# From van der Waals to Metallic Bonding: The Growth of Be Clusters

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*Ab initio* molecular-dynamics simulations were used to predict structures for beryllium clusters of two to twenty atoms. As a function of cluster size ($N$) the $sp$ hybridization converges quickly to the bulk value by $N=6$. Clusters with $N>7$ grow two dimensionally through a mechanism of prism addition and rhombus capping, beginning a growth pattern which quickly leads to an hcp lattice fragment. By $N=15$ the structure contains an element quantitatively similar to the primitive cell of the bulk. Despite strong directional bonding, the relative stability distribution obeys the predictions of the electronic shell model.

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Many materials exhibit dramatic changes in properties in passing from the molecular to the bulk state. Extreme examples are found in the group-II elements. Because these materials have a closed $ns^2$ shell and a high $np$ atomic excitation, they exhibit very weak binding in the dimer.[1] As the cluster grows in size, the unoccupied $p$ level lowers, reducing the $s$-$p$ gap.[2] The system then begins to exhibit properties associated with a metallic $sp$ band. For example, beryllium dimers are very weakly bound with a bond energy of 0.1 eV.[3] On the other hand, Be forms a strongly bound hexagonal-close-packed (hcp) metallic crystal with a cohesive energy of 3.32 eV/atom.

Recently, several experimental studies[4,5] have endeavored to probe this change in behavior as a function of cluster size for Hg. The results are consistent with a transition to metallic behavior for cluster sizes of $N>20$. The mass distributions of charged group-IIB atom clusters $Zn_n^+$ and $Cd_n^+$ have also been measured.[6] The results are consistent with the predictions of the electronic shell model and suggest that these systems are metallic for sizes as small as ten atoms. First-principles structural calculations have been carried out for some systems of higher $N$ but with very limited structural optimization. Despite the expected importance of structure to many properties, very little is known about the geometry of systems with $N>6$.

In this Letter we report calculations of the changes in fully optimized electronic and geometric structures of clusters of the group-II element beryllium as a function of size. Recently, Blaisten-Barojas and Khanna[7] (BBK) reported results using a very different approach. They fitted an empirical potential function (including up to three-body contributions) to the calculated potential surfaces of smaller clusters ($N\leq 5$) and used this potential to predict the lowest-energy structures as a function of size. The predicted geometries for the Be clusters, with the exception of $Be_8$ and $Be_{11}$, were very much like the minimum-energy structures of the rare gases. The bulk lattice was predicted to be hcp. Because several properties of the bulk were predicted correctly, BBK surmised that their fairly simple potential function gave accurate structures for intermediate clusters. If these results are correct it is remarkable because of the poor success of many others (on various systems) using even more complicated representations for the interatomic potential. However, the structures predicted by BBK are different from those obtained in this work. In fact, for $N>8$ the structures we report here bear no resemblance to those previously predicted for any system.

The structures of $Be_N$ ($N=2$–$20$) were calculated within the local-density approximation (LDA). As it is well known that cluster systems may have many nearly degenerate energy minima, simulated annealing (SA) was used to find the lowest-energy structure. An efficient approach to such a simulation within the LDA has recently been suggested by Car and Parrinello (CP).[8] This method has been successfully applied to cluster studies.[9,10] A detailed description of the CP method is given by Hohl *et al.*[10] A plane-wave basis set and generalized norm-conserved pseudopotentials[11] were chosen. These potentials were made fully nonlocal by the method of Kleinman and Bylander.[12] A simple cubic supercell with a lattice constant of $22a_0$ was found to provide adequate isolation for the cluster.

