

Calculation of Magic Numbers and the Stability of Small Si Clusters

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We present calculations of the equilibrium structures and cohesive energies for Si clusters up to the size $n = 14$. No open structures and no diamond-lattice fragments are found. Especially stable structures found for $n = 6$ and 10 coincide with experimentally observed magic numbers.

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Presently, there is much interest in small semiconductor (Si, Ge, C) clusters, which show strong and reproducible structure in both their nucleation and photofragmentation mass spectra.¹

In these materials, cluster sizes which occur in abundant number ("magic numbers") are smaller than previously observed in van der Waals² (Xe, . . .) and metallic^{3,4} (Na, Pb, . . .) clusters. In the van der Waals case, abundant occurrence of 13-, 55-, etc., atom clusters has been explained by stable icosahedral packing,² and in the metallic case (e.g., Na) the shell structure of jellium droplets seems to explain the data⁴ without pronounced structural dependence. On the other hand, the different (directional) type of bonding in semiconductors is expected to prefer other atomic arrangements whose stability shows a significantly dif-

ferent size dependence. In fact, small crystalline fragments have been proposed as stable clusters. In this Letter we present detailed calculations searching for the equilibrium structures and cohesive properties of Si₂ to Si₁₄ clusters. The main results are these: (i) Rather close-packed structures can be found significantly lower in energy than the corresponding crystal fragments and (ii) particularly stable structures occur for $n = 6$ and 10 and possibly $n = 4$ which coincide with experimentally observed magic numbers.

The calculations are done in two steps: First, we globally search in the $3n$ -dimensional space for the equilibrium geometries of Si_{*n*} using a simple empirical, nearest-neighbor, tight-binding (TB) Hamiltonian which is an extension of the formalism developed by Chadi.⁵ The total energy of a cluster (with respect to isolated atoms) is expressed as

$$E_{\text{tot}} = \sum_{\alpha} n_{\alpha} \epsilon_{\alpha} - n \sum_{\beta=s,p} n_{\beta}^0 \epsilon_{\beta}^0 + \sum_{i < j} E_r(d_{ij}) - n[\psi_1(n_b/n)^2 + \psi_2(n_b/n) + \psi_3] + U \sum_{i=1}^n (q_i - q_i^0)^2. \quad (1)$$

The first term is the one-electron energy, where the molecular levels ϵ_{α} have been obtained from a four-state TB Hamiltonian with parametrized nearest-neighbor matrix elements as given by Chadi.⁵ The second term is the corresponding reference energy of isolated neutral atoms (β denotes atomic levels). The sum of the first two terms defines a "band-structure" energy E_{bs} . The third term is a semiempirical correction to the double counting of electron-electron interactions, the exchange correlation energies, and also the ion-ion repulsion energy. It is given by a sum of pairwise repulsive interactions $E_r(d)$. Chadi originally parametrized $E_r(d)$ locally around the perfect-crystal energy minimum. This is not good enough here, since we expect a range of bond lengths and bonding configurations, drastically different from the perfect crystal. We therefore define $E_r(d) = E_{\text{tot}}(d) - E_{\text{bs}}(d)$ and construct it in a way to reproduce the total-energy curve $E_{\text{tot}}(d)$ of the diatomic molecule, as given by an *ab initio* calculation.⁶ This, by definition, exactly reproduces the entire diatomic binding-energy curve. The fourth term is an attempt to correct for energy changes arising from different numbers of bonds (n_b), found in different geometries of the same cluster size (n). In absence of this term, the nearest-neighbor-only TB Ham-

iltonian would always favor maximum coordination and metallic structures in contrast to experimental evidence. The values $\psi_1 = 0.225$ eV, $\psi_2 = 1.945$ eV, and $\psi_3 = -1.03$ eV are adjusted to reproduce the absolute cohesive energies of both diamond-structure and bcc silicon⁷ and make this term vanish for Si₂. With this correction the model reproduces a wide range of atomic coordination numbers (from ~ 1 to ~ 8). The correction for coordination changes, however, is only partial and some dependence of E_{tot} remains on the bonding to more distant atoms or on the definition of nearest-neighbor atoms. The last term finally treats intra-atomic Coulomb interactions making geometric arrangements with large charge transfer ($q_i - q_i^0$) less favorable. We here use an approximate value of $U = 1$ eV and derive the charge q_i at the site i from a Mulliken population analysis. We find our results rather insensitive to the value of U . Finally, the difference between neutral and charged clusters can approximately be described by accordingly restricting the sum in the band-structure term.

