Onset of Metallic Behavior in Magnesium Clusters

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We have measured the photoelectron spectra of mass-selected magnesium cluster anions, Mg_n^-, over the size range, $n = 3$–35. Their s-p band gaps were observed to close at $n = 18$, signaling the onset of metallic behavior. Electronic shell structure was implicated by gap "reopenings" and mass spectral magic numbers. Complementary calculations are presented in the companion paper [P. H. Acioli and J. Jellinek, Phys. Rev. Lett. **89**, 213402 (2002)].

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A collection of metal atoms does not necessarily exhibit metallic behavior. In this paper, we explore the nonmetallic-to-metallic transition in the finite size regime for the case of magnesium. Magnesium is a particularly instructive case because its electronic structure varies dramatically with the number of interacting atoms. For example, when two magnesium atoms interact, only weak, van der Waals bonding results. Yet, when large numbers of magnesium atoms interact in bulk, they form a structural material. Clearly, major changes occur as more and more magnesium atoms interact and metallic properties emerge.

The schematic in Fig. 1 provides a simplified, yet useful framework (ignoring the presence of hydridization) for visualizing the evolving electronic structure of magnesium. There, the energies of the most relevant orbitals are plotted versus increasing numbers of interacting magnesium atoms, n. The doubly occupied $3s$ energy level of the ground state atom along with the empty $3p$ level above it are shown on the left side of the figure. When two magnesium atoms interact to form a dimer, two molecular orbitals are formed and both are filled. As more magnesium atoms interact, new molecular orbitals are formed in like fashion, with n magnesium atoms giving n molecular orbitals, and with these too being filled to capacity. Above these, molecular orbitals based on the $3p$ atomic orbitals of magnesium are also formed, but these are empty. As still more atoms interact, both the filled $3s^2$-derived molecular orbitals and the empty $3p$-derived molecular orbitals broaden in energy, producing "fans" of molecular orbitals. The energy difference between the highest energy, $3s^2$-derived molecular orbital (the HOMO) and the lowest energy, $3p$-derived molecular orbital (the LUMO) is the HOMO-LUMO gap, Δ, and it becomes smaller with increasing numbers of interacting magnesium atoms. Once $\Delta \rightarrow 0$, however, the filled and empty fans overlap, and electrons from the $3s^2$-derived fan of molecular orbitals spill into the fan of previously unoccupied, $3p$-derived molecular orbitals, creating a partially filled band and meeting the usual criterion for the onset of metallic behavior.

Figure 1 can also be viewed as representing the evolving electronic structure of individual, neutral magnesium *clusters* as a function of size, n. If one next imagines adding an extra electron to each of these clusters to form their corresponding ground state cluster anions, then, for clusters smaller than that at the gap closure, that extra electron must reside at the bottom of the previously empty, $3p$-derived fan of MO's. While the energies of the MO's shown in Fig. 1 as well as the gap between them are quantitatively modified by the addition of one more electron to each cluster size, the figure itself remains a qualitatively viable picture for magnesium cluster anions.

Determining the minimum number of interacting magnesium atoms at which the onset of metallicity occurs was the main objective of this work. We approached this problem, as had Busani *et al.* [1] in the case of mercury cluster anions, by photodetaching electrons from magnesium cluster anions as a function of cluster size in order to track the closure of the energy gap in the anionic system. The electron binding energy (EBE) for an electron photodetached from the bottom of the anion's singly

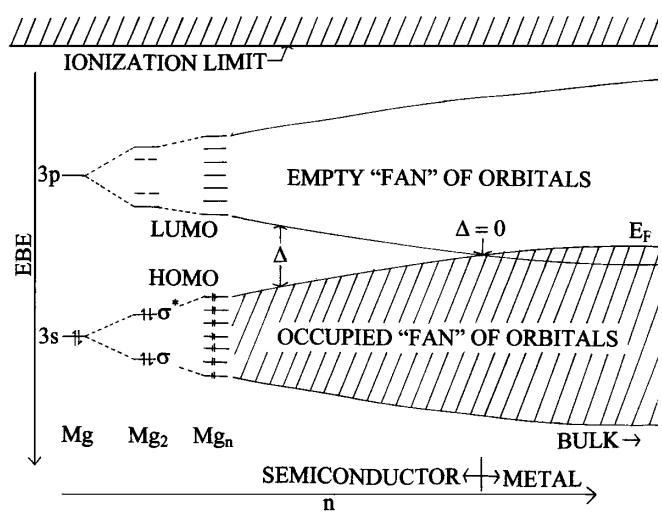

FIG. 1. Schematic of the evolving electronic structure of magnesium.

