

Nonjellium-to-Jellium Transition in Aluminum Cluster Polarizabilities

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The static dipole polarizabilities of aluminum clusters with up to 61 atoms, measured with a novel position-sensitive time-of-flight mass spectrometer, are at odds with jellium predictions for clusters with less than 40 atoms and agree for larger clusters, revealing for the first time the nonjellium-to-jellium transition in a metal cluster system.

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The electronic properties of monovalent metal clusters have been found to be consistent with the jellium model.¹ The ionic cores in these clusters play a minor role and it is found that the electronic structure corresponds to that of a spheroidal potential well giving rise to electronic shells. Shell structure is observed in the stabilities and ionization potentials for neutral as well as ionized clusters and shell closings are found when the cluster contains 2, 8, 18, 20, 40, 58, 92, . . . , electrons, in perfect agreement with the model. Most relevant for this discussion is that the measured polarizabilities² of monovalent metal clusters are in good agreement with the jellium predictions.^{3,4}

The jellium model is also expected to be valid for polyvalent metal clusters and for trivalent aluminum clusters, in particular, since bulk aluminum is very well described as a free-electron metal.⁵ Shell closings are predicted for Al₁₃, Al₂₃, and Al₃₁.⁶ However, electron-affinity (EA),⁷ ionization-potential (IP),⁸ reactivity,^{9,10} and stabilities measurements¹¹ are only in partial agreement with these predictions: There is no evidence for the predicted closing at 31 and other anomalous features are observed.^{8,10}

Upton's recent *ab initio* studies¹² of aluminum clusters with up to 6 atoms show important departures from the jellium model caused by the strong ionic-core potentials. A proper description requires inclusion of the ionic pseudopotentials which are much more important for polyvalent than for monovalent metal clusters.¹² Although shell structure is already apparent even for these clusters, nonjellium effects such as high ionization potentials and anomalous shell filling orders as well as a tendency for the clusters to assume shapes with high point-group symmetries are predicted. Properties such as ionization potentials and polarizabilities, which are sensitive to the geometry and the position and density of states near the Fermi level are expected to depart from jellium behavior.¹² As the size increases the perturbations caused by the ionic cores become less important and for sufficiently large clusters the jellium model will be valid.

In this Letter we present the experimental polarizabilities of aluminum clusters with up to 61 atoms. Polarizability measurements are especially well suited to resolve

some of the issues raised above, since polarizabilities are very sensitive to the electronic structure at the cluster surface and mainly address electronic states near the Fermi level. We find significant disagreement with the jellium predictions for clusters with less than 40 atoms, while large clusters are in good agreement.

The apparatus¹³ is shown in Fig. 1 and a brief description follows. The aluminum clusters are produced in a laser-vaporization cluster source.^{13,14} The helium-carried cluster beam is collimated with 0.7-mm slits and then passes between the pole faces of the inhomogeneous electric field, similar in design as used in Ref. 2. In this field the neutral clusters are deflected proportionally to their polarizabilities and inversely proportionally to their mass. The clusters then enter the time-of-flight (TOF) mass spectrometer where they are ionized with light from an excimer laser at 6.41 eV with a fluence of less than 0.1 mJ/cm² per pulse. The ions are accelerated perpendicularly to the neutral beam by a succession of three uniform electric fields. These electric fields are adjusted so that the time of flight of a cluster ion depends both on its mass as well as on its position when it was ionized. In Fig. 2 we show an example of two mass spectra in the position-sensitive mode, one with the deflecting field off and the other with the field activated. The shifts

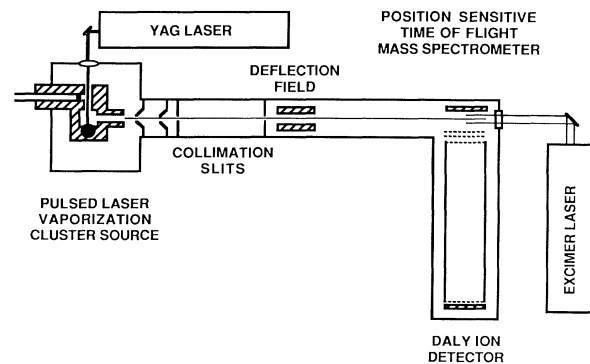


FIG. 1. Schematic overview of the apparatus (not to scale). The distance from source to the deflecting field is 1.4 m and from the source to the mass spectrometer is 2.4 m.

