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Electronic shell and supershell structures in gallium clusters containing up to 7000 electrons

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Gallium clusters have been studied by near-threshold photoionization up to 2400 atoms. An electronic shell structure is clearly observed and may be interpreted by considering three electrons per atom. A quantum supershell corresponding to the interference between the contributions of triangular and square classical electronic orbits is obtained at about 2500 electrons. This number is considerably larger than expected from self-consistent homogeneous jellium calculations and is interpreted by introducing an inhomogeneous jellium approach.

The electronic properties of alkali clusters are well understood in the framework of the self-consistent spherical jellium shell model.[1] In the spherical symmetry, the electronic energy levels *nl* have a $2(2l+1)$ degeneracy. As in atomic and nuclear physics, the closed shells have enhanced stability leading to "magic" numbers in mass spectra or to energy gaps in ionization potentials[2-5] or in cohesive energies.[6] For large sizes, the *nl* levels are called subshells and they tend to condense into highly degenerate shells. It may then be shown, using a semiclassical approach,[7,8] that this electronic shell structure can be related to quantization conditions for the closed classical orbits of the electron in a spherical potential. In fact, at nonzero temperature, the triangular and square classical orbits are dominant. Interference occurs between the contributions of both orbits with lengths close to each other and the resulting beating structure is called a supershell structure. In quantum calculations, the supershell effect appears in the electronic density of states as a beating pattern in which the oscillating part of this density is enveloped by a slowly varying amplitude. This effect was predicted in alkali metal clusters by Nishioka, Hansen, and Mottelson[9] and has been observed in sodium[10,11] and in lithium.[12]

In trivalent metal clusters, the same effects are in principle expected but we have to consider three valence electrons per atom ($N_e=3N$) and therefore, a higher electronic charge density in the cluster. Up to now, aluminum is the most studied system. Whetten and co-workers[13,14] have interpreted the results obtained in the size range $20<N<400$ ($60<N_e<1200$) within the spherical jellium model, but they were not able to explain all the observed structures. Lermé *et al.*[15] have since shown that a clear shell structure emerged at $N\approx250$ atoms and extended the range of observation up to 900 atoms. These results were tentatively interpreted in terms of electronic shell structure within the semiclassical theory (classical star orbit). Although this model could explain such a structure in clusters containing up to about 900 atoms, it predicts that this shell structure must change for larger clusters, but subsequent observations by Lermé and coworkers[16,17] reveal the same shell structure up to 2000 atoms. Finally, Martin, Näher, and Schaber[18] have shown that this shell structure goes up to 10 000 atoms and can be explained by geometric arrangement of atoms, namely, the coverage of successive triangular faces on close-packed octahedral clusters. The structure of aluminum clusters appears mainly dominated by geometric effects.

In contrast with aluminum, indium clusters are more jelliumlike, and the energy gaps observed in ionization potentials are well related to electronic shell closures.[19] In addition to different crystalline structures in the bulk, aluminum and indium have also very different melting points, respectively, 933 and 430 K. Moreover, under standard conditions, aluminum is rigid while indium is rather soft. Indium clusters are easily liquidlike and close to the spherical structure assumed in the jellium model. As discussed by Stampfli and Bennemann,[20] the occurrence of electronic shell structure depends on the size but also strongly on the closeness of the cluster temperature to the melting point of the bulk metal. Following this argument, gallium (which has a melting point of 303 K) will be a very good system in which to study the electronic shell structure of large clusters having a great number of electrons.

In this paper we present near-threshold photoionization experiments in large gallium clusters. Electronic supershell structure is clearly observed in nonalkali clusters. Our results extend up to 7000 electrons, which represents a huge increase in the number of electrons per cluster, considering that the published results concerning alkali metal clusters are limited to no more than 3000 electrons.[10] The first beating structure occurs around 2500 electrons, a number of electrons considerably larger than in sodium. This point is interpreted and discussed in the last part of the paper and we show that the supershell structure is very sensitive to the surface properties.