The TB Hamiltonian defined above yields the *ab initio* results for Si₂ exactly, i.e., $d_0 = 2.27$ Å (2.24), $E_{\text{coh}} = 3.07$ eV (3.0), and $\omega_0 = 519$ cm⁻¹ (511); for

diamond silicon it yields $a_0 = 5.47 \text{ \AA}$ (5.43), $E_{\text{coh}} = 4.6 \text{ eV}$ (4.63), and $B = 0.88 \text{ a.u.}$ (0.99) for lattice constant, cohesive energy, and bulk modulus, respectively. The experimental values are given in parentheses. For the high-pressure bcc phase the model yields $a_0 = 3.25 \text{ \AA}$ (3.12), $E_{\text{coh}} = 4.2 \text{ eV}$ (4.24) in comparison to local-density approximation (LDA) calculations by Yin and Cohen.⁷ The quality of the cluster results will be discussed in detail below.

The search for equilibrium geometries of neutral Si_n clusters is initiated by minimizing E_{tot} given in Eq. (1) using an analytic expression of the Hellmann-Feynman forces by starting with a large number (10–20) of different “seed” bonding configurations for each cluster size. Few (2–3) stable configurations result from this search. The resulting energies of the most stable structures for different cluster sizes are given in Fig. 1. Rather similar distributions are found for neutral or positively or negatively charged clusters. All tight-binding calculations were done on an AT&T PC 6300 personal computer.

We then proceed to step 2 and in detail investigate

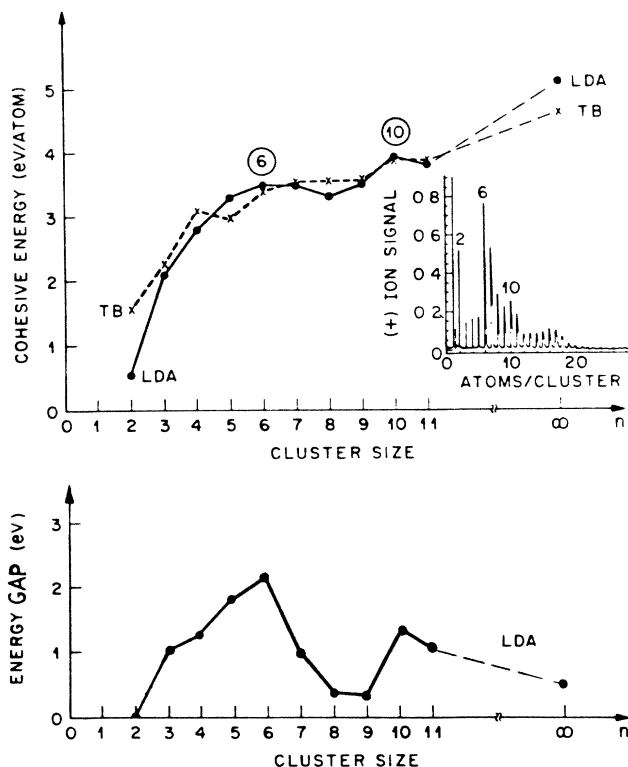


FIG. 1. Cohesive energies per atom (top panel) for the most stable arrangements of Si_n clusters. Tight-binding results (dashed line) are compared to local-density-functional results (solid line). Especially stable cluster sizes $n = 6$ and 10 coincide with clusters found abundantly in the experiment (see inset). The bottom panel shows the calculated LDA gaps and illustrates the strongly semiconducting character of the magic cluster sizes.

the several stable and metastable structures of Si_2 to Si_{10} using a self-consistent local-density-functional (LDA) scheme^{8,9} for E_{tot} . The ingredients here are the LDA functional of Ceperley and Alder, norm-conserving pseudopotentials of the Hamann-Schluter-Chiang type, and a Gaussian orbital basis with twenty orbitals per Si site. This scheme applied to bulk silicon reproduces plane-wave calculations with good accuracy.¹⁰ If applied to small clusters, however, the Gaussian orbital basis is expected to yield less accurate results and the cohesive energy will be systematically too small. This will, however, not affect the gross features of the binding-energy curve nor the general nature of the found stable structures. We also neglect spin-polarization effects which introduces additional errors on the same scale especially for small clusters.¹¹ It is rather satisfying to see how the original TB results agree qualitatively with the LDA results. Quantitative differences occur in both energies (see Fig. 1) and bond lengths as outlined below.

