

## Electron Delocalization in Magnesium Clusters Grown in Supercold Helium Droplets

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The formation of bare clusters from highly reactive metals can be achieved very effectively by the pickup of atoms into superfluid helium droplets. We report on the experimental observation of electronic shells in small magnesium clusters produced by this method. Mass spectra taken under various ionization conditions show steps and outstanding peaks, as well as pronounced minima. The abundance distribution suggests a transition to full electron delocalization which is complete at about 20 atoms. A so-far-not-reported electron reorganization is observed, leading to a novel shell structure.

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The confinement of a gas of electrons to a volume with a diameter comparable to the order of the electron's matter wave, i.e., the de Broglie wavelength, gives rise to new and interesting quantum phenomena [1,2]. In semiconductor quantum dots a restriction down to 100 nm leads to discrete electronic levels and, correspondingly, to novel optical and electronic properties [3]. In metals, distinct quantum effects will not emerge until a confinement to about one or two nanometers is reached. Objects of this size are called clusters. As in the shell model of atomic nuclei a mean field potential can be introduced to calculate the energy levels of such a system. This is the base of the jellium approach, which provides in a crude but attractive manner a qualitative understanding of physical phenomena in clusters of simple metals [4–6]. As an example it explains the higher binding energies in alkali clusters whenever the number of valence electrons leads to a complete filling of an energy level or shell. Experimental proof for the validity of such a concept comes, e.g., from the mass spectra of clusters. Under suitable conditions, species with high binding energies appear with increased intensity.

One still hotly debated problem is the influence and the proper theoretical representation of the electron exchange and correlation. In first order this is taken into account by applying the local density approximation (LDA) [7]. For high electron density systems, however, often more sophisticated approaches [8] are necessary to reveal certain features of the electron structure such as the interchange of nearly degenerate energy levels. Furthermore, details of the cluster surface and the ionic background have to be properly taken into account [5,9,10]. Therefore, experiments on clusters of simple divalent materials, where each atom can contribute two electrons to the electron ensemble, are promising for the exploration of the shell order within a dense and confined electron gas.

To date, experimental results on the electronic properties of alkaline earth metal clusters are rare [11,12]. Evidence that clusters of other divalent atoms might be described in part by the jellium approach arises from mass spectra of sputtered cadmium and zinc clusters [13]. Connected with the question of the electronic structure is a possible transition from a phase with localized electrons to one with delo-

calized electrons. In clusters of mercury atoms, which are also divalent, such a nonmetal-to-metal phase transition is still under discussion. Most probably it occurs in the range between one hundred and a few hundreds of atoms [14]. For magnesium, a transition to metallic signatures of the electronic wave functions has been theoretically predicted for  $N = 10$  [15,16], but so far no experimental verification was given. Here, we present the first proof for a transition to electron delocalization in free magnesium clusters, i.e., evidence of the onset of an electronic shell structure. In addition, a phenomenologically derived level interchange model is shown to be the key to understanding the details of the observed mass spectra and thus the shell structure.

Magnesium clusters are produced by the pickup of atoms in helium nanodroplets. This technique is currently used for the spectroscopy of atoms, molecules, and metal clusters [17]. We generate large helium droplets of approximately  $10^5$  atoms with a supersonic nozzle source which is cooled by a liquid helium cryostat to about 9.5 K. When passing an oven filled with magnesium, atoms are loaded into the droplets and form clusters (see Fig. 1). Any excess energy from cluster aggregation leads to an instantaneous evaporation of helium atoms—about 2000 atoms per 1 eV binding energy. This mechanism effectively cools the system to about 0.4 K on a time scale shorter than a microsecond. The supercold environment

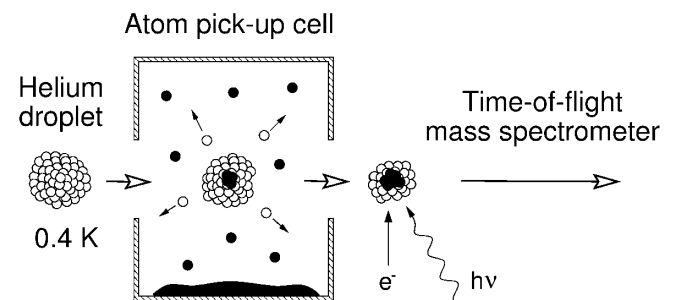


FIG. 1. In a pickup cell, magnesium atoms are loaded into helium droplets and form clusters. Photoionization by nanosecond and femtosecond laser light pulses as well as electron impact ionization serve to charge the clusters which then are analyzed by high resolution time-of-flight mass spectrometry.