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occupied, $3p$-derived fan of MO's to the ionization limit is less than that of an electron ejected from the anion's energetically wider and fully populated, $3s^2$-derived fan of MO's to the same ionization limit. The result is a photoelectron spectrum consisting of a single, relatively narrow peak at low electron binding energy and a broader spectral feature at higher electron binding energy. The energy separation between them is the anion's gap, and measuring it as a function of size, n, allows one to determine the cluster anion size at which it closes. (It should be noted that, under Koopman's approximation, the measured gap is the HOMO-LUMO gap, a property of the neutral cluster. Rigorously, however, the measured gap is the anion's gap.)

Negative ion photoelectron (photodetachment) spectroscopy is conducted by crossing a mass-selected beam of anions with a fixed-frequency photon beam and energy analyzing the resultant photodetached electrons. This technique is a direct approach to measuring electron binding energies, and it is governed by the energy-conserving relationship, $h\nu = \mathrm{EKE} + \mathrm{EBE}$, where $h\nu$ is the photon energy, and EKE is the measured electron kinetic energy. The details of our apparatus have been given elsewhere [2]. Briefly, both mass spectra and photoelectron spectra were collected on an apparatus consisting of a laser vaporization source employing a Nd:YAG laser, a linear time-of-flight mass spectrometer for mass analysis and selection, a second Nd:YAG laser for photodetachment, and a magnetic bottle for electron energy analysis. Pure magnesium cluster anions were generated by laser vaporization (2.331 eV/photon) of a magnesium rod without the use of inert carrier gas. This resulted in magnesium cluster anions, uncontaminated by impurities such as oxides which had plagued previous attempts. Size-selected magnesium cluster anions were photodetached with 3.493 eV photons. The resolution of our magnetic bottle electron energy analyzer was ~60 meV at an EKE of ~1 eV.

The photoelectron spectra of Mg_n^- ($n = 3$–35, $n \neq 21$) are presented in Fig. 2. For $n \leq 15$, each spectrum consists of two main spectral features, in accord with the description above. The lower EBE, narrower peak corresponds to photodetachment from the bottom of the anion's $3p$-derived fan, while the higher EBE, broader and sometimes structured band corresponds to electron detachment from the anion's $3s^2$-derived fan. The energy spacing between these features is a direct measure of the anion's gap. Following this spacing by eye to increasing cluster size, one observes an overall trend by which it gradually decreases, although it is also marked by reopenings of the gap spacing at several specific cluster sizes. For example, the spacing closes relatively smoothly from $n = 3$–9, except for a "reopening" at $n = 4$. The smooth closure of the gap spacing is again disrupted by the gap opening up at $n = 10$, only to resume its closure at $n = 11$ and to continue smoothly until the gap spacing disappears at $n = 16$. The gap spacing remains closed

