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Structure and Bonding in Small Aluminum Clusters

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Density-functional calculations with simulated annealing have been performed for aluminum clusters Al_n up to $n=10$. There are many local minima in the energy surfaces, with a rich variety of structures and spin multiplicities. With increasing cluster size we find transitions from planar to nonplanar structures at $n=5$, and to states with minimum spin degeneracy at $n=6$. There are stable isomers of Al_5–Al_{10} with buckled planar structures reminiscent of the layers in crystalline α-gallium. *All* structures show regular patterns of bond and dihedral angles. Trends in binding and ionization energies are compared with experiment and with the predictions of other calculations.

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Interest in clusters in general and small metallic clusters in particular has grown dramatically in the last decade. There is justifiable confidence that the developments in both theory and experiment will lead to improved understanding of many properties of atomic aggregates, particularly those that reflect the transition from atomic→ molecular→ bulk behavior.

Aluminum has been a favorite element for cluster studies, including work on the magnetic properties [1], the ionization thresholds and reactivities [2], and the static polarizabilities of Al_n [3], the collision-induced dissociation of $Al_n{}^+$ [4], and the photoelectron spectroscopy of $Al_n{}^-$ [5]. Particular attention has been paid to the existence of prominent or unusually stable clusters, such as $Al_7{}^+$, with "magic numbers" of atoms or electrons. The electronic structure of bulk aluminum is characterized by small departures from free-electron behavior, and several theoretical studies of small Al_n clusters have adopted the "spherical jellium" model [6], where both the electronic charge and positive background distributions are uniform within a sphere of appropriate size. There are, however, many experimental data that cannot be explained by this model. The static polarizabilities show a transition from "nonjellium" to "jellium" behavior near $n=40$ [3], and ionization potentials show an initial linear increase, an abrupt leveling near $n=5$, and only then a gradual approach to the results of a jellium calculation [7]. Magnetic deflection measurements [1] indicate a transition to states with low spin multiplicity as n increases. It is clear that detailed calculations of geometries are essential to explain measured properties of clusters with less than ∼40 atoms.

The stable isomers of a cluster can be found by locating the low-lying minima in the energy surface. In the aluminum dimer there is excellent agreement between the most detailed experiments and calculations [8], but in larger clusters the results are limited [9] and often contradictory [10]. There are many minima in the energy surface in all but the smallest clusters, and it is essential to perform reliable calculations of the energy surfaces *and* to avoid the energetically unfavorable minima. We study here the structures and ionization energies of aluminum clusters up to Al_{10}, using such a method [11]: a combination of density-functional calculations [12] [with a local spin density (LSD) approximation for the exchange-correlation energy] and finite-temperature molecular dynamics. The method is described in earlier applications [13], and the present calculations use the same basis functions and pseudopotential construction [14] as in the P_n calculations.

The results for Al_2 and Al_3 agree well with available data [8,15]. The ease of transfer between σ and π electrons in Al_2 is reflected in the near degeneracy between the $^3\Pi_u$ and $^3\Sigma_g^-$ states, and our calculations find the former to be slightly (0.06 eV) more stable. The equilibrium separations r_e and vibration frequencies ω_e are in excellent agreement with experiment for both states [16]. The well depth (2.03 eV compared with the experimental value 1.5 eV) [17] agrees with all-electron, basis-set-independent molecular calculations [18]. The most stable form of Al_3 is an equilateral triangle ($^2A_1$, $r_e=4.65$ a.u.) [19], and in Al_4 the planar rhombus structure (D_{2h}) ($r_e=4.75$ a.u., bond angle $\alpha=56.5°$) is ∼0.4 eV more stable than the compressed pyramid (C_{3v}) shown in Fig. 1.

The structures and spin degeneracies of the most stable planar and nonplanar ("3D") isomers in Al_4 to Al_8 are shown in Fig. 1. The corresponding binding energies [Fig. 2(b)] increase with increasing n towards the bulk cohesive energy [20] and show two important trends: (a) At $n=5$ there is a transition from planar to nonplanar ground states. In Al_5, a planar C_{2v} structure is almost degenerate with a C_s structure with similar bond lengths. (b) States with minimum spin degeneracies are favored for $n>6$. In Al_6, the lowest-lying singlet (D_{3d}) and triplet (D_{2d}) states are nearly degenerate [21].

