Magic Numbers for Sphere Packings: Experimental Verification in Free Xenon Clusters

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The existence of magic numbers for atomic microclusters has been found experimentally for the first time. The magic numbers n^* manifest themselves in the mass spectra of free xenon clusters, nucleated in the gas phase. The observed numbers $n^* = 13$, 55, and 147 coincide with the numbers of spheres required for complete-shell icosahedra. The appearance of further magic numbers (19, 25, 71, and 87) is only partially explained by previous calculations.

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A variety of experimentally observed properties of matter have been accounted for by hard-sphere-packing models during the last century such as the regular shape of single crystals,[1] the natural abundance of chemical elements,[2] the structure of liquids,[3] or the fivefold symmetry of small metallic particles.[4] The availability of fast computers allowed consideration of packing of "soft" spheres, thus simulating aggregates of real atoms more realistically. This has been applied to microscopic nucleation theory,[5] and to the explanation of structural properties of amorphous solids[6] and free argon particles,[7] of surface melting,[8] and of the catalytic activity of microclusters.[9]

Aggregates of extremely compact shape such as full-shell clusters with face-centered-cubic or icosahedral structure can be built for certain numbers of spheres. Clusters like these might be assumed to be "magic," i.e., to be especially stable. Computer calculations, however, showed that the absolute binding energy per atom depends monotonically on the cluster size n, if a central pair potential is used. Therefore, it has been argued that magic numbers of stability n^* do not exist, with the possible exception of $n^* = 13$,[10,11] or that they are not observable.[12] Evidence for the occurrence of the magic number 13 in lithium clusters has been reported[13]; but the rather weak effect could not be reproduced in a recent experiment by the same authors.[14]

We report the first experiment with atomic microclusters which demonstrates that magic numbers of stability do exist. They are manifest in the relatively high intensity of isolated clusters containing a magic number of xenon atoms. Although the appearance of magic numbers apparently contradicts the predictions quoted above,[10-12] a detailed comparison with sphere packings confirms the correctness of their basic results concerning the structure of free clusters.

The clusters are homogeneously nucleated in a supersaturated vapor phase. This is achieved by adiabatic expansion of xenon (purity 99.99%) through a capillary (diameter 0.2 mm, length 20 mm) into vacuum; the gas condenses in the supersonic jet.[15] For a given nozzle geometry, the nozzle temperature T_0 and the stagnation pressure p_0 control the mean cluster size; low T_0 and high p_0 favor the condensation. The jet is skimmed by two conical collimators and enters the time-of-flight mass spectrometer,[16] where it is ionized by a pulsed electron beam with an energy of 30 eV.

Figure 1 displays a mass spectrum, subdivided into two overlapping ranges. The cluster intensity decreases slowly with increasing n. At certain numbers, however, the intensity *increases* slightly to a local maximum and thereafter *decreases* steeply. The most prominent intensity drops occur after $n^* = 13$, 19, 25, 55, 71, 87, and 147. The numbers $n^* = 23$, 81, 101, and 135 might be tentatively added to this list. The intensity drop at $n^* = 13$, 19, and 25 amounts to a factor of 2, in contrast to the average decrease of a few percent. The steps occurring for larger n^* are even more pronounced, if the "background" of the spectrum, due to finite mass resolution, is properly taken into account.

The physical significance of the observed magic numbers has been verified in several ways; among other things we checked the reliability of the spectrometer with time-of-flight spectra of carbon dioxide clusters up to $n = 90$, covering the mass range up to Xe_{30}: Their intensity decreased strictly monotonically with increasing size.[17] Care was also taken to demonstrate that the magic numbers do not merely reflect the stability of *ionized* clusters which might stem from electron-impact fragmentation: (i) Possible contam-

