

## Polarizability of alkali clusters

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Molecular beam deflection measurements of the static electric polarizability per atom,  $\alpha/N$ , are reported for sodium clusters up to  $N=40$ . The quantity  $\alpha/N$  decreases from the atomic polarizability to approximately 150% of the bulk value, at  $N=40$ . Potassium-cluster polarizabilities follow closely the same pattern up to  $N=20$ . There is some correlation between the polarizabilities and previously observed electronic shell structure.

The static electric polarizability is an experimental parameter useful in following changes which take place as metal clusters grow larger toward the extended crystalline conducting state. In view of the recent observation of electronic shell structure in the alkali clusters,<sup>1,2</sup> it also becomes of interest to determine whether the shell structure is manifested in physical properties of the clusters. Here we report on a series of direct measurements of the polarizability of sodium and potassium clusters by electric deflection of a molecular beam.

The experimental values for sodium (see Fig. 1) follow a general downward trend toward the bulk value, becoming approximately constant between  $N=20-40$ . Between  $N=1-6$  the polarizability appears to reflect individual molecular structures. There is an abrupt drop through  $N=7$ , to a minimum at the shell closing  $N=8$ , after which

it rises somewhat, to drop again toward the shell closings at  $N=18-20$ . Corresponding results for the static polarizability of potassium follow the sodium data closely.

Several recent calculations<sup>3-5</sup> of the static polarizability are in substantial agreement with each other and follow the general trend of the experimental results on a curve which lies between the experimental results and the bulk value. The calculations assume spherical symmetry, and the results are most easily stated in terms of an enhanced classical polarizability, with sphere radii increased by approximately 1 a.u., resulting from induced surface charge at the jellium boundary.

The experimental apparatus<sup>1</sup> produces a supersonic beam of metal clusters seeded in stagnation pressures of several atmospheres of argon. Varying source conditions were established for sodium. With  $P_M$  representing alkali-metal va-

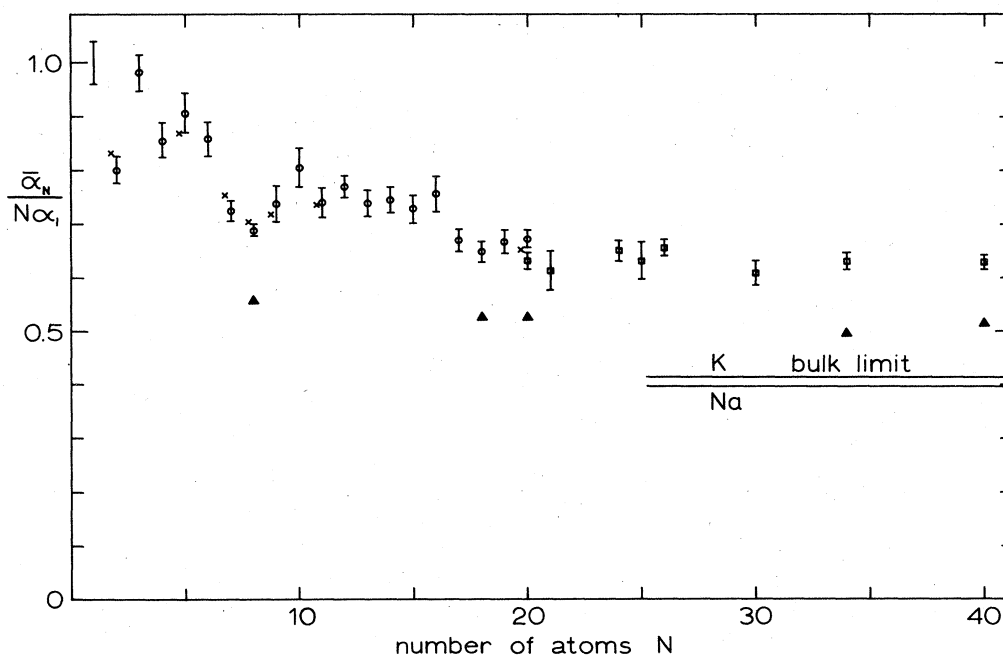


FIG. 1. Static mean polarizability (per atom) for clusters of sodium (circles and squares) and potassium (crosses), normalized to the respective atomic polarizabilities. Error bars on sodium cluster points represent one standard deviation of the data; error bars (not shown) for potassium points are approximately twice as large; the error bar on the atomic value indicates the accuracy of the vertical scale. Some representative theoretical points for sodium, derived from Refs. 3-5, with  $r_s = 4$  a.u., are indicated by triangles. They have been scaled to the bulk values shown, which are based on 300 K values for the metallic densities, and on a previous measurement of the atomic polarizability (see Ref. 11).

por pressure, and  $P_A$  representing argon-carrier gas pressure (in units of kPa): atoms,  $P_M=0.13$ ,  $P_A=250$ ; clusters,  $N=2-20$ ,  $P_M=20-33$ ,  $P_A=230-370$ ; clusters,  $N=20-40$ ,  $P_M=26-33$ ,  $P_A=400-460$ .