The most remarkable structures occur in Al_7 to Al_{10}. Our earlier work on sulphur and phosphorus led to relatively few stable minima in seven-membered clusters, and this is also true in Al_7. Two stable isomers—a nearly symmetric capping of Al_6 (D_{3d}) and a planar form ∼0.8 eV higher in energy—have large basins of attraction, i.e., each is the closest minimum for a large region of configuration space. If the "dangling" atom in the Al_8

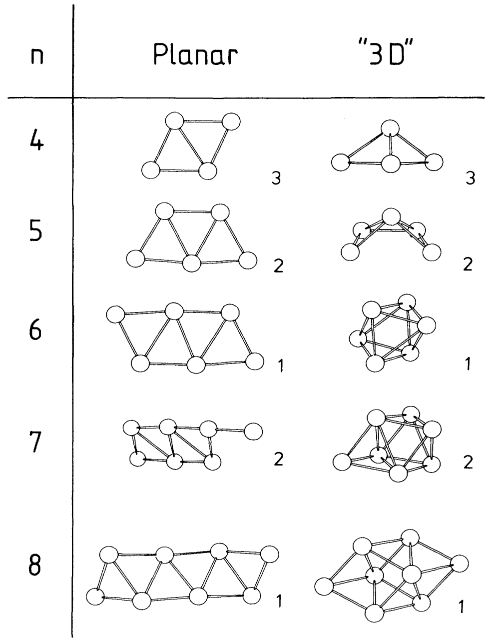

FIG. 1. The structures and spin multiplicities of the most stable planar and "three-dimensional" isomers of Al_n, $n=4$–8. Bonds are shown if the interatomic distance is less than 5.48 a.u. The planar structure in Al_8 corresponds to a saddle point in the energy surface, and buckles readily.

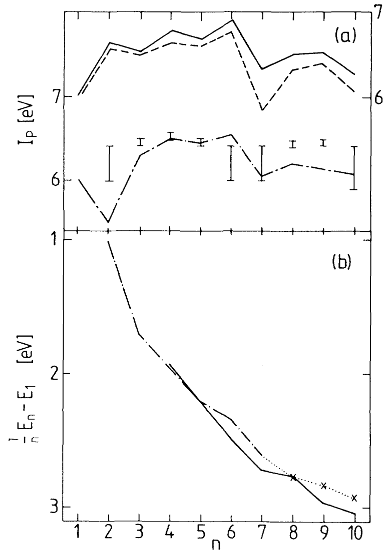

FIG. 2. Energy differences in aluminum clusters: (a) Ionization potential I_p for both vertical (full curve) and adiabatic (dashed curve) transitions. Experimental values after Cox *et al.* [1] (bars) and Jarrold, Bower, and Kraus [4] (dot-dashed curve). The experimental (left scale) and theoretical curves (right scale) are displaced by 1 eV. (b) Binding energies for 3D (full curve), planar (dot-dashed curve), and buckled planar (crosses) structures.

structure of Fig. 3(c) is removed, for example, the resulting cluster relaxes to the planar form. The results for Al_8 to Al_{10} are qualitatively different, not only because the planar forms are unstable. In addition to a C_{2h} isomer of Al_8 (a distortion of the structure familiar as the primative cell of the fcc lattice), we found numerous buckled planar arrays. The examples shown in Figs. 3(a)–3(c) are more stable (by <0.1 eV) than the bulklike fragment (Fig. 1), and all conform to the pattern found in Al_5: almost equilateral triangles, connected so that they are either coplanar (dihedral angle γ near 0°) or have $\gamma \sim 50°$. Interconversion between these structures can be observed in simulations at 300–500 K, and they also occur with a single extremal atom, as in Fig. 3(c). The energies of the isomers 3(b) and 3(c) are almost identical.