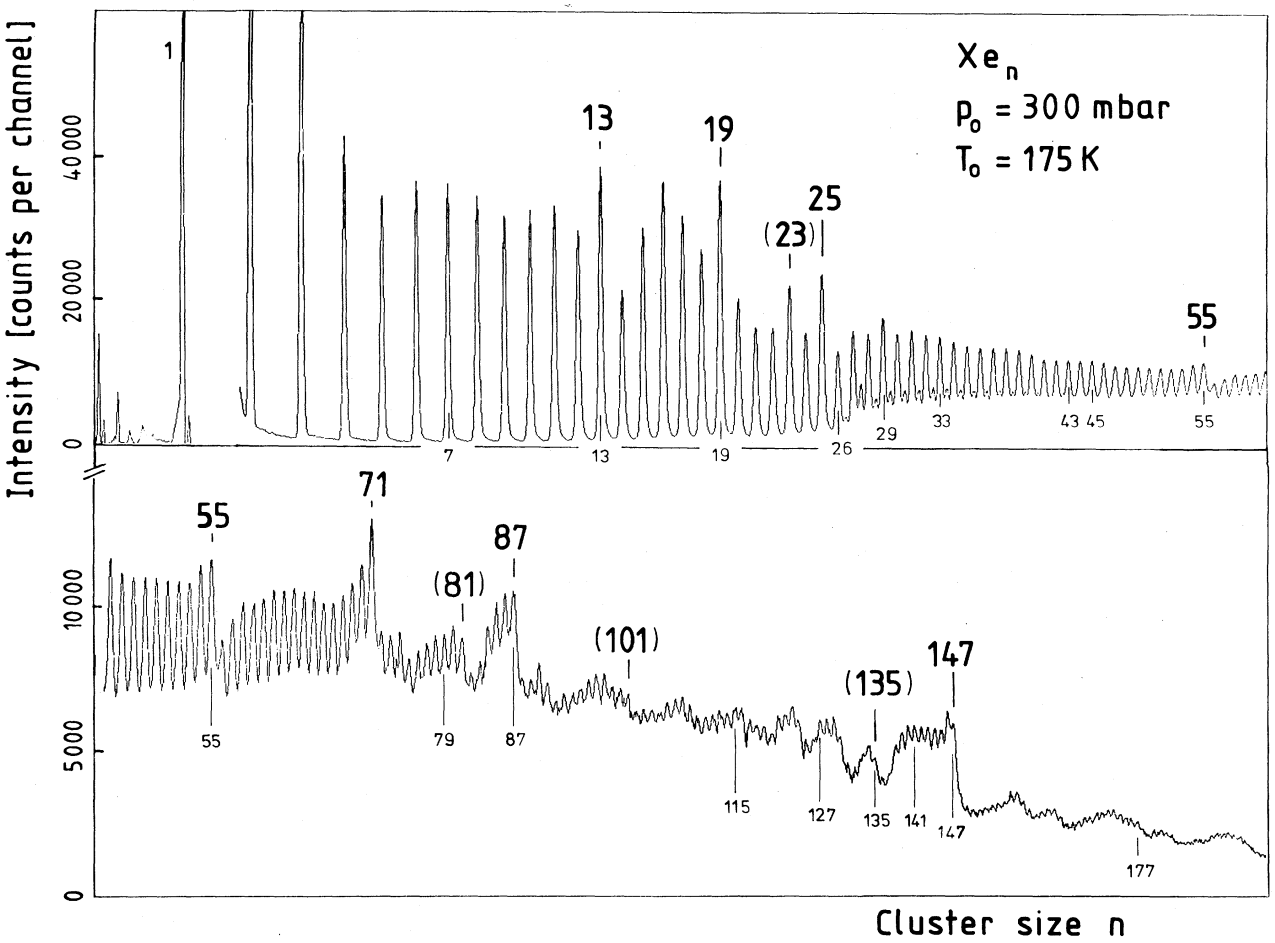

FIG. 1. Mass spectrum of xenon clusters. Observed magic numbers are marked in boldface; brackets are used for numbers with less pronounced effects. Numbers below the curve indicate predictions or distinguished sphere packings.