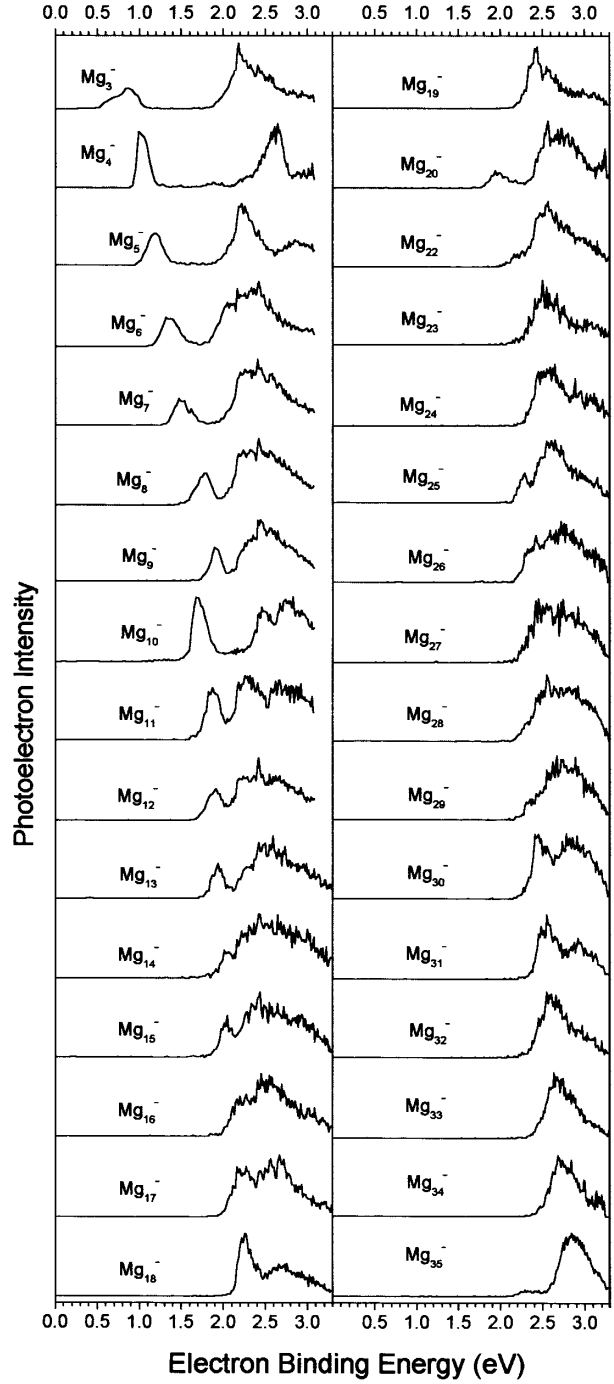

FIG. 2. Photoelectron spectra for Mg_n^-, $n = 3$–35, $n \neq 21$.

through $n = 19$, until it opens up still again at $n = 20$. Thereafter, the gap rapidly closes and remains closed for successive sizes through $n = 34$. Then, at $n = 35$, the gap spacing exhibits still another reopening.

Starting at $n = 16$, it becomes difficult to discern a nonzero gap. So, where does the gap actually close? We assert that effective band overlap first occurs at $n = 18$. At this size, the gap has become comparable to kT, and this marks the onset of metallic behavior in magnesium clusters. The overlap of bands is evidenced by the dramatic change in the shape of Mg_{18}^-'s spectral profile

relative to its immediately smaller neighbors. When overlap between the orbital fans first occurs, electrons from the $3s^2$-derived fan gain access to the high density of states associated with the $3p$-derived fan, giving them enhanced "p character." This manifests itself on the low EBE side of Mg_{18}^-'s spectral profile, where the relatively sharp feature indeed resembles the shapes of $3p$-derived peaks seen in larger magnesium cluster anions.

Numerical values for the gap in a given spectrum were determined by measuring the energy difference between the center of the lower EBE peak and a thermally corrected offset point on the low EBE edge of the broad, higher EBE spectral band. Because of the source conditions used to generate these cluster anions, the photoelectron spectra are thermally broadened. The extent of broadening (both thermal and instrumental) is best gauged from the widths of the lower EBE peaks, since they represent detachment from orbitals containing only a single electron. We have used half the base width of these peaks to thermally correct the low EBE edge of their high EBE bands. The resulting gap values are plotted as a function of cluster size in Fig. 3. The underlying trend seen in this plot is the relatively smooth closing of the gap with increasing cluster size, and it is evident that the gap closes for n values in their high teens. In addition, however, this trend is also punctuated by several sudden gap "reopenings."