and the clean nature of the droplets conserve the bare magnesium clusters and enable them to be transported into the ionization region of a high resolution time-of-flight mass spectrometer. For detection we employ electron impact and photoionization with nanosecond (5 ns at 266 nm, 0.1–20 MW/cm<sup>2</sup>), and femtosecond (200 fs at 400 nm, 1–50 GW/cm<sup>2</sup>) light pulses. These different methods are chosen in order to suppress the possible influence of resonant processes, which might affect the measured mass distribution. Since the experimental setup allows only the detection of charged particles, the role of the ionization cannot be reliably clarified at present. However, as the helium droplet environment acts as a heat bath, fragmentation of the metal core should be suppressed. As a typical example, Fig. 2 shows the spectrum of magnesium clusters (Mg<sub>N</sub>, with *N* the number of atoms) photoionized with nanosecond light pulses. Pure Mg<sub>N</sub> are recorded up to *N* = 80. The overall shape of the measured spectra roughly follows a log-normal behavior, which represents the statistics of atom accumulation in the helium droplet. Enhanced abundances highlight magic sizes which are partly followed by regions of low intensities, with exceptionally pronounced minima at *N* = 22, 37, 57, and 71. As these features appear in all measured mass distributions

irrespective of the ionization method, we are convinced that they image the relative cluster stabilities. If the magic sizes were caused by an isocahedral packing of the atoms one would expect intensity maxima for *N* = 13, (19), 55, 147, etc. Indeed, it was found that the size distribution of larger magnesium clusters with *N* ≥ 147 is governed by geometrical packing [18]. The missing of any sign of such *shells of atoms* in the spectra suggests that the whole pattern in this size range emerges from the *electronic structure* alone. Similar jellium shell closings were also found in the mass spectra of Mg<sub>N</sub><sup>-</sup> [19] and Mg<sub>N</sub><sup>++</sup> [20].

The well-defined electronic shell structure in clusters of simple-metal atoms results from the delocalized nature of the valence electrons [4–6]. In a homogeneous potential with spherical symmetry the energy levels  $E(k, \ell)$  are  $2(2\ell + 1)$ -fold degenerate, where *k* and  $\ell$  are the radial and angular momentum quantum numbers, respectively. Calculations, as well as extended experimental work on alkali and coinage metal clusters, show characteristic features (e.g., a high ionization potential) whenever an electronic angular momentum shell (*kl*) = (1*s*), (1*p*), (1*d*), (2*s*), (1*f*), (2*p*), (1*g*), (2*d*), (1*h*), (3*s*), ... is fully occupied, corresponding to a total number of valence electrons  $n_e = 2, 8, 18, 20, 34, 40, 58, 68, 90, 92, 106, 132, 138,$