The binding-energy trends in Fig. 2(b) show that the C_{2h} isomer in Al_8 is relatively weakly bound, and this is reflected in bonds that are longer than those in the related structures of Al_7 and Al_9. In Al_9 and Al_{10}, bulklike structures are significantly more stable than the buckled planes. The most stable isomer in Al_9 (C_{3v}) has the C_{2h} structure of Al_8 with an additional dangling atom, and capped structures of Al_9 are the most stable in Al_{10}. In Al_{10}, the "open" arrays of triangles in the buckled planes distort towards "closed" bulklike structures, and we observed interconversion between different capped structures. We also found a stable structure comprising Al_3 and Al_7 units. In fact, there are so many local minima in the energy surface for Al_{10} that a detailed study of even larger clusters will be extremely difficult. Full details of all structures found will be given elsewhere.

In addition to the binding energies, we show in Fig. 2 the results of two calculations of the ionization energy I_p: (a) for the structure of the most stable isomer found for Al_n; (b) for the relaxed structure of $Al_n{}^+$. Also shown

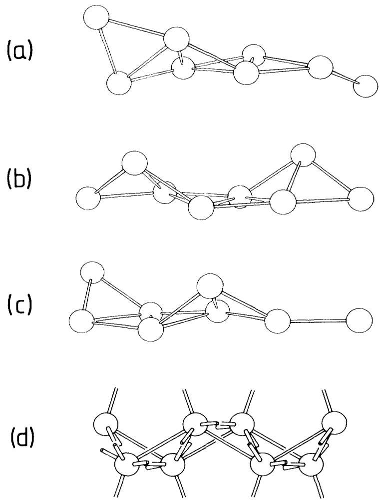

FIG. 3. (a)–(c) Three buckled planar structures of Al_8. (d) Layer structure in bulk α-Ga.

are experimental bounds on the ionization thresholds [1] and I_p values derived from the product branching ratios in collision-induced dissociation of $Al_n{}^+$ clusters [4]. The experimental trends are reproduced well: I_p increases initially to a maximum at Al_6 [4], and has a sharp minimum at Al_7 [1]. The dissociation energies of the ions decrease in the order $Al_7{}^+ > Al_9{}^+ > Al_{10}{}^+ > Al_6{}^+ > Al_5{}^+ > Al_4{}^+, Al_3{}^+ > Al_8{}^+$. The high stability of $Al_7{}^+$ and the low stability of $Al_4{}^+$ have been noted elsewhere [4].

The energy change on relaxation is much larger in $Al_7{}^+$ ($\sim$0.5 eV) than in the other ions (<0.2 eV). The final structure (C_{3v} symmetry) is very compact, with bonds from an atom in the central layer to atoms in base and apex of equal length (4.78 a.u.). The $Al_7{}^+$ ion is one of the most prominent in-beam experiments, and its stability has been related to the "magic number" of 20 valence electrons in the spherical jellium model. In the present calculations, the dissociation energy of Al_7 is larger than those of Al_6 and Al_8, and there is an unusually large separation (1.15 eV) between the highest (singly) occupied orbital and the next highest (doubly degenerate) orbital. The large gap between the energy eigenvalues of valence electrons 20 and 21 is consistent with the low ionization energy in Al_7. The gap between the corresponding eigenvalues in the planar structure ($\sim$0.8 eV) is smaller, but significantly larger than typical energy differences in other Al clusters. These large gaps are in accord with the pronounced stabilities of both $Al_7{}^+$ isomers.

The variety of structures found here is consistent with the "metallic" nature of the element: The valence *sp* shell in the atom is less than half filled, and there are usually unoccupied bonding orbitals near the highest occupied orbital. Furthermore, it is easy to transfer electrons between π orbitals (which dominate in the bonding in planar structures) and σ orbitals. The stable structures show remarkably uniform patterns of bond and dihedral angles. These are also found in bulk aluminum and in α-gallium, for which we show a single layer in Fig. 3(d) [22], and molecular dynamics simulations of liquid Al [23] show peaks in the bond-angle distributions at 60° and near 110°.

