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From atoms to solids

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Abstract

Under certain experimental conditions a periodic structure can be induced in the mass spectra of clusters of metal atoms. For example, if the clusters are heated with a laser beam, those with high stability resist evaporation. The resulting mass spectra reveal that clusters with closed electronic shells and clusters with perfect icosahedral symmetry are unusually stable. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Metal clusters; Mass spectrometry

1. Introduction

The properties of bulk metal are so different from those of a metal atom that it is sometimes hard to imagine how they might be related. However, a connection can be established by studying a succession of clusters containing 2, 3, 4, 5 ... atoms. If the properties of the solid were found to evolve gradually and continuously with increasing cluster size, this type of investigation would not really be of much interest. But nature has presented us with a different situation. The properties of clusters change not continuously, but often periodically with cluster size. This is due to the formation of shells – shells of electrons and shells of atoms.

2. Shells of electrons

If it can be assumed that the electrons in metal clusters move in a spherically symmetric potential, [1–16] one must solve only a radial Schrödinger equation,

$$\left[\frac{-\mathrm{d}^2}{\mathrm{d}r^2} + \frac{l(l+1)}{r^2} + V(r) \right] P_{nl} = E_{nl}(r)$$
$$= E_{nl}P_{nl}(r) \tag{1}$$

where l is the angular momentum quantum number and $V(r)$ is the radial dependence of the potential in which the nucleons move. A further simplification can be made by assuming that $V(r)$ is a simple potential well. Some confusion can arise as we will use a slightly different definition for the principal quantum number n.

Throughout this paper we will use the principal quantum number from nuclear physics, i.e. n denotes

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the number of extrema in the radial wavefunction. Subshells for large values of angular momentum can contain hundreds of electrons having the same energy. The highest possible degeneracy assuming cubic symmetry is only 6. So under spherical symmetry the multitude of electronic states condenses down into a few degenerate subshells. Each subshell is characterized by a pair of quantum numbers n and l, Fig. 1. Under certain circumstances the subshells themselves condense into a smaller number of highly degenerate shells. The reason for the formation of shells out of subshells requires more explanation.

The concept of shells can be associated with a characteristic length. Every time the radius of a growing cluster increases by one unit of this characteristic length, a new shell is said to be added. The characteristic length for shells of atoms is approximately equal to the interatomic distance. The characteristic length for shells of electrons is related to the wavelength of an electron in the highest occupied energy level (Fermi energy). For the alkali metals these lengths differ by a factor of about 2. This concept is useful only because the characteristic lengths are, to a first approximation, independent of cluster size.

3. Observation of electronic shell structure

Knight et al. [1] first reported electronic shell structure in sodium clusters in 1984. Electronic shell structure can be demonstrated experimentally in several ways: as an abrupt decrease in the ionization energy with increasing cluster size, as an abrupt increase or an abrupt decrease in the intensity of peaks in mass spectra. The first type of experiment can be easily understood. Electrons in newly opened shells are less tightly bound, i.e. have lower ionization energies. However, considerable experimental effort is required to measure the ionization energy of even a single cluster. A complete photoionization spectrum must be obtained and very often an appropriate source of tunable light is simply not available. It is much easier to observe shell closings in photoionization, TOF mass spectra. However, depending upon the intensity and wavelength of the ionizing laser pulse, the new shell is announced by either an increase or a decrease in mass peak height.