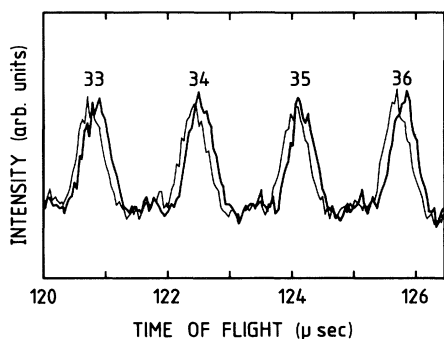


FIG. 2. Partial TOF mass spectra in the position-sensitive mode in the region $N=33-36$, one with the deflecting field off, the other with the deflecting field activated (bold). The shifts in the mass peaks correspond to deflections of about 0.2 mm.

of the mass peaks are due to the deflections of the cluster beam. By measuring the shifts of the average positions of corresponding mass peaks, the cluster deflections are determined. Auxiliary velocity measurements are made with the TOF spectrometer mounted coaxially to the beam. Because of the initial velocities of the clusters the mass peaks will be shifted compared with the perpendicular configuration. The velocities are determined from the shifts and are found to vary continuously from 1.23×10^5 to 1.18×10^5 cm/sec for Al_{15} to Al_{60} under the conditions that the deflection measurements are made. Cluster polarizabilities are determined relative to the atom from the relation

$$\frac{\alpha_N}{\alpha_1} = \frac{d_N v_N^2}{d_1 v_1^2}, \quad (1)$$

where α is the polarizability, v is the velocity, and d is the deflection and the subscripts refer to the cluster. The atom and dimer polarizabilities are measured relative to the lithium atom¹⁵ and are in good agreement with *ab initio* calculations.¹⁶

The method outlined above offers several advantages compared with the standard technique as, for example, in Ref. 2. The deflections of all clusters, from the atom to Al_{61} are measured simultaneously, thereby greatly decreasing acquisition times and eliminating many sources of systematic errors. Since complete spectra containing both position and mass information are taken with every laser pulse, fluctuations in the cluster-beam intensities do not affect these measurements as they do in measurements where a slit is scanned across the beam to measure deflections.²

The polarizabilities per atom from 1 to 61 are shown in Fig. 3. There is a gap from 3 to 15 because the ionization potentials of those clusters exceed or are very close to the ionizing light used,^{8,10} resulting in no or very weak signals. Large oscillations in the polarizabilities are observed for clusters with less than about 40 atoms with pronounced minima at 19, 23, 27, and 32 and weak-

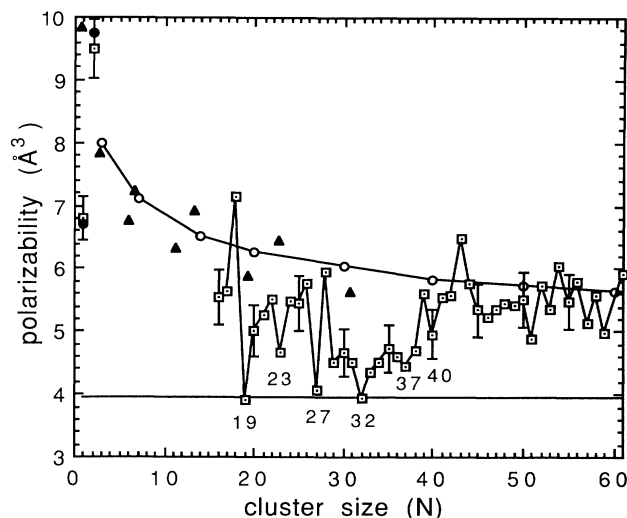


FIG. 3. Measured per-atom polarizabilities of aluminum clusters Al_N from this work (open squares); *ab initio* calculations from Ref. 16 (filled circles); self-consistent spherical jellium calculations from Ref. 17 (filled triangles); and spherical jellium calculations in the Thomas-Fermi approximation from Ref. 4 (open circles).

