from perfect symmetry in that the octahedron is stretched along one of its axes. LDA calculations in silicon suggest that the octahedral configuration is most stable, but that the capped bipyramid is very close. This agrees with our calculations with $C=0.7$ for Si which lies just above the transition from one structure to another.

For the seven-atom cluster, we tried numerous possible starting configurations and found that, at low C, the distorted sevenfold ring was stable, moving with increasing C through a capped hexagon (four double bonds) to the bicapped pentagon. This is another prototype close-packed cluster, but is significantly distorted. The reason for this distortion (also present in the capped hexagon) is that the cap atoms are fivefold coordinated (in the undistorted structure) but the inherent covalency in the model forces them to choose four ring atoms to which to bond. This, in turn, leaves two ring atoms undercoordinated. The most stable situation occurs when the undercoordinated ring atoms are adjacent and can form a double bond.

We have found that the same value ($C=0.7$) for bond repulsion strength reproduces all the configurations found from the LDA calculation for silicon, with the same trend of steadily increasing average bond length with cluster size (mainly due here to steadily reduced average bond order). We note that, in all cases, there are distortions away from close packing.

The interpretation of the model allows us to distinguish between these clusters and those found for metallic or inert-gas elements. In metals, the clusters attempt to maximize their coordination so as to allow the conduction band to be as broad as possible. In inert gases, the van der Waals forces are such that the cohesive energy scales proportionate to the coordination. In the present case, the dominant trend is toward saturated (fourfold) coordination. For very small clusters, overcoordination is impossible, so the trend appears to be to maximize coordination. It might be hoped that bond lengths would provide some information about the nature of the bonds. In inert-gas clusters, the interatomic spacing tends to be slightly larger than in the bulk (the attraction from more distant neighbors is missing); in metals it is slightly smaller (in a tight-binding picture the atoms attempt to increase wave-function overlap per neighbor). In the present model both situations can arise: double bonds reduce the bond lengths, repulsive interactions are enhanced above the bulk values due to distortion of bond angles below 109°, causing an extension in the bond lengths. The first effect is similar to that found in metals, the second effect is not quite analogous to the inert-gas case because it arises from extra repulsion and not missing cohesion. The variation in mean bond length is also found within a given cluster size. For example, in the six-atom cluster (with $C=0.7$), we find that the (strained, single-bonded) octahedron has an average bond length of 1.060 times the bulk value, for the (less strained, with four double bonds) capped bipyramid it is only 1.008 times, and for the (unstrained, double-bonded) linear chain structure it is 0.943 times.

C. Eight to twelve atoms: Open cagelike structures

For clusters containing eight or more atoms we find no tendency toward true close packing (although the structures are still considerably more closely packed than in the diamond structure). These clusters still show an evolution with increasing C away from multiply bonded structures, although, with the value of $C=0.7$ (assumed for silicon), the 8- and 11-atom clusters still contain double bonds. All structures are rather distorted, but the general topologies (nearby high-symmetry configurations) are as follows (stable structure with $C=0.7$ in italics and number of double bonds in parentheses): For 8 atoms, as C is increased, the stable structure evolves from an octagonal ring (8), a cube (4; in two antiparallel pairs), and a *bicapped octahedron* (2) to a square antiprism (0). From the LDA work in silicon, the bicapped octahedron is most stable, again in agreement with $C=0.7$ representing silicon. For 9 atoms we find (number of double bonds in parentheses) nonagonal ring (9), tricapped octahedron (2) capped cube (2, this could also be regarded as a tricapped octahedron with caps on adjacent faces), *tricapped trigonal prism* (0). For 10 atoms we find closed ring (10), quadruply capped trigonal prism (1), *hexagonal bipyramid* (with dimers at the apices) (0). For 11 atoms we find ring (11), cube with a trimer cap (3), *bicapped cube* (one dimer cap and one monatomic cap, on opposite faces) (1), tricapped cube (0). For 12 atoms we find ring (12), double cube (4), bicapped cube (dimer caps on opposite faces) (2), *hcp near-neighbor shell* (0).