For high laser intensities, multiple-photon processes cause the mass spectra to be less wavelength sensitive and also cause considerable fragmentation of large clusters. The resulting mass spectrum re-
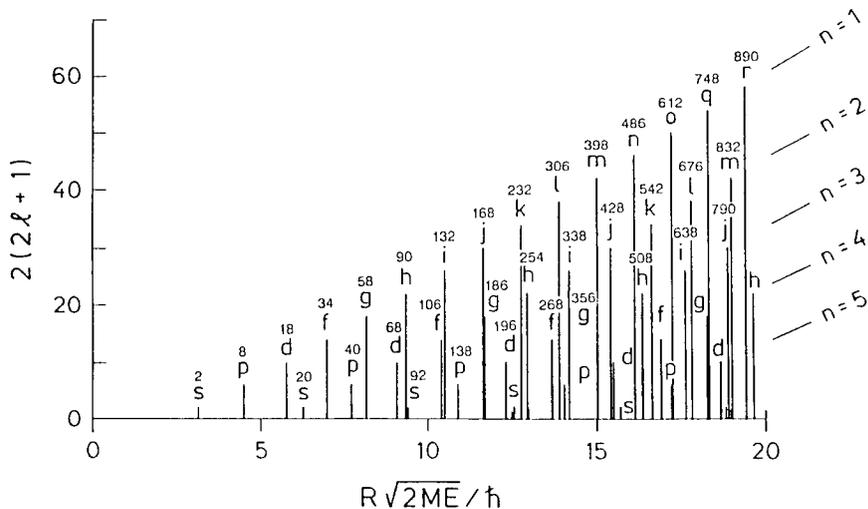
Fig. 1. The degeneracy of states of the infinitely deep spherical well on a momentum scale. The total number of fermions needed to fill all states up to and including a given subshell is indicated above each bar.
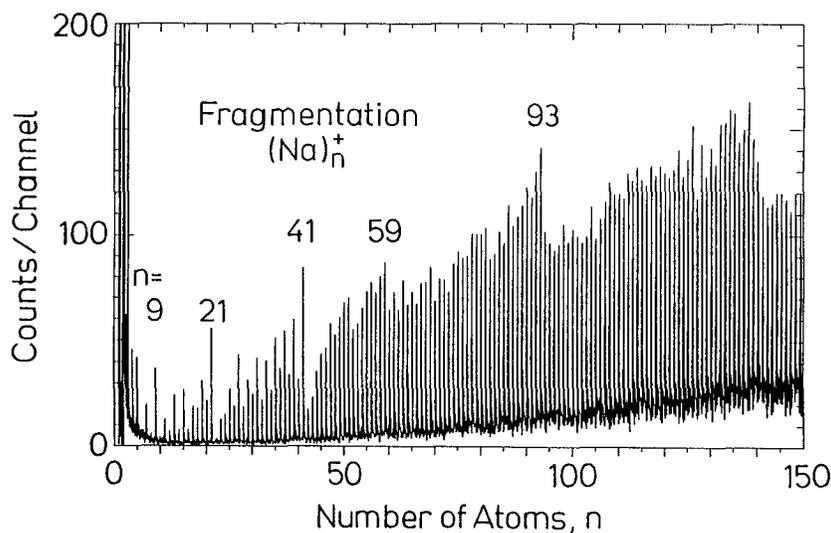
Fig. 2. Mass spectrum of $(Na)_n^+$ clusters ionized with high intensity, 2.53 eV light. The clusters are fragmented by the ionizing laser. Fragments having closed shell electronic configurations are particularly stable.

flects the stability of cluster ion fragments. Clusters with newly opened shells are less stable and are weakly represented in the mass spectra. Notice in Fig. 2 that as each new shell is opened there is a sharp step downward in the mass spectrum. Remember that cluster ions containing 9, 21, 41, 59, ... sodium atoms contain the magic number (8, 20, 40, 58, ...) of electrons.

4. Shells of atoms

One might think that the definition of a shell of atoms is straightforward – one layer of atoms arranged on the surface of a core such that the newly formed, larger unit has the same (overall) outer symmetry as the core itself. However, as one begins to construct examples, it becomes quickly clear that this definition might lead to confusion. For example, consider a cluster composed of atoms placed at the sites of a simple cubic lattice and having the overall outer shape of a cube. The first such cube that can be formed around a central atom contains 27 atoms, three atoms on a side; the next, 125 atoms, i.e. 5 atoms on a side, etc. But what happened to the 64 atom cube with 4 atoms on a side? It has no central

atom. That is, this simple example might be considered to describe two distinct shell sequences, one set of shells possessing a central atom; the other set has a central 8-atom cube. One way of getting around this difficulty is to combine the two sets into a single set. Each successive member of this combined set is obtained by adding atoms to only three of the six faces of the preceding member. We will see that it is useful to designate a set of such shells as irregular shells in order to distinguish them from, for example, the regular shells of an icosahedron where atoms must be added to all faces in order to complete the next shell.