These reopenings occur at sizes, $n = 4$, 10, 20, and 35. For the case of a three-dimensional harmonic oscillator potential, electronic shell closings occur at 2, 8, 20, 40, 70, . . . , valence electrons [3]. Assuming that each magnesium atom contributes two valence electrons to a given cluster, neutral Mg_4, Mg_{10}, Mg_{20}, and Mg_{35} all meet the criterion for being closed shell species. In general, the next energy level above a closed shell level is separated from it by more energy than typically separates levels in that system. Thus, when an extra electron is added to the above closed shell neutral clusters to form anions, their photoelectron spectra reflect this "closed shell plus one electron" property by exhibiting gap reopenings. The same effect that makes the gap unusually large necessarily minimizes the electron affinity at that same cluster size, and indeed this correlation is observed for $n = 10$, 20, and 35. Thus, these three reopenings observed in this system are clear manifestations of electronic shell model behavior. For $n = 4$, on the other hand, its gap reopening is not accompanied by a minimum in its electron affinity relative to its immediate neighbors. Thus, this reopening is probably not a shell effect. Calculations by Sin *et al.* [4] reach the same conclusion.

Shell structure is even more apparent in the mass spectra of magnesium cluster anions. Figure 4 presents our mass spectrum of $Mg_{n=3-70}^-$. Dramatic maxima in ion intensity are observed for $n = 4$, 9, 19, 34, 46, 55, and 69, while striking minima are observed for $n = 11$, 21, 36, 48, and 57. This intensity profile is reproducible. The mass spectral magic numbers at $n = 9$, 19, and 34 are due to the same shell closings that gave rise to photoelectron spectroscopic reopenings at $n = 10$, 20, and 35. For example, Mg_9^- has 19 valence electrons, just one less than the 20 required for a shell closing. Likewise, Mg_{19}^- has 39 valence electrons, just one short of the shell closings at 40, while Mg_{34}^- has 69, just one less than 70. While magnesium cluster anions can never have an even number of valence electrons and therefore can never perfectly coincide with shell closing numbers, they do gather stability as they approach shell closures. In each case, this enhanced stability manifests itself as a local ion intensity maximum (a magic number) in the mass spectrum. The magic numbers observed at $n = 9$, 19, 34, and 55 correlate with 3D harmonic oscillator shell closings.

Because of the occurrence of reopenings and magic numbers, it is clear that the shell model plays an important role in describing the electronic structure of magnesium clusters. The situation, however, is more complex than it might appear at first sight. The applicability of the

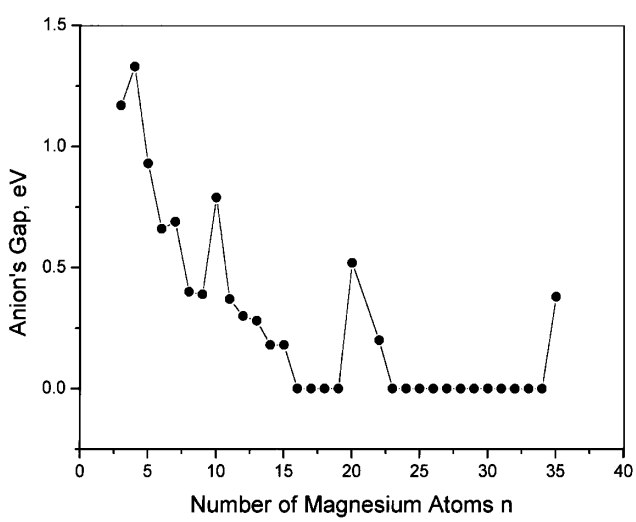

FIG. 3. Plot of Mg_n^- gap values versus their sizes, n.

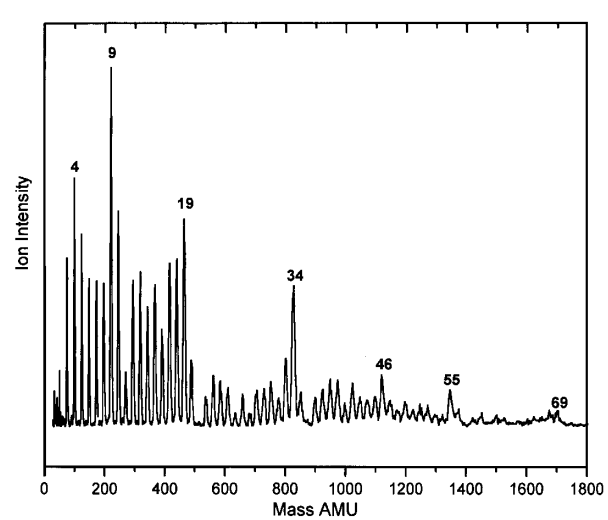

FIG. 4. Mass spectrum of $Mg_{n=3-70}^-$.