Because of the extensive distortions found when the structures are allowed to relax, each configuration could have been described in more than one way. In comparison with the LDA calculations in silicon, our predictions for clusters of up to eight atoms are in agreement (assuming $C=0.7$). For Si_9, the LDA predicts that the capped Bernal structure[11] or reconstructed tricapped octahedron[22] (two alternative descriptions of the same structure) is the most stable. We find this to be stable in the range $0.35 < C < 0.58$ and 0.02 eV/atom higher than the tricapped trigonal prism at $C=0.7$. For Si_{10}, the LDA predicts a quadruply capped triangular prism. We find this to be stable in the range $0.27 < C < 0.35$, but 0.02 eV/atom higher than the "distorted hexagonal bipyramid with skew dimers at the apices." In each case the transition value (relative to the value which stabilizes the Si_2 to Si_7 structures) is sensitive to the choice of functional form, but close-packed structures could never be stabilized.

In spite of the difficulties encountered in describing the relaxed clusters, certain universal factors emerge. Although Fig. 1 suggests that the cluster energy is tending toward an asymptotic value, the actual bulk value (4.63 eV/atom) is significantly greater than the highest cluster values might suggest. This prediction is in excellent agreement with *ab initio* calculations. In each case there are no atoms which can be truly regarded as internal (each can be surrounded by at least a hemisphere through which no bonds pass). The close-packed hcp shell is the most symmetric of the high-C configurations, but does not represent close packing (and nor do any others) because there is no central atom. The addition of a thirteenth atom to the center of this configuration leads to large distortions and an unstable configuration. Unlike metallic clusters, 13 is not a magic number for covalent materials.[23,24]

In each case the average bond length is greater than that found in bulk silicon. It appears to have reached an asymptotic value at about 4% greater than in the bulk. This is shown in Table I. The expansion arises as a result of enhanced repulsion from second neighbors due to reduced bond angles. It is in good agreement with the expansions found in the LDA calculations.

TABLE I. Mean bond lengths relative to the value in the bulk diamond structure, and the number of bonds over which the average was taken for stable clusters with $C=0.7$.

Cluster size	Mean bond length	Coordination
2	0.944	1
3	0.955	1.33
4	1.031	2.50
5	1.028	2.80
6	1.060	4.00
7	1.041	3.71
8	1.034	3.75
9	1.034	4.00
10	1.031	4.00
11	1.025	3.82
12	1.025	4.00

IV. DELOCALIZATION

One aspect of bonding which is explicitly missing from the model is the possibility of delocalization of the electrons. It is to be expected in cases where the choice of double-bonding sites is degenerate: in graphite and in the chain structures which characterize carbon clusters. The present model with $C=0.25$ predicts closed chains for all clusters, whereas *ab initio* calculations in carbon suggest linear chains for clusters containing an odd number of atoms, and rings for clusters containing an even number. In each case, the total number of bonds is even, suggesting delocalized band effects. While the difference in energy is small, it cannot be accounted for by a pair-potential model without using a judiciously oscillating function. We believe that the failure to predict the linear structure is thus due to the nature of the model itself, and not to poor optimization of the functional forms. A possible solution would be to introduce a resonance energy for degenerate structures.

Resonance would suggest that the electron can be in any of a number of bonds, and hence that the material becomes conducting. This would imply that the fully bonded reconstructed surface structures found in silicon[1] are nonconducting, while the degenerate unreconstructed surfaces are conducting. This observation is again consistent with the calculated band structures.

V. POINT DEFECTS AND SURFACE STRUCTURES

Without bond-bond terms, the lowest-energy configurations for vacancies and interstitials were found to be asymmetric reconstructions which had not previously been considered for calculation by *ab initio* methods. We examined the effect of the bond-bond term on these reconstructions.

For the vacancy, only two configurations were found to be relevant—the rebonded[1] and the symmetric (dangling bonds). The lowest-energy configuration is determined by the competing effects of energy gained by rebonding against that lost through bond-bending distortions.

For the self-interstitial, there are many possible rebonding configurations which give very low energy if bond-bond forces are not considered. As the bond-bond repulsion is increased, a preferred rebonded configuration emerges, until at very high C the dangling bond configuration, with the interstitial atom unbonded in the hexagonal configuration, becomes favored. The energies

TABLE II. Interstitial formation energies of the structures considered in Ref. 1 at various strengths of bond-bond interaction. The most stable configuration is shown in boldface.

