Magic triangular and tetrahedral clusters

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(Received 30 July 1997)

Using the methods of density functional theory and the jellium model we show that clusters with triangular [in two dimensions (2D)] or tetrahedral [in three dimensions (3D)] shapes have a strong shell structure and enhanced stability. Moreover, the shell closings correspond to the lowest magic numbers of a 2D and 3D harmonic oscillator and at the same time to the number of divalent atoms in close-packed triangles and tetrahedrons. *Ab initio* molecular dynamics simulations for Na and Mg clusters support the results of the jellium model. [S0163-1829(97)00943-0]

The enhanced stability of alkali metal clusters with certain numbers of valence electrons was discovered experimentally by Knight *et al.*[1] The large abundancies of such clusters could be attributed to a similar physical phenomenon as in the case of chemically inert noble gas atoms or so-called ''magic'' nuclei:[2] The emergence of shell structure as a direct consequence of single-particle motion in a mean field, being reflected in many of the physical properties of finite fermion systems.

Metallic clusters with a large energy gap between the lowest unoccupied (LUMO) and highest occupied (HOMO) level are especially stable. Spherical clusters with full electronic shells are basic examples.[3,4] It should be noted, however, that the Jahn-Teller[5] deformation opens up a marked gap also in all nonmagic clusters (see Ref. 6 for a review).

Metal clusters also show magic numbers corresponding to *geometrical packing* of atoms.[7] This is seen clearly for large clusters at low temperatures. Having in mind the electronic as well as the atomic shell structure of such clusters, one would expect that clusters with both filled electronic *and* atomic shells have a particularly large stability. However, for icosahedral packing (as for alkali and alkali earth metal clusters) or octahedral packing (for Al clusters) the electronic magic numbers do not match with the geometric ones. But an icosahedron with 12 Al atoms surrounding a carbon or a silicon atom forms a system with optimal packing of atoms and, at the same time, a magic number of 40 valence electrons. Indeed, calculations have shown that this cluster can have a reduced reactivity.[8]

The purpose of this article is to show that quasi-two-dimensional (2D) *triangular* and three-dimensional (3D) *tetrahedral* clusters can be magic in several ways: (i) They have especially strong shell structure. (ii) These geometries are in some cases preferred as opposed to spherical geometries. (iii) The first few magic numbers in triangles and tetrahedrons coincide with those of 2D and 3D harmonic oscillators. (iv) The triangular and tetrahedral clusters made of divalent atoms have magic numbers of electrons.

In alkali metal clusters, a strong magic number is observed at $N=40$. Indeed, from a detailed analysis[10] of the experimental mass abundancies[9] weaker intensity maxima were seen around 70 and 112. Moreover, in divalent Zn and Cd clusters intensity maxima for cluster sizes of 10, 20, and 35 are observed.[11] These magic numbers coincide with the strong shell closings for tetrahedral symmetry.[12]

In the following, we study the shapes of quasi-two-dimensional and three-dimensional clusters with closed shells of electrons. To this end we use density functional theory and the so-called ''ultimate'' jellium model (UJM):[13] For a *completely deformable* jellium, the positive ionic background has the same density as the electrons at every point of space, the total charge density being zero. The total energy of the cluster then consists only of the kinetic and exchange-correlation energies of the electrons. The electronic many-body problem can be solved using the Kohn-Sham method with the local density approximation.[14] We compute the ground-state structures of 2D and 3D clusters using a plane-wave technique which allows a shape relaxation without restrictions. For small sodium clusters with up to 20 atoms, it was shown that this technique describes the equilibrium shapes qualitatively very well.[13]

To study the shell structure of quasi-two-dimensional clusters we first consider a jellium confined between two planar, parallel surfaces of distance $z_0=3.9$ a.u. (i.e., the Wigner-Seitz radius of sodium).[15] Allowing shape relaxation in the (x,y) plane, the Kohn-Sham equations are then solved iteratively for various forms of the initial potential. Figure 1 shows the contours of the self-consistent electron density for quasi-two-dimensional electron gas clusters with closed shells and enhanced stability for either circular or triangular shape.