The prediction of new structures in aluminum clusters underlines the advantages of a method using finite-temperature simulated annealing. Studies of the relative stabilities of these structures using other methods would be of interest, although buckled planar structures are less accessible to methods that focus on spherical cluster forms. Also interesting are the departures from regular trends, such as the low dissociation energy in Al_8 and the low I_p in Al_7. Finally, the large relaxation energy found in $Al_7{}^+$ indicates that precise measurements of the variation in ionization energies should provide information about the relaxation of ionic structures.

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[1] D. M. Cox, D. J. Trevor, R. L. Whetten, E. A. Rohlfing, and A. Kaldor, J. Chem. Phys. **84** 4651 (1986) ($n=2$–25). These experiments indicate that Al_6 and Al_8 are probably triplets, with Al_{10} a singlet.

[2] D. M. Cox, D. J. Trevor, R. L. Whetten, and A. Kaldor, J. Phys. Chem. **92**, 421 (1988) ($n=2$–13).

[3] W. A. de Heer, P. Milani, and A. Châtelain, Phys. Rev. Lett. **63**, 2834 (1989) (up to $n=61$).

[4] M. F. Jarrold, J. E. Bower, and J. S. Kraus, J. Chem. Phys. **86**, 3876 (1987) ($n=3$–26); L. Hanley, S. A. Ruatta, and S. L. Anderson, J. Chem. Phys. **87**, 260 (1987) ($n=2$–7).

[5] G. Ganteför, M. Gausa, K. H. Meiwes-Broer, and H. O. Lutz, Z. Phys. D **9**, 253 (1988) ($n=3$–14); K. J. Taylor, C. L. Pettiette, M. J. Craycraft, O. Chesnovsky, and R. E. Smalley, Chem. Phys. Lett. **152**, 347 (1988) ($n=3$–32).

[6] See W. A. de Heer, W. D. Knight, M. Y. Chou, and M. L. Cohen, in *Solid State Physics,* edited by H. Ehrenreich and D. Turnbull (Academic, New York, 1987), Vol. 40, p. 94, and references therein.

[7] K. E. Schriver, J. L. Persson, E. C. Honea, and R. L. Whetten, Phys. Rev. Lett. **64**, 2539 (1990).

[8] Al_2: Recent experimental work [M. F. Cai, T. P. Djugan, and V. E. Bondybey, Chem. Phys. Lett. **155**, 430 (1989)] supports theoretical predictions [C. W. Bauschlicher, Jr., H. Partridge, S. R. Langhoff, P. R. Taylor, and S. P. Walch, J. Chem. Phys. **86**, 7007 (1987); K. K. Sunil and K. D. Jordan, J. Phys. Chem. **92**, 2774 (1988)] that the $^3\Pi_u$ $(1\pi_u^1 2\sigma_g^1)$ is slightly (less than 0.025 eV) more stable than the $^3\Sigma_g^-$ $(1\pi_u^2)$ state.

[9] Calculations of clusters up to $n=15$ have been reported by K. Raghavachari, Bull. Am. Phys. Soc. **35**, 606 (1990).

[10] G. Pacchioni and J. Koutecký [Ber. Bunsenges. Phys. Chem. **88**, 242 (1984)] predict the most stable structures in Al_3–Al_5 to be deformed fragments of the bulk (face-centered cubic) lattice, with high spin multiplicities. By contrast, Upton [T. H. Upton, J. Chem. Phys. **86**, 7054 (1987); configuration-interaction calculations of the energy for geometries optimized using generalized valence bond calculations] found ground states of C_{2v} symmetry in Al_3–Al_5, and D_{2h} symmetry in Al_6, and states with *minimum* spin degeneracy are favored in Al_3, Al_4 and Al_5. The structures are three dimensional starting with Al_4. Other calculations for Al_4 led to a planar rhombic (D_{2h}) ground state [Pacchioni and Koutecký, *op. cit.;* J. Koutecký, G. Pacchioni, G. H. Jeung, and E. C. Hass, Surf. Sci. **156**, 650 (1985); U. Meier, S. D. Peyerimhoff, and F. Grein, Z. Phys. D **17**, 209 (1990); L. G. M. Petterson, C. W. Bauschlicher, Jr., and T. Halicioglu, J. Chem. Phys. **87**, 2205 (1987)], and Petterson, Bauschlicher, Jr., and Halicioglu also found a planar ground state in Al_5, with Al_6 having O_h symmetry.