Coefficient C eV	Unreconstructed eV/Å^3	Tetragonal recon. A eV/Å^3	Hexagonal recon. C eV/Å^3
0.0	5.52	0.06	**0.03**
0.5	5.68	1.71	**1.33**
1.0	5.76	3.29	**2.59**
1.5	5.81	6.01	**3.84**
2.0	5.86	6.37	**4.08**
2.5	**5.89**	7.89	6.31

of various configurations are given in Table II. The reconstructions A and C are taken from Ref. 1.

We note that energies for these asymmetric configurations have not yet been evaluated using *ab initio* methods,[25–28] but from diffusion data we can obtain an estimate of formation+migration energy which provides an upper bound to the formation energy. Values for this lie between 4.0 and 5.1 eV.[29] Our calculations for those configurations which have been investigated with *ab initio* techniques are generally in good agreement.[1]

Notice that the values for C required to destabilize the asymmetric point-defect configurations are much higher than those suggested by the cluster calculations. This result is again independent of the parametrization: nonoscillatory forms of the bond-bond term predict that the asymmetric configuration is the most stable. The predictions of the previous paper are thus unaffected.

The other significant, correct prediction of the previous model was for the surface reconstructions of silicon. Once again, the strength of the bond-bond interaction required to destabilize these reconstructions was found to be well in excess of that suggested by the cluster calculations, so that qualitative predictions of the previous work are unaffected.

It should be noted that the quantitative values of the surface and defect energies are strongly dependent on the choice of functional form for the bond-bond repulsion. This suggests that they would be good candidates for fitting parameters in a more comprehensive parametrization of the model.

VI. CONCLUSIONS

The essential aspect of silicon clusters is that they are three dimensional, yet neither close packed nor fragments of the diamond lattice. We have shown that these essential features can be explained at the level of a pair potential which is also transferable to bulk energetics. No previous model at this level of simplicity has been able to account for either, and more complex models have recently been shown to be inadequate for both.[11]

We have shown that interbond forces are required to explain the structure of small clusters. Even with this very simple force model we find subtle competing effects between optimum coordination, bond-bond repulsion, and multiple-bond formation. We have shown that there exist various regimes of bond-bond repulsion strength which give rise to completely different structures of covalent clusters. These regimes can be associated with different covalent elements.

We make a division between the pseudo-close-packed clusters of $N=2-7$ and the more open structures of $N=8-12$. When a single-parameter functional form for $F_{\text{bond-bond}}$ is chosen, and the value which gives rise to siliconlike small clusters determined, the $N=2-7$ clusters tend to be the same, whilst the relative stability of the $N=8-12$ clusters varies between different cagelike structures. If it were desirable to concentrate entirely on silicon, it is certainly possible to choose $F_{\text{bond-bond}}$ in such a way as to stabilize the LDA structures. This is not the aim of the present work, and so we have concentrated on a form which is both familiar and simple.

The simplicity and intuitive basis of the model allows us to offer new physical explanations for the variation in average bond length with cluster size. It is smaller than in the bulk for very small clusters because of multiple bonding, but larger for bigger clusters because of the distortion-enhanced bond-bond repulsion. For a given cluster size, the average bond length between competing configurations can be very different, depending upon the degree of distortion and the number of double bonds. Similarly, the rise in coordination which goes analogously with close packing up to a coordination number of about four, and then levels off, finds a clear physical interpretation in terms of saturation of the bonding.

With reference to results for all-electron calculations in silicon, we suggest that the correct ratio of bond strength to bond-bond repulsion from Eq. (2) corresponds to a value of $C=0.7$, although we do not believe that the choice of the function is optimized. This is still within the regime where formation of double bonds is a viable alternative to highly strained, but fully coordinated, structures. For clusters greater than five, we still find that fourfold coordination is favored over undercoordination (undercoordination can occur with larger values for C). Figures 2 and 4, showing the dependence on C of the stable configuration, show that the region around $C=0.7$ is a transitional one, allowing double bonds but tending toward all single bonds. The fact that silicon lies in this transitional region explains the wide variety and complexity of stable and metastable structures for clusters with high N, and the difference in stable structures suggested by various authors. Graphs for higher N clusters yield similar results to Figs. 2 and 4. In Fig. 5, for example, we show the variety of structures which can occur for $N=11$, depending on the value of C.