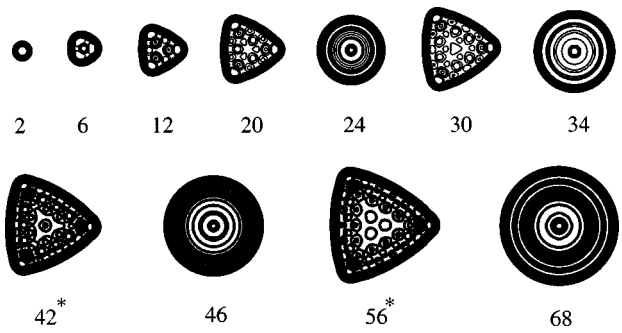

FIG. 1. Contours of the self-consistent densities for quasi-two-dimensional closed-shell clusters. The lowest contour is drawn at 14% of the 2D bulk density. The diameter of the perfect disk with $N=34$ is $d\approx 33a_0$ (where a_0 is the Bohr radius), giving the length unit in this figure. The stars indicate isomeric states (see text).

Having in mind the strong shell structure of spherical sodium clusters,[3,4] one would correspondingly expect the magic numbers in 2D to have a circular disk shape for the closed shells with electron numbers 2, 6, 12, 24, 34,.... From Fig. 1, however, one can see that the ground state of clusters with 6 and 12 electrons is triangular, even though these numbers are ''magic'' for a circular disk. It is interesting to compare the results of the self-consistent calculation to the single-particle motion in a *triangular* 2D cavity. Its exact quantum spectrum is written as $\epsilon_{n,m}=a(n^2+m^2-nm)$, where a is a constant and n, m are positive integers with $m\geqslant 2n$.[16] Large gaps in the energy spectrum are found for 2, 6, 12, 20, 30, 42, 56... particles.

The triangular shape for the magic numbers 6, 12, 20, and 30 is obvious from Fig. 1. For bigger sizes the increasing surface energy, which is larger for the triangle than for any other 2D shape, makes nontriangular shapes energetically more favorable. But in all the cases studied the triangular shapes were found as isomers (indicated with a star in Fig. 1), being only some meV higher in energy than the ground state. A systematic study of the 2D ground-state shapes for clusters with up to 34 particles showed[17] that only the triangle and circle appear as closed-shell configurations, whereas other possible shapes of high symmetry, as, for example, a square or pentagon-shaped ground state, have not been seen.

For three-dimensional clusters, the situation is analogous to the quasi-two-dimensional case discussed above. 3D clusters with 40, 70, and 112 electrons were found to have tetrahedral ground-state shape. Figure 2 (left) shows a constant density surface for $N=112$ as an example.

Our interpretation of the strong tetrahedral deformations of 3D clusters follows the same arguments as for the 2D case discussed above. From a numerical computation[18] the first shells were found at 2, 8, 20, 40, 70, and 112, again coinciding with those of a 3D harmonic oscillator. The smallest ones (2, 8, 20, and 40) are also magic numbers for a sphere. Indeed, the ground states of clusters with 8 or 20 electrons are spherical, but the 40-electron cluster has a clear tetrahedral deformation. This has been observed earlier in jellium calculations which include octupole deformations[19,20] as well as by using the Nilsson model.[12] Using Monte Carlo growth simulations in a distance-dependent tight binding model, an

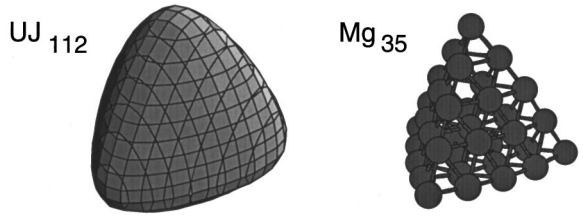

FIG. 2. Left: Tetrahedral equidensity surface of a 3D ''ultimate jellium'' (UJ) cluster with 112 electrons, drawn at 60% of the 3D bulk density. The height of the tetrahedron is $h\approx 38$ a.u. Right: Atomic view of a tetrahedral Mg_{35} cluster, having a height of $h\approx 18$ a.u. (Note the different scale for both figures.)

energetically favorable regular tetrahedral geometry of a sodium cluster with $N=40$ was found by Poteau and Spiegelmann.[21]

Here we wish to point out that it is a natural consequence of 40 being a strong magic number for tetrahedral symmetry: The electrons favor tetrahedral shape when the number of electrons equals an electronic magic number in a tetrahedron. This might explain the strong abundance of 40-atom peak in the mass spectrum as compared to the 34-atom peak.[1] If both clusters were spherical, 34 would be a stronger magic number.