The beam passes along the axis of a pair of electrodes which produce an inhomogeneous transverse electric field.<sup>6</sup> Following deflection in this field, the clusters are admitted through a movable slit to an ionizing chamber and exposed to ultraviolet light. The resulting ions are mass selected in a quadrupole mass analyzer (QMA) of  $\sim 5$ -amu resolution, and converted to pulses by means of a Daly<sup>7</sup> dynode, plastic scintillator, photomultiplier, and counter system. The basic measurement is one giving the deflection profile for clusters containing a specific number of atoms  $N$ . Since the deflection is proportional to the product of dipole moment and electric field gradient, both of which are proportional to the applied field  $E$ , the deflection  $z$  is proportional to  $E^2$ ,

$$z = K\alpha E^2/Mv^2, \quad (1)$$

where  $\alpha$  is the mean polarizability averaged over the relevant molecular states. The constant  $K$  depends on apparatus configuration,  $E$  is the rms electric field over the path length  $L$  in the electrodes, and  $M=Nm$ , where  $N$  is the number of metal atoms of mass  $m$  in the cluster.

Sets of deflection measurements were bracketed by measurements of time-of-flight (TOF) profiles, which provided values for the mean velocity  $v$  with better than 2% precision. Each deflection profile was compared with a computer simulation based on an assumed value of  $\alpha$ , and using a velocity distribution based on the TOF data. We chose the value of  $\alpha$  which produced the best fit. Although  $K$  and  $E$  are not known directly, they are eliminated when the ratio is taken between cluster and atomic polarizability. Polarizability measurements for each sodium cluster (except  $N=21$ ) were made several times on each of two or more days. The experimental points for potassium represent fewer experimental trials, but all of these were made in a single day. The statistical accuracy of the sodium  $N=21$  point is lower than for the other clusters, because of the low signal intensity (see Fig. 1 of Ref. 1).

Potentials between 27 and 40 kV were applied to the deflection plates. The maximum potentials of 40 kV produced a field of  $\sim 200$  kV/cm and atomic beam deflections of the order of 0.015 cm, which were comparable to the profile widths. Various supplementary experiments, including substitution of optical filters on the ionizing light source, have failed to give evidence that fragmentation effects are appreciably affecting the results.

ciably affecting the results.

We conclude that the general trend of the experimental values of polarizability is in satisfactory qualitative agreement with the latest theoretical calculations for  $N \geq 8$ . It is worth noting that the reduced screening predicted earlier<sup>8</sup> is not apparent for clusters of any size. The largest cluster investigated here is still small compared with bulk material, and the trend for large clusters is yet to be measured. However, comparing the experimental and theoretical trends, it appears that the experimental polarizability is unexpectedly high. A careful study of the effect of temperature on the polarizability may give some insight into the reasons for the discrepancy. At any rate, it is not easy to compare the experimental values with either the theoretical ones, or the bulk, since the atomic volume in the cluster is not known. Theoretical estimates<sup>9</sup> of the atomic volume, in fact, predict a contraction in clusters compared with the bulk, which would actually seem to worsen the comparison of experiment and theory. Aside from the general trend of the experimental results, the correlation with observed shell structure is significant, and can be shown<sup>10</sup> to be related to aspherical deformations in the clusters between shell closings.

These experiments are not expected to relate to the development of crystal structure, because of the small size of the clusters. In fact, the observed shell structure is strong evidence for the degeneracies appropriate to spherical symmetry. Consequently it may be useful to consider the small metallic spheres to be like "liquid drops," following a well-known model of the nucleus. The question of why the experimental polarizabilities are somewhat higher than expected may be partly addressed by measurements of larger clusters. In fact, since Eq. (1) indicates that the deflection sensitivity is retained even for very large clusters, these experiments may be extended to approach the classical limit for large spheres.

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<sup>6</sup>See, for example, H. K. Hughes, *Phys. Rev.* **72**, 614 (1947); R. G. J. Fraser, *Molecular Rays* (Macmillan, New York, 1931).

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<sup>11</sup>R. W. Molof *et al.*, *Phys. Rev. A* **10**, 1141 (1974); *J. Chem. Phys.* **61**, 1816 (1974). The polarizabilities of the sodium and potassium dimers given in Fig. 1 are significantly different from those given in the latter reference. Because of the use of the supersonic beam and refined TOF measurements, we believe that the present values are more accurate.