In carbon, the preference for a two-dimensional bulk structure (graphite) and the increased occurrence of double bonds leads us to suggest that a lower value of $C=0.25$ may be applicable. Our calculations then suggest that the structure of small carbon clusters will be chainlike. This is different from that of silicon clusters, although the same physics of covalency is present. This is in agreement with *ab initio* work which suggests that small carbon clusters form chains, but the model is unable to explain the mechanism which causes these chains to be closed (i.e., rings) for even-numbered clusters and

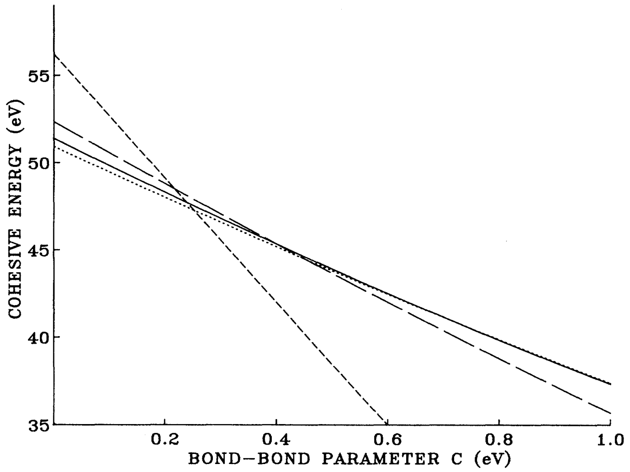

FIG. 5. Cohesive energy of various cluster configurations for $N=11$, shown as a function of the bond-bond repulsion parameter C. The short-dashed line represents the double-bonded ring, the long-dashed line the cube with a single trimer cap, the dashed line the cube with one monatomic cap and one dimer cap, and the dotted line the cube with three monatomic caps.

linear for odd-numbered clusters. We believe that this failure is related to delocalization (resonance) effects which are not considered by the model. In germanium, another material to which the model could reasonably be applied, the structure of small clusters is broadly similar to silicon.

We also note that the onset of covalent bonding can be seen in clusters as small as three atoms (the acute isoceles triangle cannot be explained by metallic-type dissociated electrons), but that the equilateral triangle can occur as a result of either covalent or metallic bonding. The four-atom cluster is the smallest which gives a topological divergence from the close-packing result for silicon.

We have shown that the same empirical model can be used to predict both bulk structures and cluster configurations in agreement with all-electron calculations. We believe that the localized electrons must be considered explicitly (their positions defined) in a widely applicable model for covalent materials, and that the possibility of multiple bonds must be allowed for.

The addition of the bond-bond term does not affect the conclusions of our previous paper with regard to surface reconstruction or defect formation. The formation energies are increased slightly, which actually improves their agreement with *ab initio* calculations marginally.

The relative insensitivity of the stable configurations to details of the parametrization is powerful evidence that the model captures the essential physics behind covalent bonding, and compares favorably with other empirical schemes which work well in certain regimes (for which they were parametrized) but lack transferability. Only one parameter was varied in this work, so that, while we have found regions which give configurations akin to carbon and germanium, the bulk potential parameters in these regions are not fitted to these materials (although, interestingly, the correct bulk structures are obtained, including the high-pressure graphite-diamond transition in carbon), and so the quantitative results are not reliable. The important aspect of this work is to show the transferability of the restricted bonding pair-potential scheme, and not to produce definitive parametrizations.

More generally, while simple physical principles can be used to derive useful empirical models for certain properties, the actual parametrization of these models may lead to vastly different answers for other properties when based on the extrapolation of an arbitrary function. In this work we have indicated, for one empirical model, which properties are well described as a result of the underlying physics (surface reconstructions, cagelike cluster structures, and asymmetric point defects) and which are strongly dependent on parametrization and arbitrary choice of functions (difference between covalent elements, quantitative energies). It is important to note that, whilst this second group may be well reproduced by judicious parametrization, they cannot be explained using the physics incorporated in the model.

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