Small clusters ($N=2$–$7$) were efficiently optimized by a steepest-descent (SD) algorithm[8] applied to different assumed structures, rather than by SA. A cutoff energy of 20.9 Ry produced converged results. For larger clusters ($N=8$–$20$), SA was used because they have too many possible local minimum-energy structures. To save computing time a low cutoff energy of 8.1 Ry was chosen. A fictitious mass $\mu$ of 300 a.u. and an integration time step of 5 a.u. gave sufficient accuracy. In the SA runs the systems were equilibrated for 2000 time steps at a temperature above the bulk melting point. They were then cooled (cooling rate $10^{14}$–$10^{15}$ K/sec) until solidlike dynamics appeared. At this point the SA run was terminated and the system was finally quenched by SD using a cutoff energy of 20.9 Ry. In order to ensure that the global minimum had been obtained, the systems were reheated and again cooled. These runs in

nearly every case led to the same final configurations despite the rapid cooling rate, supporting the assertion that the ground state had been obtained. Repeated annealing runs were only feasible for systems up to $N=16$. To ensure that the structures we obtained were improvements over the previously proposed geometries, several local minimum-energy structures including those proposed by BBK were calculated using the SD algorithm. In all cases the configurations we obtained by SA were lower in energy than those obtained by SD. Triplet and quintet states were also calculated up to $N=10$. For $N \geq 6$, the triplet states are nearly degenerate with the singlet states, except for $Be_9$ whose triplet state is 0.27 eV lower in total energy. As the difference in the cohesive energy and other properties shown here is so small, we emphasize only the singlet states in this paper.

For $N<7$ our calculated structures agree with those calculated by others[13,14] and are qualitatively similar to those formed by rare-gas elements. However, it should not be inferred that the binding is related to that of van der Waals systems. The population of $p$-type orbitals [Fig. 1(a)] approaches the bulk value very quickly as a function of cluster size. The band of mostly $p$-type molecular orbitals broadens and begins to overlap the $s$ band by $N=4$. The highest filled orbital of the singlet $Be_6$ has pure $p$ character instead of the nearly pure $s$ character expected for rare-gas clusters. In addition, a triplet state is slightly lower in energy for this system. This is dramatically different from the singlet ground state of a rare-gas system. Furthermore, the $N=6$ and 7 systems show considerable deviation from the highly symmetric rare-gas clusters. The cohesive energy rises less quickly, reaching half the bulk value by $N=6$ [Fig. 1(b)].

The structures for systems $N=8$–11, shown in Figs. 2 and 3, are very different from those of rare-gas systems. The structure of $Be_8$ is a dicapped trigonal prism with a fairly large distortion [Fig. 2(a)]. A similar structure was predicted by BBK. For $N>8$ the minimum-energy structures differ markedly from those of BBK. $Be_9$ is a tricapped trigonal prism [Fig. 2(b)] of $C_{3v}$ symmetry formed by capping the remaining rectangular face [1-2-5-4 in Fig. 2(a)]. $Be_{10}$ results from capping the rhombus face [1-7-4-9 in Fig. 2(b)]. The structure obtained has $D_{4d}$ symmetry. Capping another rhombus face [2-8-5-9 in Fig. 2(c)] leads to $Be_{11}$ [Fig. 3(a)].

The structure of $Be_{11}$ is very close to a fragment of bulk hcp. A twelve-atom fragment of the bulk is shown in Fig. 3(b). Band-structure calculations[15] indicate that triangles which are coordinated with atoms above and

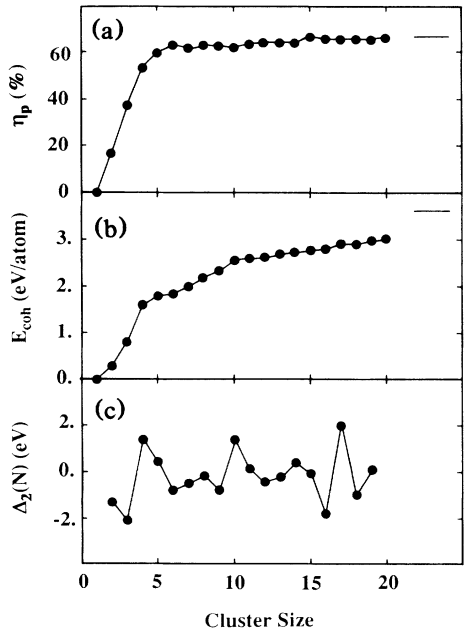


FIG. 1. (a) Population of $p$-character electrons, (b) cohesive energy, and (c) second finite difference of the total energy $\Delta_2(N)=E(N+1)+E(N-1)-2E(N)$. Theoretical bulk values (Ref. 15) are shown at the top right corner.