We now discuss the cluster structures in some detail. Si_2 was used as input for the tight-binding scheme. The LDA calculations yield the same bond length but a different binding energy.¹² The Si_3 structure is a triangle with an opening angle of $\sim 80^\circ$ which agrees with the singlet state found in independent first-principles calculations.¹¹ The restoring forces for bond-angle changes are rather small. Remarkably, the TB results for bond length, bond angle, and cohesive energy are within less than 5%. Si_4 is a flat rhombus with one diagonal about equal (2.4 \AA) to the side length of 2.3 \AA . The TB bond lengths are 2.5 and 2.4 \AA , respectively. In Si_5 a “squashed” trigonal bipyramid with base length of 3.1 \AA is favored over the tetragonal pyramid. A metastable minimum ($\Delta E \approx 0.3 \text{ eV/atom}$) exists for a “pointed” bipyramid with base length of 2.3 \AA . The corresponding TB results are 3.3 \AA , 0.6 eV , and 2.5 \AA , respectively. The structure of Si_6 is a tetragonal bipyramid or distorted octahedron with a base length of 2.6 \AA and cap bond lengths of $\sim 2.3 \text{ \AA}$ which is much more stable ($\sim 0.6 \text{ eV/atom}$) than the relaxed sixfold ring, a fragment from bulk Si. The corresponding TB results are 2.8 \AA , 2.5 \AA , and 0.6 eV . Another, more distorted structure is found for Si_6 at slightly higher energy. From Si_7 to Si_9 stable structures are found by addition of atoms as caps to the Si_6 distorted octahedron in such a way that their mutual distance is maximal. This leads for Si_{10} to a regular octahedron structure with four caps leaving alternating sides empty. Another high-symmetry, but metastable, decahedron structure exists at $\sim 0.4 \text{ eV}$ higher energy. The open adamantane cage structure, a fragment of bulk Si, is far less stable ($\sim 0.9 \text{ eV/atom}$) although it is topologically connected to the octahedral equilibrium structure¹³ (see details below). For Si_{11} through Si_{14} additional caps are added to Si_{10} and the

structures are allowed to relax. Some of the structures show Jahn-Teller distortions when a symmetry reduction is needed to lift the degeneracy of the highest occupied molecular orbital. A detailed discussion of these results will be given elsewhere.¹⁴ The calculated equilibrium structures agree well with recent accurate *ab initio* calculations^{12,15} where available.

We now analyze the results. The TB curve suggests that Si₄, Si₆, and Si₁₀ should be especially stable while the LDA emphasizes only Si₆ and Si₁₀. It is interesting to note that the structure in the stability curve displayed in Fig. 1 (top) reflects the size dependence of the "band-structure" energy, while the other terms in Eq. (1) seem to play only a secondary role. This feature is well known¹⁶ and has been used to analyze bonding trends. From the inspection of our results we find a bonding highest occupied molecular orbital and antibonding lowest unoccupied molecular orbital and a large gap between these orbitals to be a favorable stability criterion. The calculated LDA gaps, shown in Fig. 1 (bottom), clearly illustrate this point.

In contrast to some recent speculations about the equilibrium structure^{1,17} for Si clusters, our calculations suggest that for cluster sizes $n \leq 14$ open bulk-like structures are much less stable than partially close-packed arrangements. If we consider, e.g., Si₆ in its tetragonal bipyramid configuration, the calculated (LDA) bond lengths are 2.3 Å for the fourfold apex atoms and 2.6 Å for the base, which is only weakly bound. The main bonding therefore originates from the two caps. As one decorates alternating pyramidal faces with threefold caps and produces Si₁₀ the bipyramid becomes perfectly octahedral (*O*) with a bond length of 2.55 Å still yielding some weak bonding. The main bonding now arises from the new, catenated threefold caps (*T*) with a bond length of 2.3 Å. Thus, although extra stability seems to derive from close packing, the main bonding is contained in the surface caps. However, adding more caps onto the free faces of the octahedron up to $n = 14$ does not produce extra stability (see Fig. 1, TB results) for the fully decorated octahedron. This is a result of over-coordination of Si atoms and clearly indicates that the bonding is different from the simple octahedral-type packing of spheres.¹⁸

There is a simple *topological* connection between the Si₁₀ equilibrium structure and the adamantane cage obtained by moving the *O* atoms outwards by ~ 0.9 Å and simultaneously the *T* atoms inwards by ~ 0.9 Å. Upon this structural inversion level crossing occurs and the bonding changes drastically in character and no octahedral bonding remains. In Fig. 2 we show the calculated LDA configurational energies along the minimum-energy path connecting the stable octahedral structure (*O*) and the metastable tetrahedral (relaxed) adamantane cage (*A*) (full curve). The energy differ-