er minima at 29, 37, and 40. The region between 29 and 38 is particularly low, after which there is a rise and a recovery. Clusters with less than 40 atoms clearly disagree with jellium predictions in the values as well as in the general trend.^{4,17} In contrast, the polarizabilities beyond 40 are in good agreement with the spherical jellium model.⁴

The observed behavior can be understood if the metal sphere and the spherical jellium models are taken as starting points. External electric fields are completely screened within a metal sphere and the polarizability is the cube of the radius. For a jellium sphere the polarizability is enhanced because the electronic charge density spills out beyond the jellium radius and the polarizability per atom a_N may be written as¹⁸

$$a_N = \frac{(R + \delta)^3}{N}, \quad (2)$$

where R is the jellium radius (for Al_N , $R = 1.579N^{1/3}$ Å) and δ (which is related to the electronic spillout) is predicted to be approximately constant for all sizes.¹⁸ For aluminum, in the Thomas-Fermi approximation, δ varies from 0.70 to 0.79 Å for clusters 14 to 60.⁴ The straight line in Fig. 3 at 3.94 Å^3 corresponds to $\delta=0$ in (2), and for clusters 19, 23, 27, and 29–38, δ is close to or equal to 0 demonstrating the departure from jellium predictions even more clearly.

As pointed out by Upton,¹² in aluminum clusters, perturbations due to the configuration of the ionic-core potentials cause departures from jellium and we attribute the anomalous polarizabilities to this effect. When the

polarizabilities do agree with jellium predictions over an extended range of cluster sizes we conclude that the perturbations are no longer important, so that for clusters with more than 40 atoms the jellium model is valid.

Electronic shell structure may nevertheless still be observed for the smaller clusters provided the effective single-particle potentials are approximately spherically symmetric.¹ However, due to geometrical and surface effects, the shapes of these potentials may change discontinuously from one cluster to the next, influencing the shell filling order. We expect nonjellium effects of this kind in view of our results and they are most likely observed in other measurements as discussed below.

Maxima in the EA's (from 2 to 32) from photoelectron spectra of cluster anions⁷ are found at 13, 17, 19, 21, 23, 27, and 29 (the underline indicates a major feature). Note that these features correspond very well with the minima observed in the polarizabilities. Studies of Al_N anions show that 13^- , 23^- , and 37^- are almost unreactive with O_2 ,⁹ and high stabilities are found for 13^- and 23^- .¹¹ Reactivities of 7^+ , 13^+ , 14^+ , and 23^+ cations are exceptionally low¹⁰ and, finally, minima and steps in the IP's of neutral clusters from 1 to 70 (Ref. 8) are found at 14, 19, 21, 23, 25, 29, 33, 37, The major features in the EA's, reactivities, and stabilities are consistent with a spherical-harmonic-well potential, which has shell closings for . . . , 40, 70, 112, . . . , electrons. The IP measurements, however, indicate shell openings for 23 and 37. This is difficult to reconcile in the jellium model, but may still be consistent with shell structure if cluster-dependent level reordering is considered. Nonjellium effects are also responsible for the rich fine structure observed in the IP's, the EA's, and the reactivities. In this context it is interesting to note the correspondence between the spherical numbers observed here and the magic numbers for argon clusters: 13, 19, 23, 26, 29, 32, 34, . . . ,¹⁹ indicating stable geometrical structures.

In conclusion, our measurements provide the first clear evidence of the expected nonjellium-to-jellium transition in a polyvalent metal cluster system. We find that the jellium model is valid only for aluminum clusters with more than 40 atoms. Important cluster-size-dependent surface and geometrical effects caused by the ionic-core potentials are responsible for anomalous polarizabilities of small clusters and are expected to account for features in the ionization potentials and electron affinities. In any case, calculations which take into account the ionic cores will be necessary¹² to accurately describe the electronic properties of aluminum clusters with less than 40 atoms.

For clusters with more than 40 atoms our results indicate that ionic-core perturbations are no longer important so that the jellium model is valid.

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