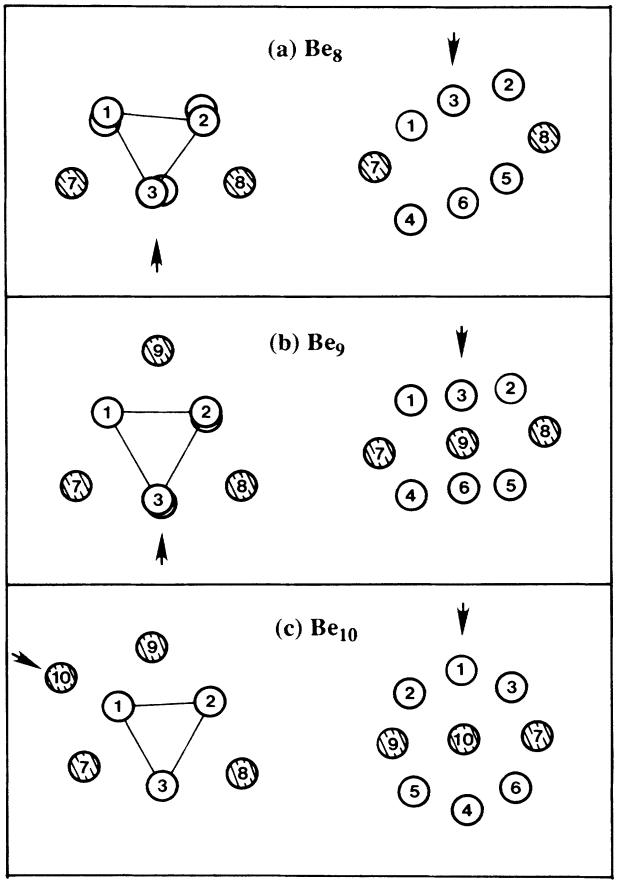


FIG. 2. Structures of beryllium clusters of size $N=8$–10. Atomic configurations are projected onto the plane normal to the $D_{3h}$ symmetry axis of the prism (left). Shaded particles indicate the capping atoms. Another view (the view direction is indicated by the arrow in the left figure) is shown on the right.

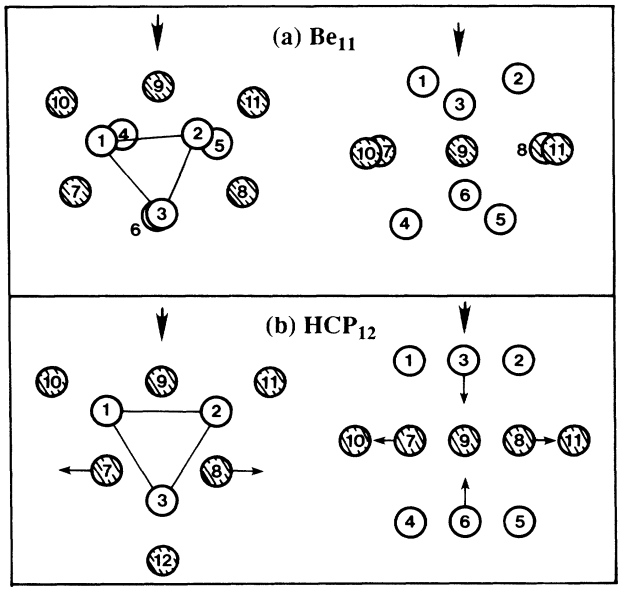


FIG. 3. Structures of (a) $Be_{11}$ and (b) a fragment of the hcp lattice. Small arrows indicate the directions of distortion due to removal of atom 12.

below [triangles 7-9-10, 8-9-11, and 7-8-12 in Fig. 3(b)] have high electron densities. The three corner atoms of these triangles interact strongly. If atom 12 is removed from the cluster, the binding between 7-8-12 is destroyed. Atoms 7 and 8 are no longer bound to each other and move apart. On the other hand, atoms 3 and 6 now move together to form a strong bond. The small arrows in Fig. 3(b) show the directions of distortions due to the removal of atom 12. Apart from small Jahn-Teller distortions, the resulting structure is close to that of $Be_{11}$. The distances 1-2 and 1-4, which correspond to the bulk lattice constants $a$ and $c$, respectively ($a=4.3a_0$ and $c=6.8a_0$), are $3.8a_0$ and $6.0a_0$.