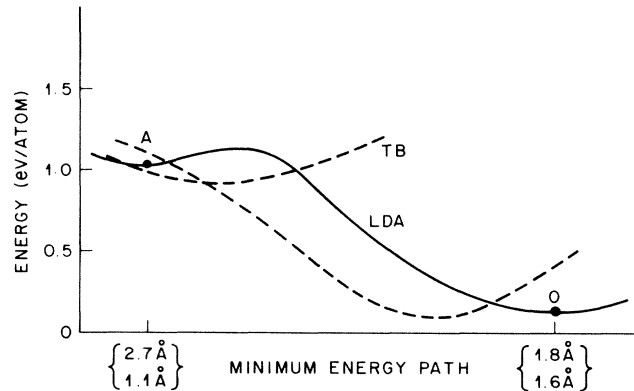


FIG. 2. Total-energy variation for Si₁₀ along the minimum-energy path connecting the stable octahedral structure *O* and the metastable adamantane structure *A*. Local-density-functional results (solid curve) are compared to two tight-binding results (dashed curves), obtained for *O*-type and *A*-type bonding. The octahedral atoms have coordinates $(X, 0, 0)$ with $2.7 \text{ \AA} > X > 1.8 \text{ \AA}$; the tetrahedral atoms have coordinates (Y, Y, Y) with $1.1 \text{ \AA} < Y < 1.6 \text{ \AA}$.

ence is large (~ 0.9 eV/atom) and the barrier is small (~ 0.1 eV/atom), virtually ruling the relaxed adamantane cage out as candidate for observable structures. Also shown are TB results along that same path. The two curves correspond to *O*-type and *A*-type nearest-neighbor connectivities. Both bonding configurations individually yield metastable minima; however, not along the LDA energy path shown in Fig. 2. The TB bond lengths are generally ~ 0.1 to 0.2 Å larger than the corresponding LDA values. This tendency of the TB Hamiltonian can be traced to the Si₂ total-energy curve which is too attractive at large distances ($d \geq 2.5$ Å) if applied to cluster bonding. One may use the LDA cluster results and *post hoc* adjust the TB Hamiltonian for large distances.¹⁴

The equilibrium structures of larger clusters are determined by the competition of bulklike atoms in sp^3 configuration preferring a network structure and the surface atoms which tend to minimize their number of broken bonds. Using the (calculated) energies of the diamondlike and close-packed arrangements from Si₁₀ and Si_{bulk} and using surface-to-volume ratios, we estimated the critical cluster size for the transformation from close packed to diamond to be in excess of $\sim 10^2$ atoms.¹⁴

It is interesting to note that the maxima in our total-energy curve for neutral Si_{*n*} clusters coincide with cluster sizes (positive ions) observed in abundant numbers during both the condensation and the photofragmentation¹ (see inset in Fig. 1). This has to be some surprise since (i) the role of charge states has not been fully considered and (ii) it is not clear from the experiment whether equilibrium conditions have

been reached during cluster growth. Clearly, both energetic and kinetic considerations are in general necessary to interpret these spectra. If we interpret the results of photofragmentation purely on energetic grounds, a binding-energy curve increasing smoothly with cluster size results in *single* atoms being preferentially ejected.¹⁴ This prevails until particularly stable fragments can occur, i.e., until the clusters are large enough to decay into $n=6$ or 10 fragments. This theoretical result is in accord with experimental findings¹ and thus underlines the importance of energetic considerations.

In Ge clusters, the similar type of bonding as in Si suggests similar stable structures. This hypothesis finds support in the observed¹⁹ mass spectra of Ge_n yielding the same magic numbers as Si and in calculated²⁰ equilibrium structures of Ge_2 - Ge_6 . A very different behavior, on the other hand, is expected for C_n clusters, where π bonding plays a significant role.^{17,21}

In conclusion, we investigated structural stability and cohesive energies for Si_n clusters up to $n=14$. The stable structures are found for rather close-packed atomic arrangements. The most stable clusters are, however, typical "semiconductors," i.e., with a large band gap between bonding and antibonding states. These clusters of size $n=6$ and 10 and possibly $n=4$ coincide with magic numbers observed in mass distribution spectra.

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¹³We thank K. Raghavachari for pointing this out to us.

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