ination of the ion signals by fragment ions would be reduced, if the cluster intensity decreases rapidly with increasing size. Variation of the mean cluster size, however, *did not* influence the intensity drop after the magic numbers.
(ii) The probability of possible fragmentation can be reduced by lowering the energy of the ionizing electrons. We varied this quantity between 50 and 15 eV (3 eV above the ionization threshold of atomic Xe), but the ratio between neighboring peaks in the investigated size range ($10 \leq n \leq 30$) remained virtually constant.[17]

The relatively high intensity of xenon clusters having a magic number of atoms must therefore be attributed to intrinsic properties of these clusters. The most obvious explanation for the appearance of magic numbers is in terms of energy. Unfortunately we cannot derive the binding energies of the clusters from our spectra, because the nucleation is a nonequilibrium process. A quantitative calculation of the cluster concentration c_n within a microscopic nucleation theory would require values for the size-dependent capture cross sections (including sticking probabilities) and decay-rate coefficients, which depend on the structure of the clusters. The treatment of this problem has been restricted to very small clusters ($n \leq 5$) until now.[18]

As mentioned above, the binding energy E_n of the energetically most favorable structure of the n-mer, divided by n, approaches montonically the bulk value with increasing n.[10] The sublimation energy $\Delta E_n = E_n - E_{n-1}$, however, is more appropriate to reveal the existence of magic numbers of stability. We used data from Ref. 5 (up to $n = 20$, including zero-point contribution) and Ref. 10 (for $n \geq 20$, without zero-point contribution) for a plot of the sublimation energies in

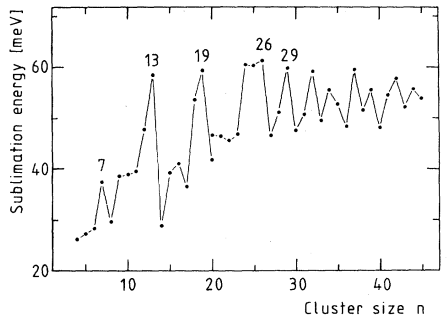

FIG. 2. Sublimation energy $\Delta E_n = E_n - E_{n-1}$, calculated for argon clusters (data from Refs. 5 and 10).

Fig. 2. They were evalutated for argon clusters, assuming a Lennard-Jones potential. The superiority of the 13-mer, having icosahedral structure, and the 19-mer (icosahedron plus pentagonal cap of six atoms) is evident from Fig. 2, in agreement with our findings.

Figure 2 does not account for $n^* = 23$ and 25. Of course, one should take into consideration the influence of finite cluster temperature on the sublimation energy; but (i) the entropy is believed to yield a comparatively small contribution,[19] and (ii) the temperature of the clusters is unknown. If we assume a temperature deduced from electron diffraction at rare-gas particles in a supersonic beam[20] and use energies calculated for clusters at finite temperatures[5,10] for a plot of the sublimation energy, we still find pronounced maxima for $n = 13$ and 19; but $n^* = 23$ and 25 remain unexplained. Sphere-packing calculations have been extended up to $n = 100$ using a truncated Lennard-Jones potential.[21] Apart from 55 (see below), no additional magic numbers are anticipated. This partial failure of the theory may be due to the difficulty of computer simulations to find the minimum-energy configuration for a given size. The virtual impossibility of solving this problem reliably for large n has been pointed out by Hoare and McInnes.[22] Because of this, the beauty of derived geometrical structures has somehow served as a guide in computer simulations. Some numbers for which beautiful clusters can be built are indicated in Fig. 1 below the curve: $n = 7$ (pentagonal bipyramid), 33 (dodecahedron), 43 (icosidodecahedron), 45 (rhombic triacontahedron), 115 (rhombicosidodecahedron), and 127 (icosahedron of icosahedra). None of them is found to be magic in our measurement.