5. Shells obtained from close-packed spheres

A limited number of symmetric clusters can be constructed from the close-packing of hard spheres; e.g. tetrahedra, octahedra, and their truncated forms. The truncated forms can have triangular, square or hexagonal faces. For example, the cuboctahedron, an octahedron truncated by a cube, Fig. 3, has 6 square faces and 8 triangular faces. Although this figure is constructed from close-packed layers, the cut form-
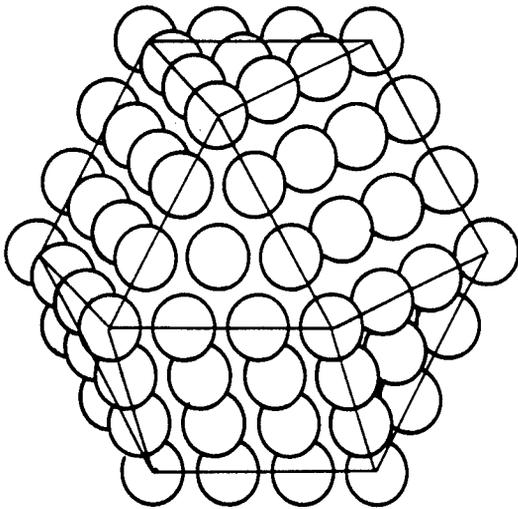
Fig. 3. A closed-shell 147 atom cuboctahedron. Notice that the atoms in the square faces are not close-packed.

ing a square face reveals a surface which is not close-packed. Such a surface is relatively unfavorable energetically and is a good candidate to accept the first atoms of a new shell.

6. Shell structures related to the bcc lattice

In a previous section we used the example of a cube-shaped cluster cut out of a simple cubic lattice. This was convenient to illustrate the concept of irregular shells, but is unrealistic in that elemental matter does not usually condense into a simple cubic structure. However, if such a cube is squeezed along a body diagonal, the cube deforms into a rhombohedron which can be cut out of a bcc lattice, Fig. 4. The bcc rhombohedron represents a set of irregular shells containing, of course, the same number of atoms as simple cubic shells. The bcc lattice contains also a set of regular shells. The first member in this set is shown in Fig. 4. The atoms of such clusters are contained within 12 rhombic faces.

7. Shell structures with five-fold symmetry

Until now we have discussed shell structure in clusters of close-packed atoms or of atoms on crystal lattice sites. Clusters in the form of icosahedra or decahedra are neither close-packed nor are they small pieces cut out of a crystal. A five-fold symmetry axis is not consistent with the crystalline requirement of translational symmetry. Icosahedra form a set of regular shells around a central atom, Fig. 5.

Fig. 4. A smaller geometric figure found in a bcc lattice is outlined with heavy lines. This figure can be found in shells of increasing size.
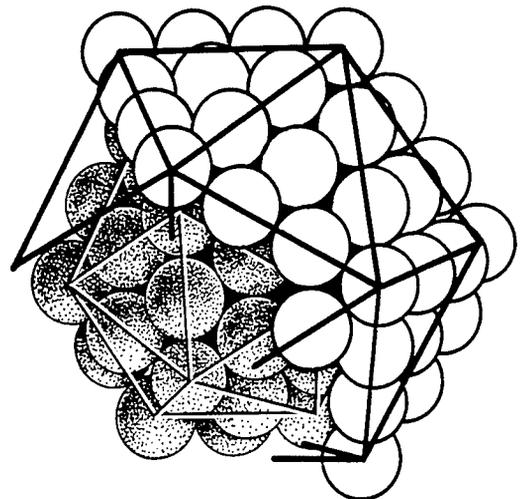
Fig. 5. A closed-shell 55 atom icosahedron and a portion of the next shell.
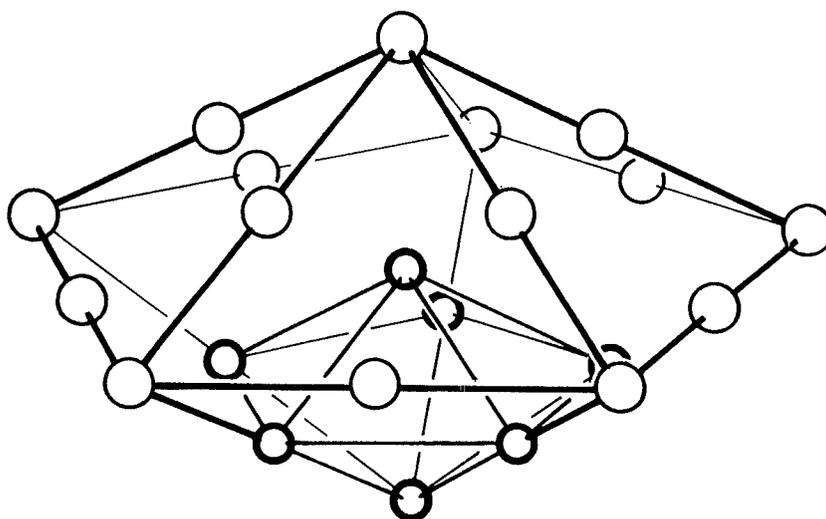
Fig. 6. Decahedra form a set of irregular shells. Successively larger shells are formed by adding an umbrella-shaped partial layer.