shell model has itself often been put forth as a criterion for metallic behavior. Yet, we see both a reordering and a magic number at $n = 10$ and 9, respectively, well below the observed gap closure at $n = 18$. Adherence to the predictions of the shell model is a working criterion for metallic behavior to the extent that it reflects electron delocalization within a finite size environment. Most likely, what we are seeing here is a hierarchy of criteria for metallic behavior, with the applicability of the shell model having some merit but with gap closure providing a somewhat stricter criterion.

Numerous investigators have preceded us in the quest to find the onset for metallic behavior in metal clusters. Mercury clusters have been the most thoroughly studied in this regard. Experiments on these aggregates were performed in the late 1980s and early 1990s by Brechignac *et al.* [5], Rademann and co-workers [6], and Haberland *et al.* [7], these including studies of inner shell excitations, photoionization size dependencies, plasmon excitations, mass spectrometric intensities, and cohesive energies. Collectively, this work indicated an onset for metallic behavior between ~40–100 mercury atoms per cluster. Then, more recently, Busani *et al.* [1] tackled this problem using anion photoelectron spectroscopy to monitor the closing gap in mercury cluster anions as a function of increasing size, n. While Busani did not observe gap closure, he was able to extrapolate his results to a gap closing at $n \sim 400$.

In addition, the onset of metal-like behavior in other metals has also been studied. In aluminum, for example, both Li *et al.* [8] and Gantefoer *et al.* [9] used anion photoelectron spectroscopy to observe the onset of *sp* hydridization and thus trivalency in relatively small clusters, and calculations by Rao *et al.* [10] supported their findings. The clusters of alkali and coinage metals have also been widely studied. If the criterion of partially filled bands is used to signal metallicity, then they should be considered metallic even at $n = 1$, i.e., at their atoms.

Both experimental and theoretical work has been conducted on magnesium. As the second simplest divalent metal and as the element with one electron less than aluminum, magnesium is well positioned to complement the work on mercury and aluminum. In the mid-1980s, Meiwes-Broer recorded the photoelectron spectra of the first few magnesium cluster anions ($n = 3$–6), and, although that work was not published, the electron affinities extracted from his spectra appear in the literature [11]. Theoretical work by Reuse *et al.* [12] explored structural and electronic properties of neutral and charged magnesium clusters. Kumar *et al.* [13] calculated HOMO-LUMO gaps for neutral magnesium clusters over the size range, $n = 2$–13, finding trends which followed those measured here by us. Calculations by Akola *et al.* [14] found that certain sizes of magnesium clusters favor tetrahedral geometries. Computations by Koehn *et al.* [15] investigated energetic and structural properties of neutral magnesium clusters. Very recently, Acioli and Jellinek have performed rigorous calculations which quantitatively reproduce most of the pertinent spectroscopic results derived from our photoelectron experiments. Their work is complementary to ours and is presented as a companion paper [16,17].

A recent experiment by Diederich *et al.* [18] is especially relevant to our work. These investigators recorded mass spectra of magnesium clusters grown in helium droplets and observed extensive electronic shell structure in cluster cations larger than $n = 20$. They interpreted their data as pertaining to neutral magnesium clusters and explained the observed shell structure in terms of a reordered shell level scheme, concluding that electron delocalization must be complete by about $n = 20$. Thus, their and our conclusions about the onset of metallicity in magnesium clusters (at $n = 20$ vs $n = 18$, respectively) are in close agreement. Even though their work was performed on a different charge state and at a much lower temperature than ours, the size onset for metallicity was nevertheless found to be essentially the same via both approaches.

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