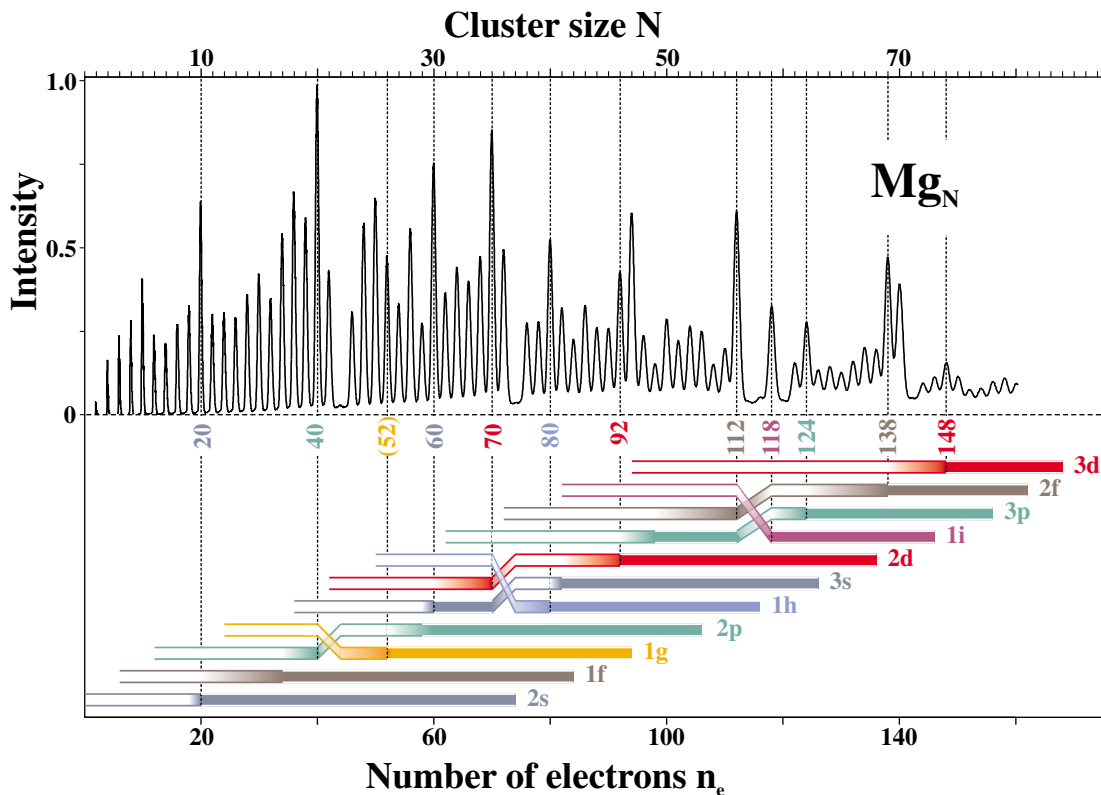


FIG. 2 (color). Mass spectrum of bare magnesium clusters photoionized with nanosecond laser pulses at 266 nm. The original spectrum shows isotopic resolution which, for the sake of clearness, is smoothed here. Enhanced abundances of clusters with specific sizes can be explained by assuming level interchanges. The magic electron numbers associated with the proposed model are given below the spectrum and indicated by the vertical dashed lines. With increasing shell filling, which is illustrated by the rising color strength, some levels reorganize.

168, . . . . These clusters are called magic. Note that, in magnesium clusters, shell effects are expected to appear at  $N = n_e/2$ . Some features in Fig. 2 coincide with the predicted pattern. But many others do not (i.e.,  $n_e = 60, 70, 80, 112, 118, 124, 148$ ). In order to check the influence of the higher electron density, we have performed LDA calculations using spherical symmetry for magnesium clusters [21]. No additional magic numbers appear. These computations reveal, however, that high angular momentum states decrease faster in energy with increasing  $N$  than the low- $\ell$  states, reflecting, in particular, the electronic motion in the outer region of the potential (see also Ref. [7]). In order to explain the observed shell closings in  $Mg_N$  we have to presume that this effect is even more pronounced than when calculated by LDA for spherical jellium. As a consequence, level crossings might occur upon shell filling. With this modification, practically all features of the mass spectrum can be explained (see the level crossings indicated at the bottom of Fig. 2 and the phenomenologically derived sketch of the new shell structure in Fig. 3). The enhanced intensities at  $n_e = 20$  and 40 agree well with results from the standard spherical jellium model. In larger clusters, electron reorganization now leads to additional magic numbers. For an illustration of how the new shell closings arise, let us consider  $Mg_{35}$  which has a high abundance in accordance with the  $(3s, 2d)$  closing in a 70 electron system. From the LDA calculations we know that the next unoccupied shell is  $(1h)$ , and thus the following magic number should be  $Mg_{46}$ . In order to explain the high intensity at  $N = 40$  ( $n_e = 80$ ), we assume that in the process of electron accumulation this  $(1h)$  level shifts below  $(3s)$  and  $(2d)$ , leading to a complete transfer of the  $(3s)$  and  $(2d)$  electrons into this level. Hence a new shell closure appears at  $n_e = 80$ , in accordance with the experimental finding. A further increase of the cluster size refills the  $(3s)$  and  $(2d)$  levels, which is completed at  $n_e = 92$ . The corresponding, very pronounced, feature in the mass spectra is found at  $N = 46$  and 47. Similar

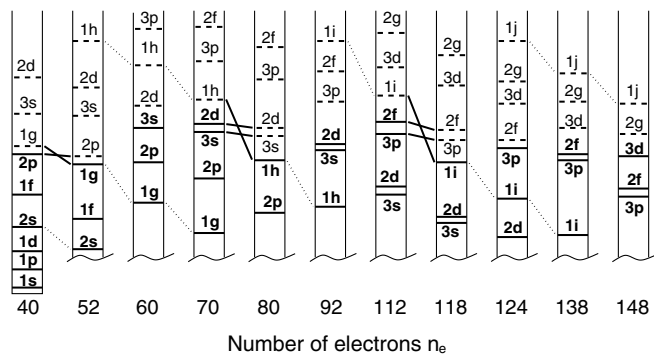


FIG. 3. Schematic illustration of the energy level order for magnesium clusters with a corresponding number of electrons. Solid lines: fully occupied energy levels, dashed lines: unoccupied levels. With the proposed level crossings the additional magic numbers in magnesium clusters can be explained.