Nature has played a strange trick on us here. The number of atoms needed to complete icosahedral shells is exactly that needed to complete cuboctahedral shells. For this reason, the experimental observation of magic numbers corresponding to shell closings is not sufficient to allow us to distinguish between non-crystalline icosahedra and fcc cuboctahedra.

Decahedra represent a set of irregular shells. The shells possess alternately a central atom and a central 7-atom decahedron and are formed by placing a large overlapping 'umbrella' on top of the previous member of the set, Fig. 6.

8. Observation of shells and subshells of atoms

Both calculations and experiments [17–25] indicate that inert gas clusters containing from 13 to 923 atoms have icosahedral symmetry. These might be referred to as precrystalline structures since the inert gases are known to condense into fcc crystals. Precrystalline structures have also been observed for metallic materials in condensed units large enough to yield sharp electron diffraction patterns [26–28]. These quasicrystals present a fascinating challenge to scientists to develop methods for describing a regular but nonperiodic state of bulk matter. Smaller

icosahedral metal particles have been observed directly using the technique of high-resolution electron microscopy [29].

Additional evidence exists for icosahedral symmetry in metal clusters. Calculations predict that very small alkaline earth clusters prefer noncrystalline structures [30–34]. The pattern of NH_3 and H_2O binding energies with Co and Ni clusters has been interpreted as indicating icosahedral symmetry in metal clusters containing from 50 to 150 atoms [35,36]. Mass spectra of Ba and Ba–O clusters seem to indicate an icosahedral growth sequence in the size range from 13 to 35 atoms [37–39].

Recently we observed a slow modulation in mass spectra of Na clusters, Fig. 7, which we interpreted as evidence for the existence of shell structures, i.e. a highly symmetric, onion-like cluster structure [14]. The modulation appeared only if the energy of the ionizing photons was chosen to coincide with the ionization potential of the clusters and was found to be almost periodic when plotted on a cube root of mass scale. The cusp-like minima of the mass spectra pointed to characteristic masses or numbers of atoms. Within the accuracy of reading the minima, these magic numbers correspond to the number of atoms in complete Mackay icosahedra [40]. However, on the basis of such observations, it is not possible to conclude that the clusters have icosahedr-
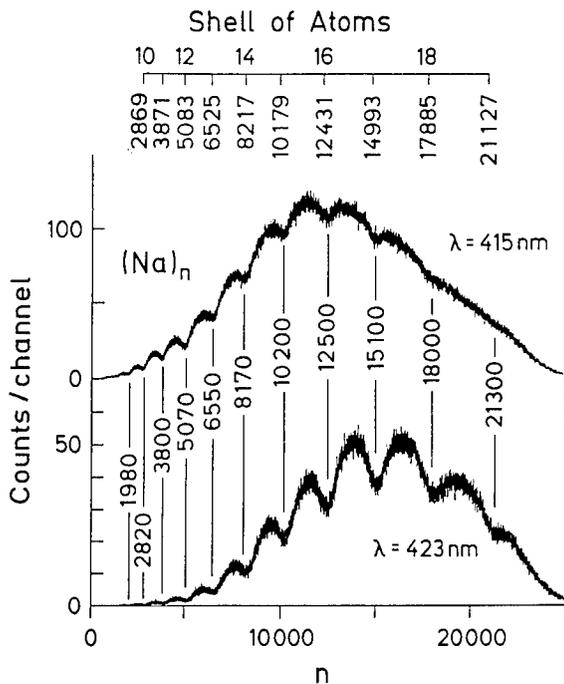
Fig. 7. Averaged mass spectra of $(Na)_n$ clusters photoionized with 2.99 and 2.93 eV light. Well-defined minima occur at values of n corresponding to the total number of atoms in close-packed cuboctahedra and nearly close-packed icosahedra (listed at top).