The most interesting structure for large clusters, however, has been found in hard-sphere-packing studies by Mackay.[23] The "Mackay icosahedra" contain 55, 147, 309,... spheres, in striking agreement with the observed magic numbers 55 and 147. The superiority of the 55-atom icosahedron has been confirmed in soft-sphere-packing studies.[21,24] The Mackay icosahedra can be imagined to consist of 20 close-packed fcc tetrahedra sharing a single vertex; they might therefore constitute the nuclei for crystalline growth. If the clusters should grow in the fcc structure, one might expect magic numbers for clusters having complete shell, i.e., $n = 13$, 19, 43, 55, 79, 87, 135, 141, 177,... (also indicated in Fig. 1 below the curve). Some of these numbers coincide with the observed magic numbers and with the numbers of spheres for complete-shell icosahedra, but the absence of any effect for $n = 43$, 79, and 141 clearly contradicts the assumption that clusters in this size range already possess bulk structure. On the other hand, all the magic numbers predicted for icosahedral clusters (13, 19, 55, and 147) are indeed observed.

The observation of magic numbers implies that for each n the geometrical structure of the cluster is well defined, i.e., the clusters are solid. This agrees with the findings of Farges *et al.*,[7,20] who proposed that the clusters might be liquid during their growth, but cool down and solidify, after the nucleation has ceased, via evaporation of atoms. Such a mechanism would easily explain that clusters having a size n slightly larger than n^* are less frequent, because they can easily evaporate atoms in excess of n^*, while a high energy barrier prevents further evaporation if $n = n^*$ is reached.

Comparison of our measurements with mass spectra of argon clusters[25,26] shows a surprising difference. Apart from a minimum for $n = 20$, equivalent to $n^* = 19$, no distinct structure was observed for argon. On the basis of the material now available, it is impossible to decide whether the difference arises from differences in the experimental arrangement or from different properties of argon and xenon. Comparative experiments with Ar and Xe and possibly Kr at the same apparatus are highly desirable.

In conclusion, the predicted superiority of complete-shell icosahedra could be confirmed. Additional oscillations in the size dependence of thermodynamic cluster functions, however, are more important, even for large clusters, than hitherto assumed. This partial failure of previous calculations may be due to an inadequacy

of central pair potentials or due to difficulties in finding the minimum-energy configurations of simple microclusters.

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Radical Redistribution of the 4*d* Oscillator Strength Observed in the Photoabsorption of the Ba, Ba^+, and Ba^{++} Sequence

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The vacuum-ultraviolet absorption spectra of isolated Ba, Ba^+, and Ba^{++} have been measured. In Ba and Ba^+ most of the 4*d* absorption oscillator strength is in the continuum, but in Ba^{++} several very strong discrete transitions are observed. Such behavior has never before been observed in the 4*d* photoabsorption of vapors, solids, or compounds. An interpretation is given in terms of the partial collapse of the *nf* bound states in Ba^{++}.

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The vacuum-ultraviolet (VUV) photoabsorption of the rare-earth elements and the elements directly preceding them can be shown, in a Hartree-Fock model, to depend critically on the details of the effective potential for an *f* ($l=3$) electron.[1] In this region of the periodic table this potential has a double-well character, the wells being separated by a potential barrier originating from the competition between the nuclear attraction (a negative term), a combination of electrostatic terms (both positive and negative), and a positive term (often called the centrifugal repulsion) of the form $(h^2/2m)l(l+1)/r^2$ (with $l=3$) associated with a particle with angular momentum l. For atoms with $Z \leq 57$ the 4*f* wave function resides in the outer well, penetrating the barrier only slightly, and is an excited state. At $Z=58$ (Ce) the 4*f* is in the inner well (collapsed) and is part of the ground-state configuration, a condition that also applies for all $Z>58$. These features were first recognized by M. G. Mayer in her explanation of the properties of the rare