If another atom [11 in Fig. 3(b)] is removed, the interaction between atoms 8 and 9 weakens and atoms 2 and 5 are bound together. This leads to the structure of $Be_{10}$. Similarly, the structure of $Be_9$ can be obtained by removing atom 10. There is no high-electron-density triangle in $Be_9$ and thus the capping atoms (7, 8, and 9) do not interact strongly with each other. $Be_8$ and $Be_9$ do not look like an hcp fragment. However, continuous capping of rhombus faces from $Be_8$ leads the system to hcp-like $Be_{11}$.

If the twelfth atom capped the rhombus 3-7-6-8 in $Be_{11}$, the structure would be a perfect hcp fragment. However, the lowest-energy structure predicted by the SA is quite different. The growth of structures beyond $Be_{11}$ can be characterized as prism addition and rhombus capping. $Be_{12}$ and $Be_{13}$ have very disordered structures, but two trigonal prisms are clearly identified. Those structures are closely related to the structure of $Be_{14}$ shown in Fig. 4. The structure of $Be_{13}$ may be obtained

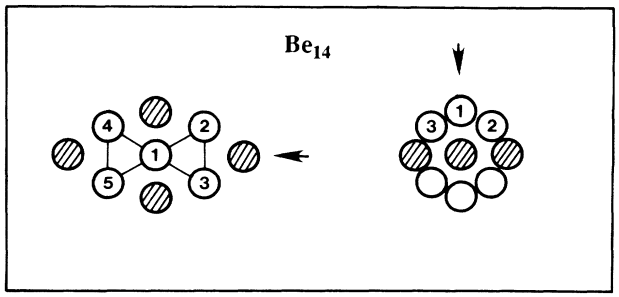


FIG. 4. The structure of $Be_{14}$.

from $Be_{14}$ by removing one of the capping atoms adjacent to atom 1 in Fig. 4, and then atoms 3 and 5 make a direct bonding. This structure is very different from the icosahedral structures predicted by BBK and hcp or fcc fragments studied in the Hartree-Fock approximation.[16,17] In order to ensure that the $Be_{13}$ geometry we obtained is lower in energy, we performed SD optimization on the icosahedral structure. The optimized icosahedron showed a large distortion from the ideal configuration and its energy was 0.7 eV higher than our thirteen-atom structure.

At $N=15$ an important new kind of addition takes place. The first interior atom appears in a three-prism structure [Fig. 5(b)]. This structure is again quantitatively similar to a fragment of the beryllium hcp crystal [Fig. 5(a)] and includes a primitive cell of the lattice. Rapid quenching in the fifteen-atom system also pro-