[11] R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985).

[12] For a survey of the density-functional formalism, see R. O. Jones and O. Gunnarsson, Rev. Mod. Phys. **61**, 689 (1989).

[13] D. Hohl, R. O. Jones, R. Car, and M. Parrinello, J. Chem. Phys. **89**, 6823 (1988) (S_n); P. Ballone, W. Andreoni, R. Car, and M. Parrinello, Phys. Rev. Lett. **60**, 271 (1988) (Si_n); R. O. Jones and D. Hohl, J. Chem. Phys. **92**, 6710 (1990) (P_n).

[14] We use the nonlocal pseudopotential of G. Bachelet, D. R. Hamann, and M. Schlüter, Phys. Rev. B **26**, 4199 (1982), with *sp* nonlocality, a plane-wave basis with energy cutoff 5.3 a.u., and a fcc unit cell with lattice constant 30 a.u.

[15] Al_3: The most stable isomers have bond angles $\alpha \sim 60°$. Configuration-interaction calculations lead either to a $^2A_1$ ground state [H. Basch, Chem. Phys. Lett. **136**, 289 (1987); ($r_e = 4.855$ a.u., $\alpha = 56.2°$), with $^2B_2$, $^4A_2$, and $^4B_2$ states 0.22–0.31 eV higher; J. S. Tse, J. Mol. Struct. (Theochem) **165**, 21 (1988): (4.82 a.u., 60°), with $^4A_2$, $^4B_1$, and $^2B_1$ states 0.29–0.45 eV higher] or a near degeneracy between $^2A_1$ and $^4A_2$ states [Meier, Peyerimhoff, and Grein (Ref. [10]); Petterson, Bauschlicher, Jr., and Halicioglu (Ref. [10])]. Electron-spin-resonance measurements of matrix-isolated Al_3 indicate a quartet ground state [J. A. Howard, R. Sutcliffe, J. S. Tse, H. Dahmane, and B. Mile, J. Phys. Chem. **89**, 3595 (1985)], while magnetic deflection measurements (Ref. [1]) point to a doublet.

[16] $^3\Pi_u$: ($r_e = 5.104$ a.u., $\omega_e = 290$ cm^{-1}), experiment (5.10 a.u., 284.2 cm^{-1}) [Cai, Djugan, and Bondybey (Ref. [8]); $^3\Sigma_g^-$: (4.675 a.u., 340 cm^{-1}), experiment (4.660 a.u., 350.01 cm^{-1}) [K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979)].

[17] Huber and Herzberg (Ref. [16]).

[18] A. D. Becke, J. Chem. Phys. **84**, 4524 (1986).

[19] The $^2B_1$ state (4.83 a.u., 60°) is 0.32 eV above the ground state, with the $^4A_2$ and $^4B_1$ states ~0.1 eV higher.

[20] The measured cohesive energy is 3.33 eV [K. A. Gschneidner, in *Solid State Physics,* edited by H. Ehrenreich and D. Turnbull (Academic, New York, 1964), Vol. 16, p. 275] and an LSD estimate is 3.84 eV [V. L. Moruzzi, J. F. Janak, and A. R. Williams, *Calculated Electronic Properties of Metals* (Pergamon, New York, 1978)].

[21] In Al_6, there are numerous states with similar stabilities. The octahedral (O_h) structure found by Petterson, Bauschlicher, Jr., and Halicioglu [10] distorts to the D_{3d} structure, with bond lengths of 4.76 a.u. and 5.41 a.u.

[22] J. Donohue, *The Structures of the Elements* (Wiley, New York, 1974), Chap. 5. The fcc structure comprises equilateral triangles with dihedral angles 0°, 54.7°, or 109.5°. The α-Ga structure has dihedral angles of 0°, 40°, and 76°.

[23] V. A. Polukhin and M. M. Dzugotov, Phys. Met. Metall. **51**, 50 (1981); J. Hafner, J. Non-Cryst. Solids **117/118**, 18 (1990).