al symmetry because icosahedral shells and fcc cuboctahedral shells contain exactly the same number of atoms.

Fig. 8 shows a mass spectrum of pure Mg clusters containing up to 3000 atoms [41]. The choice of ionizing photon energy and laser intensity is important. We have used 50 mJ/cm^2 of 308 nm radiation per 10 ns pulse. With such high intensities massive fragmentation of the clusters is to be expected. For this reason we believe that strong peaks in the mass spectrum indicate cluster ion fragments with high stability. Even though we are using a high laser intensity, the signal is weak, about one cluster per laser shot. Over 200 000 shots at 50 Hz were required to obtain this spectrum. Because of the low signal, some averaging is necessary to bring out the spectral features. First, an average is made over 500 time channels. This, plus the fact that magnesium has three natural isotopes (79% ^{24}Mg, 10% ^{25}Mg, 11% ^{26}Mg), limits the mass resolution. In a next step the spectrum is averaged over 5000 time channels. The resulting curve contains no structure but is merely an envelope of the original data. Finally, we form the ratio of the slightly averaged spectrum to the strongly averaged (envelope) spectrum. The resulting ratio spectra are shown in Figs. 8 and 9.
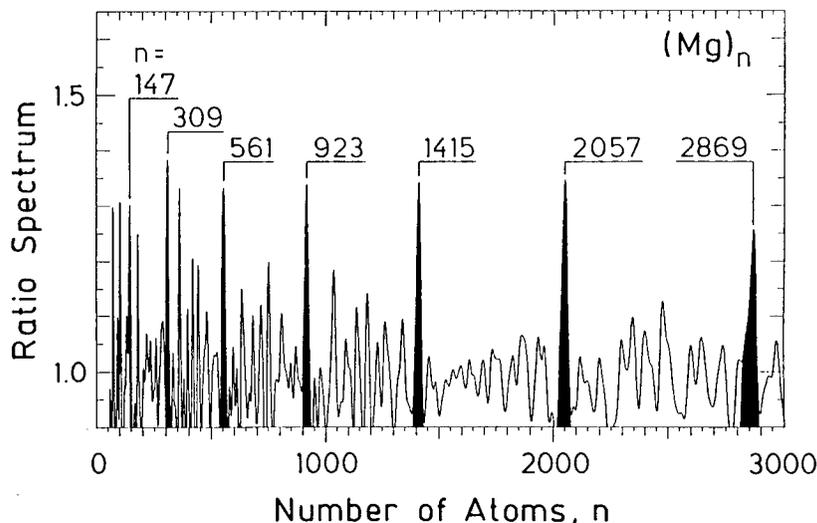
Fig. 8. Ratio spectrum (slightly smoothed mass spectrum divided by highly smoothed envelope spectrum) for Mg clusters. The filled mass peaks correspond to completely filled icosahedral shells.
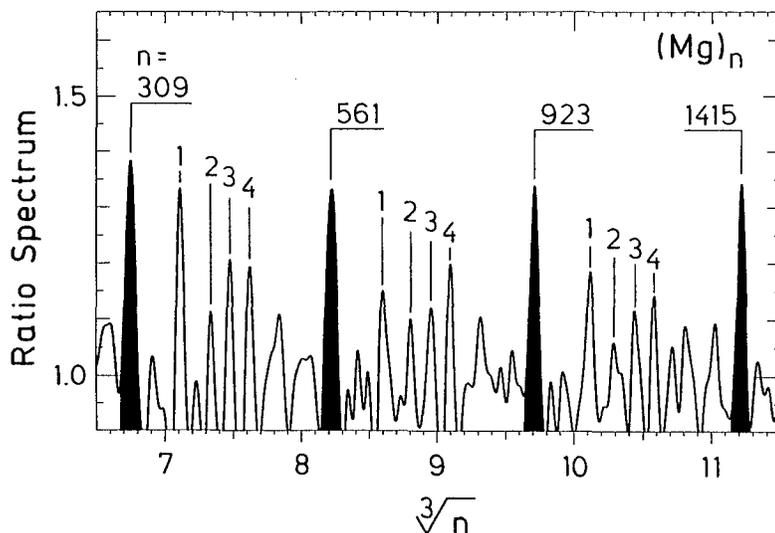
Fig. 9. Ratio mass spectrum of $(Mg)_n$ clusters. The filled mass peaks, corresponding to completely filled icosahedral shells, are nearly equally spaced on this $\sqrt[3]{n}$ scale. The four mass peaks observed between shell closings indicate highly stable partial shells.