The experimental setup is similar to the one used in previous experiments on aluminum and indium.[17,19] The clusters are produced by the laser vaporization technique. Two kinds of cluster sources have been used: one with a disk, the other with a rod. The block source is cooled to about 100 K by liquid nitrogen, to stop the gallium from melting. The clusters are photoionized by a UV laser having a photon energy very close to the ionization

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threshold. They are then analyzed through a Wiley McLaren time-of-flight (TOF) mass spectrometer, perpendicular to the beam. The initial transverse velocity of the clusters in the TOF is compensated by an electric field applied between deflector plates. With this geometry, the mass resolution is good (450 in our case[17]) but the mass range of the spectrometer is limited. However, it allows us to observe the oscillations in mass spectra, and it may be increased by applying a linear ramp voltage to the deflector plates.[21]

In the small size range, $40 < N < 200$, the mass spectra of gallium clusters are very similar to those obtained in indium[19] with shell closings at $N = 46, 66, 90, 112$ corresponding to a number of electrons $N_e = 138, 198, 268, 338$. These results are in good agreement with an electronic shell structure. Gallium clusters may therefore be considered as good candidates for the observation of a supershell structure.

Figure 1(a) shows a mass spectrum of larger gallium clusters in the size range $400 < N < 1800$. The ionization energy (4.76 eV) is close to the ionization threshold. Because the mass transmission of our perpendicular TOF spectrometer is limited, Fig. 1(a) corresponds to the summation of three mass spectra with a transmission centered on three different masses. Clear and regular oscillations appear in the mass spectrum. They correspond to oscillations in the IP or, for very large clusters, to oscillations in the electronic density of states at the Fermi level. The oscillations have a steplike shape for small clusters ($N < 800$); they are smoother for larger ones. This is not surprising: the ionization energy is closer to the threshold for the smallest clusters, and the energy gaps become smaller for the largest clusters. In order to analyze the signal oscillations, we subtract from the raw signal the strongly smoothed bell-shaped envelope. After a slight smoothing, the oscillating pattern obtained by this method is shown in Fig. 1(b). Strong oscillations are observed in the region $400 < N < 700$ and again in the region $N > 1000$. For $700 < N < 1000$, the oscillations are much less intense and two times faster on a $N^{1/3}$ scale. This kind of pattern is characteristic of the supershell structure, i.e., the quantum beat mode resulting from the interference between classical triangular and square orbits. The doubling of the oscillation period in the node region has been also observed in lithium clusters.[12] This doubling corresponds to contributions of two-turn triangular and square orbits which are in phase (2π phase shift) when the single-turn ones are in opposite phase (π phase shift).

In order to better characterize the electronic shell and supershell structures of gallium clusters, we have plotted the $N_e^{1/3}$ values corresponding to the observed dips in experimental spectra as a function of the dip index [Fig. 2(a)]. A straight line is fitted to the points lying below the beating region. The corresponding slope (0.603) is close to that obtained with sodium or lithium (0.61). In the beating region, a plot of observed minima yields a slope which is only half as steep. On Fig. 2(b) is plotted the difference between this fit and all the experimental data. It clearly shows that before and after the node region the

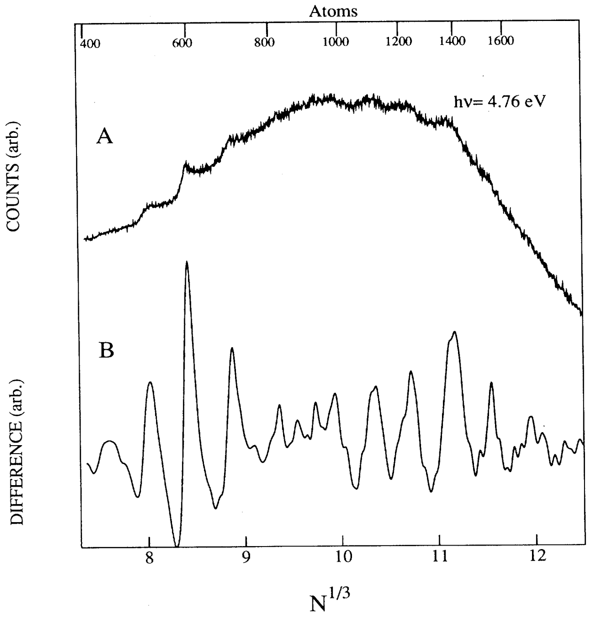

FIG. 1. (a) Photoionization mass spectrum of Ga_N clusters obtained at 4.76 eV in the mass range $400 < N < 1600$ and given on a $N^{1/3}$ scale. (Three spectra, respectively, centered around $N = 600$, 1000, and 1400 atoms have been added to display a larger domain of sizes.) (b) Slightly smoothed difference between (a) and its highly smoothed envelope. It clearly enhances the intensity fluctuations observed in (a).