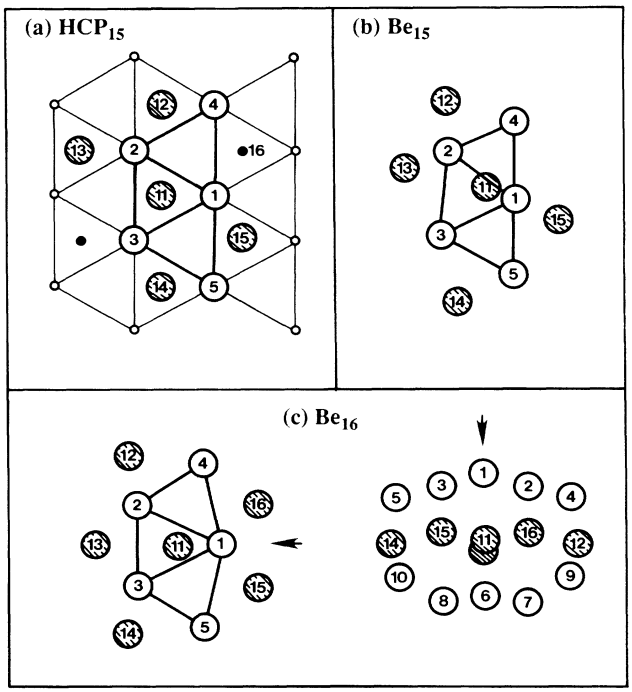


FIG. 5. Structures of (a) a fragment of the hcp lattice, (b) $Be_{15}$, and (c) $Be_{16}$.

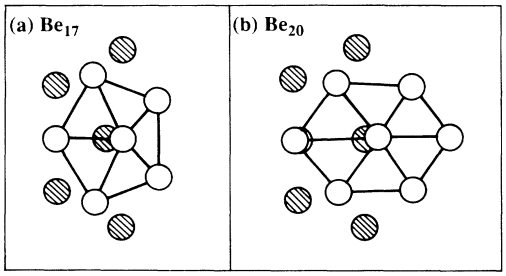


FIG. 6. Structures of (a) $Be_{17}$ and (b) $Be_{20}$.

duced a local minimum in one run. In this case the structure was characterized by two staggered hexagonal layers. Again, this is very similar to a fragment of the hcp lattice and emphasizes the importance of these fragments in the growth pattern. $Be_{16}$ is constructed by placing an atom at site 16 in Fig. 5(a). A highly symmetric structure ($D_{3h}$) is obtained. This structure is also similar to the hcp structure except for atom 13 in Fig. 5(c). The distances 11-16 and 1-6 are $4.1a_0$ and $6.4a_0$, respectively. These values are closer to the bulk lattice constants than those of $Be_{11}$ because of the interior atom.

In the sixteen-atom system all the faces are capped. There is no position for another interior atom. Rather than capping a triangular surface, the seventeen-atom system grows two dimensionally by adding two prisms resulting in a highly symmetric structure ($D_{4d}$) with pentagonal faces [Fig. 6(a)]. This structure does not look like the hcp structure and appears to be intermediate on the way to forming the complete hexagonal structure. A hexagonal face appears in $Be_{19}$ and $Be_{20}$ [Fig. 6(b)].

The remarkable persistance of a two-dimensional growth pattern related to the hcp lattice, even with the extremely rapid cooling rates, suggests that directional binding is very important in beryllium clusters and crystals. Therefore, although beryllium clusters are not expected to display simple metallic behavior, it is interesting to compare the present results with the electronic shell model. This model has had considerable success predicting the stability of simple metal clusters as a function of size.[18] The second-order finite difference of the calculated total energy [Fig. 1(c)], which can be related to the abundance of clusters measured in experiments,[18] shows large maxima at $N=4$, 10, and 17. Remarkably, these numbers correspond exactly to those predicted by the electronic shell model. They are very different from the results of BBK. Further insight into the general applicability of the electronic shell model to metallic systems can be obtained from the behavior of the Kohn-Sham eigenvalues as a function of cluster size. In the Be system the orbital energies form bands, each of which contains exactly $2l+1$ ($l$ is the angular momentum) states. The nodal properties of the orbital wave functions in these bands correlate well with the predictions of the shell model. For the magic numbers where clusters show highly symmetric structures the bands are noticeably narrower and the band gaps between different manifolds are large. On the other hand, in some cases the bands are extremely broad. No band gap can be identified for the highly disordered $Be_{12}$ and $Be_{13}$.

Above we have shown that the growth of beryllium clusters can be analyzed in terms of simple patterns of prism growth and four-coordinated capping. Bulklike hcp structures appear at $N=11$, 15, and 16. The bonding pattern indicates rather strong directional effects. On the other hand, stability and orbital energy spectra are consistent with the electronic shell model suggesting that the electronic shell model can provide useful interpretations even for the divalent systems which are not simple metals.

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