In some experimental results there are weak indications that also the 70- and 112-atom Na clusters could show increased intensity[10] in accordance to the tetrahedral magic numbers. It is expected that for much larger sizes than 112, the surface energy would win against the shell energy, making nontetrahedral shapes more stable. This is again analogous to the 2D case, where already for 42 electrons the triangle is not the shape with the lowest energy.

The strong shell structure for deformations having the symmetry of the T_d group has already been discussed by Hamamoto *et al.*[12] in the framework of the Nilsson model known from nuclear physics. Indeed, the deformation energies were found to be maximal for sizes around 40, 70, 112, and 156, as well as in the neighboring regions of these numbers (see Fig. 14 in Ref. 12). These results agree with the fully self-consistent Kohn-Sham calculations discussed above.

Clusters with well-defined geometry can be formed by packing shells (layers) of *atoms* on top of each other.[7] If this geometrical packing yields a special shape with a high symmetry and stability, one speaks about ''geometric'' magic numbers. Complete tetrahedrons can be formed using close packing of atoms in an fcc lattice structure (see Fig. 2). The number of atoms in such close-packed tetrahedrons are

$$N=\frac{1}{6}K^3+\frac{1}{2}K^2+\frac{1}{3}K, \tag{1}$$

where K is the number of atoms at an edge of the tetrahedron. The corresponding equation for equilateral triangles in 2D is

$$N=\frac{1}{2}K^2+\frac{1}{2}K. \tag{2}$$

These numbers, when multiplied by a factor of two for the spin degeneracy, are exactly the same as numbers of fermions filling 3D and 2D harmonic oscillator shells (K being

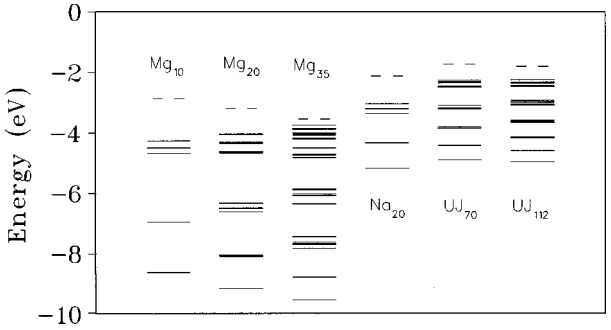

FIG. 3. Kohn-Sham single-electron eigenvalues (in eV) for tetrahedral Mg_{10}, Mg_{20}, Mg_{35}, and Na_{20} clusters, calculated with the BO-LSD-MD method, compared to the UJM result for the 70- and 112-electron clusters, which also have a tetrahedral symmetry. The uppermost pair of short lines depicts the LUMO level for each cluster, the gap below being the Fermi gap.

then the shell index). Moreover, the small electronic magic numbers in tetrahedra and triangles agree with those of the harmonic oscillators, as discussed above. These observations allow us to study clusters which *at the same time have magic number of atoms for geometrical packing and a magic number of electrons for a full electronic shell*. Obviously, tetrahedrons formed from divalent simple metals are such clusters.

As a test case we used magnesium and performed total energy calculations for tetrahedral clusters using the Born-Oppenheimer local-spin-density molecular dynamics (BO-LSD-MD) method.[22] There, the interaction of the valence electrons and ions is taken into account via *ab initio* norm-conserving nonlocal pseudopotentials.[23] The electronic structure is solved concurrently with the dynamics of ions on the BO energy surface. The calculation of the electronic structure relies on the Kohn-Sham formulation of the density functional theory, with the exchange-correlation interaction described by a chosen LSD parametrization.[24] Our results for very small Na and Mg clusters agree with *ab initio* computations of Bonačić-Koutecký *et al.*[25]