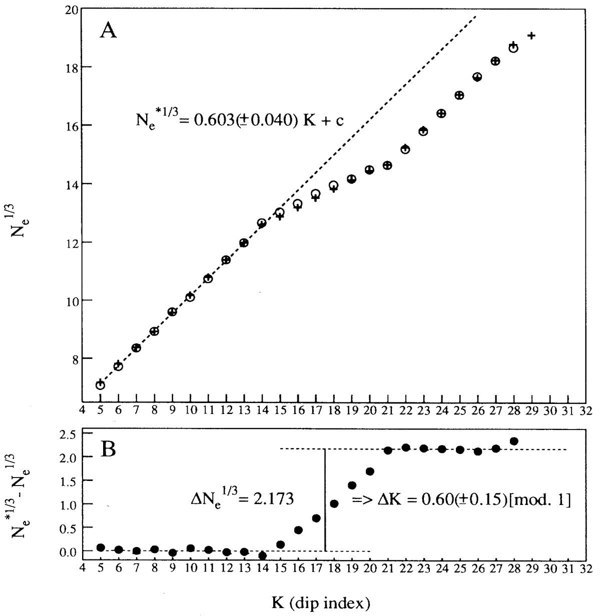

FIG. 2. (a) Cube root of the most pronounced shell closing numbers ($N_e = 3N$) observed in the mass spectra (circles) as a function of the dip index K. The shell closures given by the inhomogeneous jellium calculations are indicated by crosses. In the node region the most intense effects are reported for both curves. (b) Difference between a straight line fitted to the experimental points lying below the beating region and the experimental data. This line is drawn on the upper part [dotted line in (a)].

points are aligned on straight lines with identical slopes. A shift of 0.60 (modulo 1) in the dip indexes for these two antinodal regions can be deduced from this curve. This shift is close to half an integer which corresponds to a phase shift of π. Such a phase shift will occur between triangular and square orbit contributions when passing through the node of the beating structure. It must be also remarked that if we plot the index of the shells as a function of $N^{1/3}$ (N is the number of atoms), the obtained slope (0.418) does not correspond to any known geometry. Even without supershell, our results could not be interpreted in terms of atomic shells. Moreover the supershell is a signature of an electronic effect.

However, the beating structure occurs in gallium at $N_e \approx 2500$ electrons (≈ 830 atoms), while it occurs at $N_e \approx 900$ or 1000 electrons in sodium and lithium clusters depending on the authors. Self-consistent homogeneous jellium calculations,[22] as well as independent-electron calculations using jellium-type potentials,[23] have indeed predicted a shift of the node region when the Wigner-Seitz radius r_s decreases: the node region of the beating is calculated to occur around $N_e = 750$ electrons for $r_s = 3.93$ a.u. (sodium case) and around $N_e = 1150$ electrons for $r_s = 2$ a.u. ($r_s = 2.19$ a.u. for gallium). Since the node region extends over 300 electrons, the agreement between theory and experiment may be considered as reasonable for sodium but the calculations are in marked disagreement with our experimental results for gallium. Nevertheless, one should remember that the position of the beating region strongly depends on the surface potential of the clusters: the beating region is very sensitive to the differences of the phases of the triangular and square orbit contributions to the density of states. The surface softness modifies these classical orbits and the square orbit is more modified because the electron lies closer to the surface in a square orbit than in a triangular orbit. As it may be shown by detailed calculations,[26] the surface softness induces at first approximation a shift between the phases of the triangular and square orbit contributions and this results in a significant shift in the predicted beating position.

In order to perform calculations taking into account a possible softness of the surface potential profile, we have slightly modified the square shape of the jellium density profile. The approach is similar to the inhomogeneous jellium model introduced by Martin and co-workers.[24] In our calculations, we have used a trapezoidal density for the positive ionic sea: the jellium density is assumed constant except close to the surface where it varies linearly over a thickness ε. The physical basis for such a model may be related to the atomic vibrations in a liquid droplet: the surface atomic shell vibrates with an amplitude close to the average interatomic distance. This tends to smooth the average ionic density in the cluster surface region. We therefore consider that it is reasonable to take a thickness ε smaller than or comparable to the average interatomic distance (6.3 a.u. in gallium) and we use ε as an adjustable parameter. For a given ε value, we perform self-consistent jellium calculations for some selected sizes between 300 and 6600 electrons and we extract for each size the effective potential experienced by an electron. We have used this procedure to check that the shape of the effective potential does not vary significantly with the cluster size, especially in the surface region. We then use this optimized average effective potential to obtain the shell energy for all sizes by an independent-electron quantum calculation. We have also checked that this method, using an optimized potential, gives the same results for closed-shell numbers as a complete self-consistent jellium calculation over a large size domain.[25] This procedure allows us a fast exploration of the beating shift as a function of ε.