The strongest mass peaks correspond to the number of atoms in closed shells having either icosahedral or cuboctahedral symmetry. The Mackay icosahedra can be constructed from nearly close-packed spheres. These structures might be called noncrystalline since they possess a point group which is not consistent with translational symmetry. Cuboctahedra on the other hand, can be constructed from close-packed spheres. In fact, cuboctahedra containing an arbitrary number of shells can be cut out of a fcc crystal. The main sequence of strong mass peaks does not allow us to distinguish between these two structures. We have to look elsewhere for decisive experimental data. We believe these data are contained in the weaker mass peaks between shell closings.

Fig. 9 shows a portion of the previous mass spectrum but now plotted against $n^{1/3}$. Notice that the four main peaks are equally spaced. This is a characteristic common to all types of shell structure. The reason for this can be seen in the following way. Every time the radius (proportional, of course, to $n^{1/3}$) of a growing cluster increases by one unit of a characteristic length, a new shell is said to be added.

Notice in Fig. 9 that the spectral features between complete shells repeat exactly within the statistical accuracy of the experiment. In particular, we will focus our attention on the repetitive peak structure labeled 1, 2, 3 and 4, and suggest below that this structure corresponds to partial icosahedral shells.

The clusters most probably grow by adding shells of atoms to a rigid core. The number of atoms contained in a growth shell is dependent on the preferred coordination and local symmetry of the atoms and on the overall symmetry of the shell. If we assume that the magnesium atoms are close-packed, or nearly so, and that the outer form is that of an cuboctahedron or an icosahedron, then the total number of atoms N_k in a cluster containing K shells of atoms is [41].

$$N_k = (10 K^3 + 15 K^2 + 11 K + 3)/3. \qquad (2)$$

Clusters constructed of complete shells can be expected to be highly stable. For inert gas clusters both experiments and calculations indicate that partial icosahedral shells of atoms also show enhanced stability [19–23]. For example, one might expect that completely covered facets of a cluster surface represent intermediate structures of high stability. Since the facet structure of the icosahedron (20 triangular faces) and the cuboctahedron (8 triangular and 6 square faces) are quite different, a determination of

partial shell sizes should make it possible to distinguish between the two structures.