Figure 3 shows the single-particle levels of relaxed tetrahedral magnesium clusters with 10, 20, and 35 atoms (i.e. 20, 40, and 70 valence electrons). The clusters have been first built up in a perfect tetrahedral structure with a nearest-neighbor separation between atoms being about 3.5 Å. The total energy has then been minimized by allowing for relaxation of atomic coordinates by conjugate-gradient methods. For all the clusters investigated here a strong electronic shell structure was found, with a gap at the Fermi level of 1.4, 0.8 and 0.3 eV, respectively. In the case of the largest cluster with 35 atoms the relative Fermi gap is rather small (if compared, e.g., to the width of the occupied ''band'' just below the gap) indicating that for even larger tetrahedral magnesium clusters the shell structure does not reach up to the Fermi level. For comparison Fig. 3 also shows the energy levels of the ground state of the 70-electron jellium cluster in the UJM calculation. Its shell structure is found to be qualitatively similar to that of the tetrahedral Mg_{35} cluster, with the Fermi gap of 0.5 eV being of comparable size.

For monovalent alkali metal clusters, the BO-LSD-MD calculations show that also the 20-atom cluster can form a complete tetrahedron having a filled electronic shell. The single-particle spectrum of the tetrahedral Na_8 cluster is shown in Fig. 3. The stability of this cluster is reflected by the fact that the Fermi gap of 0.9 eV is comparable to those (≈ 1 eV) found in low-lying isomers of the magic cluster Na_8.[26,27] Indeed, a tetrahedral structure is one of the calculated low-lying isomers for Li_{20} and Na_{20}.[25] However, the calculated photoabsorption spectrum of Na_{20} (Ref. 25) is not consistent with the experimentally measured spectrum,[28] indicating that in a cluster beam a majority of Na clusters is more spherical in shape. The stability of the tetrahedral Mg_{10} and Na_{20} clusters was studied by molecular dynamics runs (in a time scale of a few ps) where the clusters were heated to about 80 K. Both clusters were stable at this temperature, i.e., atoms were found to vibrate around their zero-temperature equilibrium positions without any signs of a change in structure.

Experimentally, mass spectra of several divalent metal clusters have been measured.[11] For alkali earth metals the intense peaks in the mass spectrum do not seem to correspond to electronic magic numbers but rather to geometrical packing in icosahedral structures. In fact, spectra of these elements are interpreted as evidence that clusters are nonmetallic. This interpretation is not supported by our results for the tetrahedral clusters which show clear shell structure of nearly independent valence electrons. On the other hand, Zn and Cd have intense peaks at atomic numbers 10, 20, 28, 35, 46, etc. The numbers 10, 20, and 35 correspond to closed atomic shells in tetrahedral structure which hence could play a role in Zn and Cd clusters.[29]

Two-dimensional clusters can be grown on surfaces. If the interaction between the surface and the cluster is nonmetallic, a metal cluster on the surface is expected to be rather weakly disturbed by the surface.[26,30,31] In this case 2D metal clusters will tend to form geometries preferred by the 2D electron gas.[17,32] For divalent clusters a similar situation exists as for 3D tetrahedrons: triangular clusters are magic both electronically and geometrically. We thus expect, for instance, small Mg clusters on a graphite or NaCl(001) surface to prefer triangular shape, if the number of atoms match Eq. (2). It should be stressed that this preference to triangular shapes is due to the valence electrons, contrary to the observed triangular metal clusters on fcc(111) metal surfaces, which can be explained by considering the preferential growing directions and the lattice symmetry.[33]

In conclusion, we have shown that tetrahedral shapes of 3D metal clusters can be magic both in geometrical packing and in the electronic structure, and that liquid clusters with 40, 70, and even 112 electrons prefer tetrahedral shapes: *Electronic shell effects can enhance the stability of geometric structures resulting from dense ionic packing.* In small 2D clusters, the freely deformable clusters frequently prefer the shape of an equilateral triangle. More experiments are needed to study tetrahedral metal clusters and triangular clusters on inert surfaces.

We would like to thank S. Bjørnholm and B. R. Mottelson for discussions. This study has been supported by the Academy of Finland. S.M.R. acknowledges financial support from the Studienstiftung des deutschen Volkes, the BASF AG and CNAST and thanks the University of Jväskylä for its hospitality. Calculations were performed at the Center for Scientific Computing, Espoo, Finland.

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