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Competition between atomic shell and electronic shell structures in aluminum clusters

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Since the discovery by Knight[1] of the electronic shell structure in Na_N clusters, many attempts were done to apply the same concepts to nonalkali metal clusters. The same kind of electronic shell structure was obtained in noble metal clusters[2–4] for small sizes ($N \leqslant 100$) even if some competition occurs with specific geometric structures.[3–5] The same effects were also observed in cadmium and zinc metal clusters.[6,7] In contrast, the alkali–earth clusters[8–10] were found to be dominated by icosahedral geometric structures.

In trivalent metal clusters, aluminum was the most studied system. Whetten *et al.*[11,12] interpreted most of their results by the electronic shell model. However, some features in the size range $20 < N < 400$ cannot be explained in this frame. Competition with geometric structures was invoked[13] and was recently studied by mobilities measurements[14] for $N < 100$. For larger sizes, Lermé *et al.*[15] showed that a clear and regular structure emerges from $N > 250$. Martin[16] observed this new shell sequence up to 10 000 atoms and gave a quite convincing interpretation: It corresponds to the coverage of triangular faces on octahedral clusters. The temperature of the large clusters produced in molecular beams is expected to be close to the nozzle temperature (300 K in Ref. 15). At this quite low temperature, large aluminum clusters have well-defined geometry and may be considered as solidlike. This is not surprising because the aluminum melting point is quite high (933 K). In contrast to this situation, indium and gallium have much lower melting points (respectively 430 K and 303 K). Recent studies[17,18] reveal the occurrence of an electronic shell structure in these clusters, probably because they may be considered as liquidlike clusters. In this note, we show how, by changing the source conditions, we can observe the transition between the atomic shell structure and the electronic shell structure in aluminum clusters.

The experimental setup has been already described in a previous paper:[15] Clusters are generated in a laser vaporization source, with a waiting room.[19] They are photoionized by a tunable (uv) laser and analyzed through a perpendicular time-of-flight mass spectrometer. The vaporization chamber and the nozzle may be heated up to 300 °C above the room temperature, while the pulsed He valve is thermally isolated from the source and continuously cooled by a water flow. The mass spectra are recorded for photon energy very close to the ionization threshold. Under these conditions minima are observed in the mass spectra as well for closed electronic shells,[17,18,20] as for closed atomic shells.[20]

Thermodynamical equilibrium conditions are not fulfilled during the cluster generation in a vaporization laser source, mainly because of its pulsed operating mode. The cluster temperature is generally estimated to be close to the nozzle temperature for long residence times, and lower for shorter residence times.[21,22] However, we have not only to consider the cluster temperature, but also the fact that metastable structures may be formed. For example for a nozzle at room temperature, no particular structure is observed in aluminum mass spectra with $N > 250$ for a long residence time. However, by shortening this time delay, it is possible to obtain reproducible mass spectra with octahedral shaped clusters [Fig. 1(A)].

In order to produce warmer liquid-like clusters, we heated the nozzle. Figure 1(C) shows aluminum mass spectra for a source temperature of about 473 K. A completely different structure emerges with a periodicity about two times slower. We may also observe in the same spectrum the coexistence of these two structures [Fig. 1(B)], the octahedral one at large sizes and the new structure of Fig. 1(C) at smaller sizes.

Let us concentrate now on the new shell sequence of Fig. 1(C). If we plot $N^{1/3}$ as a function of the shell index, we obtain a straight line with a slope of 0.42 which does not correspond to any known close packed geometry. However if, instead of $N^{1/3}$, we plot $N_e^{1/3}$, the cubic root of the valence electrons number ($N_e = 3N$), the slope becomes 0.61, very close to the slope observed for electronic shells in alkali metal clusters or in melted gallium. The agreement with the magic numbers of gallium is also perfect. We conclude that aluminum clusters produced in conditions of Fig. 1(C) are dominated by the electronic shell structure and are liquidlike. We therefore observe in Fig. 1 the transition between the atomic shell structure (octahedral symmetry) and the electronic shell structure (liquidlike clusters).

These electronic shells are linear as a function of $N_e^{1/3}$ up to 1800 electrons (600 atoms). This means that as in gallium, the beat in the supershell structure[23] does not occur at 1150 electrons, as predicted by standard self-consistent jellium model,[24] but is shifted at larger sizes. In gallium, the beat is observed at 2500 electrons.[18] Our preliminary results seem to indicate a beat around 2000 electrons in aluminum, but the present sensitivity of our experiment at large sizes ($N_e > 1800$) is not sufficient for a definitive conclusion.

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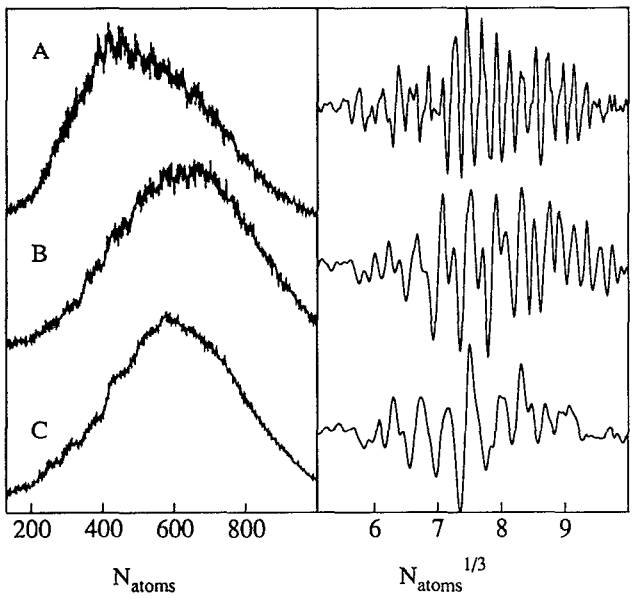

FIG. 1. On the left-hand side, aluminum mass spectra for different nozzle temperatures: (A) $T=273$ K; (B) $T=373$ K; and (C) $T=473$ K. On the right-hand side, same mass spectra but the bell shaped envelope has been removed. Spectrum (A): the fast oscillations correspond to the octahedral structure. Spectrum (C): the oscillations correspond to the electronic shell structure. Spectrum (B): competition between the two structures.

Nevertheless, our results show that the source heating process promotes the production of liquidlike aluminum clusters. The question arises if the clusters are completely melted, or if we have only a surface melting.[25] Our aluminum clusters may also be supercooled, the nucleation process being quite complex in our source.

In conclusion, we have observed for the first time the electronic shell structure in Al_N clusters in a size range $200 < N < 600$. We have also observed the transition between the atomic shell structure and the electronic one in the same size range. Further experiments are in progress in order to achieve a better characterization of this transition on a thermodynamic point of view.

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