The square faces of the cuboctahedron would be likely candidates to accept the first atoms of a newly deposited layer because the atoms in these faces are not close-packed. However, no arrangement of atoms on these faces alone or in combination with other cuboctahedral faces could be found which matched the observed subshell magic numbers. Next, we turned to the icosahedron for which subshell struc-
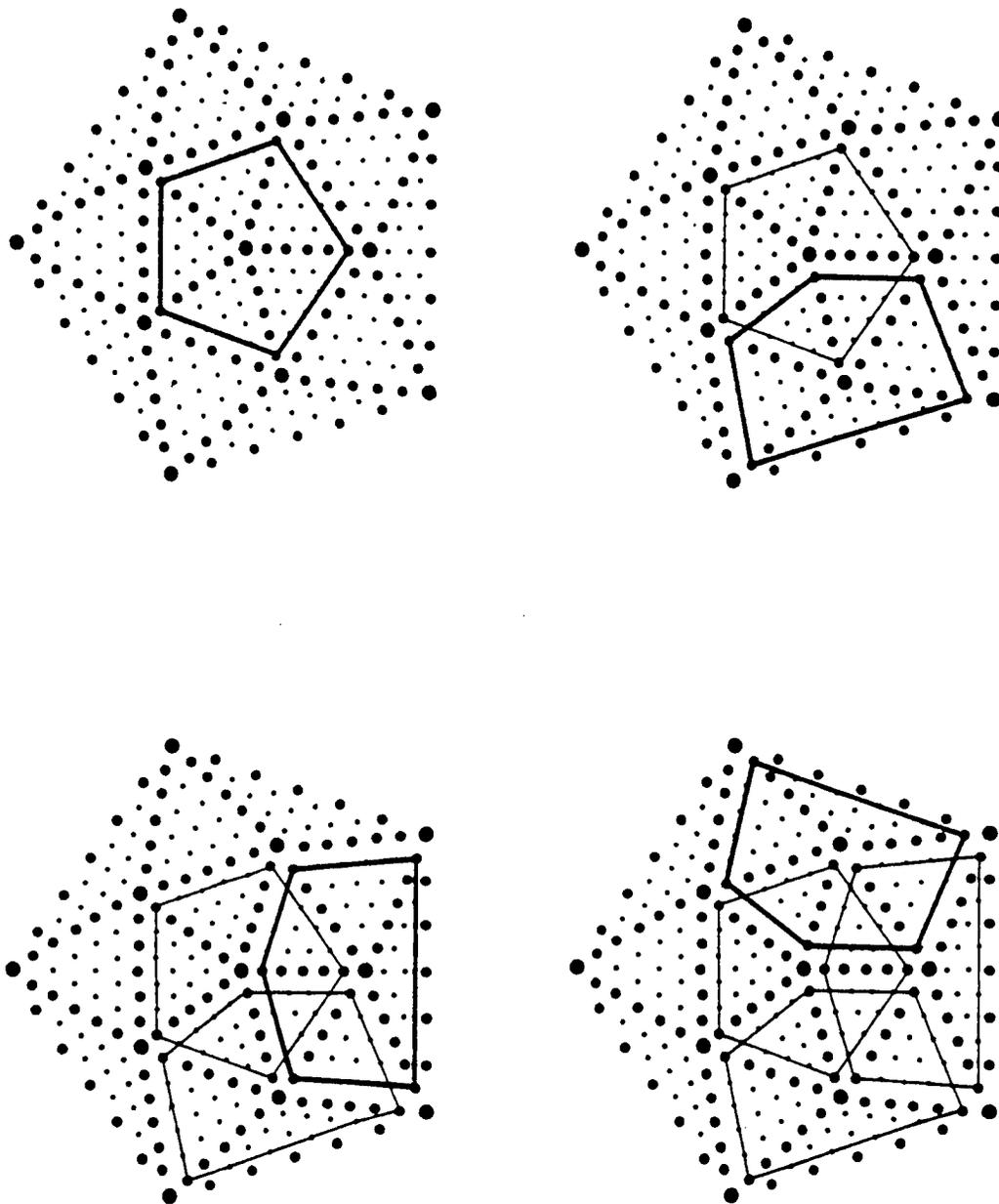
Fig. 10. The dots represent the atoms of the 7th shell of an icosahedron projected onto a plane. The bottom 76 atoms are not shown. The umbrella-shaped structures are identical, each containing 76 atoms. We suggest that the umbrellas represent highly stable partial shells of magnesium atoms.

ture had already been studied [19–23]. The first
atoms to form a new shell on an inert gas icosahed-
ron apparently do not immediately take their final
positions. This would force atoms on the border
between two triangular faces to have contact with
only two substrate atoms. Instead, the triangular
faces are first filled with a close-packed layer. Only
after the shell is more complete do the atoms
rearrange into their final icosahedral positions. This
shell filling sequence, observed in inert gas clusters,
although close, seems to deviate significantly from
the observed magic numbers for Mg clusters. There-

fore, we would like to suggest an alternative se-
quence.