We find the best agreement with the experiment for $\varepsilon = 6$ a.u. Figures 2(a) and 3 display a comparison between the shell energy obtained by this method and the experimental spectra. In Fig. 3, we present the oscillation pattern of three experimental spectra recorded with the mass-spectrometer transmission centered at three different size domains. They cover the whole studied mass range ($100 < N < 2300$). The minima in the shell energy correspond to most stable clusters and to highest IP. They therefore lead to minima in our experimental oscillation pattern. The agreement between the experiment and the calculation is very good, at the cost of an adjustment of the thickness ε.

As explained above, the beating position is very sensitive to the shape of the effective potential. For example, it shifts from $N_e = 1350$ to 2500 electrons when the thickness ε goes from 3 to 6 a.u. Since the electronic density is lower in sodium clusters, the same potential shape close to the surface leads in sodium to a much smaller shift in the beating position.[26] In fact, the homogeneous jellium

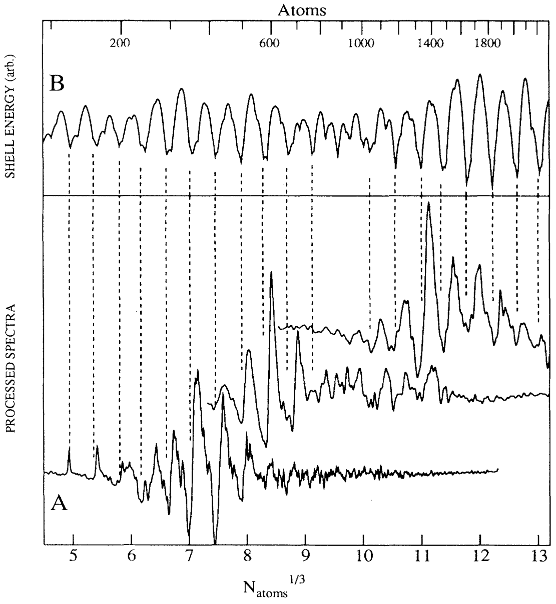

FIG. 3. Comparison between the dips observed in three processed experimental mass spectra (a) (see Fig. 1) and the minima in the oscillations of the total shell energy of the clusters vs $N_{\text{atoms}}^{1/3}$ (b). The shell energy is computed using an optimized deformation of the jellium density ($\varepsilon = 6$) and location of the minima are indicated by dotted lines.

model is not in perfect agreement with the experiments even in the sodium case. For example, the node region is predicted at 750 electrons[22] and is observed around 1000 electrons in Ref. 10. Probably the same kind of inhomogeneous jellium could be also introduced to interpret the sodium experiment.

Our model of a smoothed inhomogeneous jellium predicts shell and subshell closing numbers, which differ slightly from those given by homogeneous jellium calculations even for quite small clusters. This point will be discussed in detail in a forthcoming publication, but our model is consistent with the experimental results throughout the studied size range. This is well illustrated in Figs. 2(a) and 3, which correspond to $100 < N < 2200$.

In conclusion, we have observed electronic shell structure in a system having such a high number of electrons (up to 7000). We have also obtained quantum supershell structure in non-alkali-metal clusters. The first beating occurs in gallium at a number of electrons (2500) considerably higher than in alkalis (900–1000). We have shown that for small r_s the beating position is very sensitive to the effective potential shape at the surface. We can interpret our results by a simple model of smoothed jellium which is consistent with the observed shells, from small sizes up to 7000 electrons. The second beating structure is expected at about 8000 electrons, not very far above the present upper limit of our experiment. In fact, the number of shells between two beating structures is almost not affected by the softness of the surface because it depends mainly on the increase in the cluster radius, the surface effect being already taken into account in the position of the first beating. The deviation from the straight line for the last shell, in Fig. 2, seems in agreement with our model and could correspond to the beginning of the second beating. Further experiments are in progress to test the predictions of our model at larger cluster sizes.

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