level crossings explain the magic numbers at  $N = 26$  and  $N = 59$ , whereby the former is less prominent [22]. Note that the new level order works particularly well for high electron numbers, e.g.,  $n_e = 112, 118, 124, 138$ , and 148 (see the vertical lines in Fig. 2). Moreover, our approach provides a clue for the physical origin of the missing peaks at  $N = 22, 37$ , and 57. Obviously, a level crossing accompanied by the change in occupancy destabilizes the system to such an extent that clusters with specific sizes are practically missing. It is well known that closed-shell clusters of monovalent metals exhibit large separations between the highest occupied and lowest unoccupied energy levels (HOMO-LUMO gap) which leads to a pronounced drop in the intensity distribution beyond these clusters [6]. In this sense the missing peaks in Fig. 2 hint at strong energy gaps in the corresponding closed-shell  $Mg_N$ .

Whereas the phenomenologically derived level interchanges appear to explain the measured intensity distribution, the physical origin for the new level order still has to be interrogated. One reason could be an inhomogeneous atom density profile. As an example, this was found to be the key to explain the ordering of shells in large gallium clusters  $Ga_N$  [9]. A situation very similar to our observation was theoretically found for a completely different finite fermion system, i.e., clusters of  $^3He$  atoms [23]. The calculated potential shows an exceptionally pronounced well close to the edge of the cluster, the *Friedel dip* [24]. This causes a strong inhomogeneity of the fermion density. In detail, the wave functions of the high angular momentum states reside more in the outer part of the cluster and thus are more sensitive to the Friedel dip. As a consequence, an increased downward shift occurs, with the highest angular momentum levels even “diving” into the lower shell [23]. We believe that for magnesium clusters this occurs right at the Fermi energy. The existence of a Friedel dip in  $Mg_N$ , however, requires a peak in the electron density close to the surface which is usually suppressed in a high electron density system.

De Heer used an  $l$ -dependent correction term in the harmonic oscillator model which allows for an anharmonic distortion [6]. A slight increase of the anharmonic parameter induces new magic numbers at  $n_e = 52$  and 80. Also nonspherical deformations of the jellium potential might lead to new shell closings [5,25]. This is conceivable as the Fermi surface of magnesium is more complicated when compared to the simple alkali metal surfaces. A more recent theoretical work beyond the jellium model reveals instabilities of magnesium clusters towards Jahn-Teller deformations. Along this line, Reimann *et al.* [26] found structurally enhanced closings in tetrahedral geometry. Their stable clusters at  $N = 20$  and 35 coincide with prominent features in the mass spectra of magnesium clusters. Both the distortion and the deformation yield only partial agreement with the experimental findings. Particularly, the bulk of outstanding peaks at larger  $N$  (see Fig. 2) finds no thorough explanation with these approaches.

The last point to be addressed is the minimum cluster size to complete electron delocalization, i.e., the possible transition from nonmetallic to metallic bonding. The high intensity of  $\text{Mg}_{10}$  could correspond to a magic number at  $n_e = 20$ , but no signs of shell-closing effects are present in the spectrum for  $n_e = 8, 18,$  and  $34$ . These findings would allow the interpretation that at  $N = 10$  the delocalized phase is reached for the first time, whereas, in the size range up to about  $N = 20$ , the bonding might be less metallic. The enhanced intensity of  $\text{Mg}_{10}$  in the mass spectra is in accordance with results obtained by the density functional molecular dynamics method [15,16]. In clusters of up to 20 atoms, less distinct jelliumlike signatures of the electronic wave functions are found in the calculations. For  $N \geq 20$  the shell-closing effects are very significant in the experimental spectra, thus an upper limit for the final transition to electron delocalization is  $\text{Mg}_{20}$ , in agreement with the theoretical prediction by Kumar *et al.* [16].

In conclusion, the mass spectra of small magnesium clusters grown in supercold helium droplets provide clear proof of the existence of electronic shells and indicate a transition to electron delocalization with increasing  $N$ . Under the assumption that both valence electrons of each atom contribute to the electron ensemble confined to the cluster volume, a level interchange model provides a reasonable explanation for the measured cluster distribution. The exact theoretical background of the proposed model, however, still has to be established.

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