Assume that the atoms in the new shell take
immediately their final positions. In Fig. 10 the
positions of the atoms in the seventh shell have been
projected onto a plane in the manner of Northby
[20,21]. We suggest that umbrella-shaped inter-
mediate groups have enhanced stability. Each of the
umbrellas contains 76 atoms and each has the same
shape (although they appear distorted in the projec-
tion shown in Fig. 10). Only 51 additional atoms are
necessary to complete the second umbrella because it
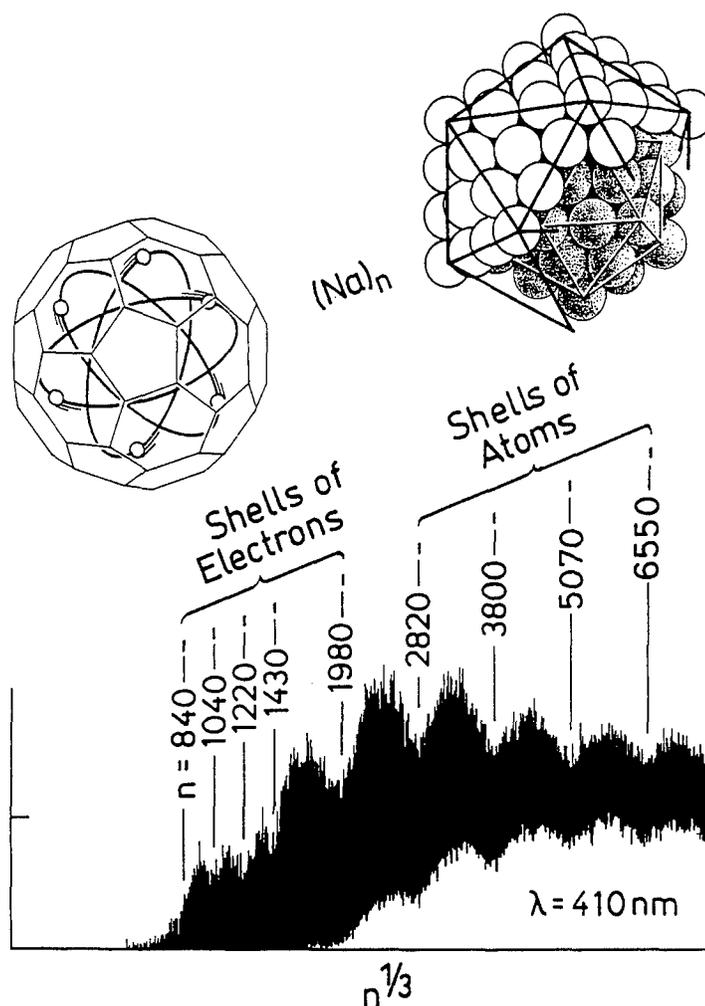
Fig. 11. Mass spectrum of $(Na)_n$ clusters photionized with 3.02 eV photons. Two sequences of structures are observed at equally spaced intervals on the $n^{1/3}$ scale – an electronic shell sequence and a structural shell sequence.

shares atoms with the first. The third and fourth umbrellas overlap two others. Therefore, they require only 36 additional atoms for completion.

9. Transition from shells of electrons to shells of atoms

Two types of shell structure have been observed in the same mass spectrum of large sodium clusters, Fig. 11. For small clusters ($n \leq 1500$) the pattern appears to be due to the filling of electronic shells. For large clusters the shells seem to be composed of atoms.

Why might one expect a transition from electronic shell structure to shells of atoms? For very small clusters the atoms are highly mobile. There is no difficulty for the atoms to arrange themselves into a sphere-like conformation if this is demanded by the closing of an electronic shell. At a size corresponding to about 1500 atoms under our experimental conditions, the clusters become rigid. Thereafter, each newly added atom condenses onto the surface and remains there. Further growth takes place by the accumulation of shells of atoms.

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