Melting and Freezing of Aluminum Clusters*

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Aluminum and sodium clusters have emerged as prototypes for understanding the thermal properties of metal clusters. In this talk I will describe new results for aluminum clusters.

Most of the experimental information on the melting transitions of size selected metal clusters has been obtained from heat capacity measurements. These measurements have now been performed for aluminum cluster cations (and some anions) with 16 to 130 atoms. Results for n>80 are reported here for the first time. Most clusters with n>80 show a single sharp peak in their heat capacities that can be fit with a two state model (i.e., a model that only includes completely solid clusters and completely liquid clusters, and no partially melted intermediates). On the other hand, clusters with 80-90 and 110-120 atoms show two clearly-resolved and well-separated peaks in their heat capacities. The two peaks may be due to partial melting, where part of the cluster melts and then the balance melts at a higher temperature, or it may indicate that there are two structures that melt at different temperatures. I will describe measurements that probe the internal energy distribution of the melting clusters and distinguish between these two possibilities.

Experimental studies of the melting of metal clusters have focused on the thermodynamic behavior (i.e., determining the melting temperature and latent heat). There is virtually no experimental information available on the rates of melting and freezing transitions and how they change with temperature and cluster size. We have performed experiments to investigate the kinetics of metal cluster freezing. In these experiments the clusters are heated to above their melting temperature, rapidly quenched, and then the heat capacity is measured after a fixed time. These studies show that the clusters do not always freeze into the lowest energy structure. At high cooling rates the liquid cluster can bypass freezing into the thermodynamically preferred solid and freeze into a higher energy solid at a lower temperature. In addition, the peaks in the heat capacities measured for freezing are for some clusters shifted to lower temperature than the peaks in the heat capacity measured for melting. This confirms that some of the clusters' super-cool.

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