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# Melting of free sodium clusters

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**Abstract.** Heat capacities have been measured across the solid to liquid phase transition for free, mass selected sodium cluster ions, $Na_n^+$, with $55 \leq n \leq 199$. Results for the melting point and the latent heat of fusion are presented here. The melting points are about 30% lower than the bulk value, and show large variations ($\pm 50$ K). They seem to be highest in a mass range, where both an icosahedral and an electronic shell closing occurs.

**PACS.** 64.70.Dv Solid-liquid transitions – 36.40.Ei Phase transitions in clusters – 36.40.Qv Stability and fragmentation of clusters

## 1 Introduction

Phase transitions in bulk material have been studied since a very long time. Their microscopic analogues differ in three main aspects from the bulk counterparts [1–9]: 1) The melting point decreases with decreasing particle size, which is mainly due to the large percentage of atoms on the surface. Here atoms have fewer nearest neighbours and are thus weaker bound and less constrained in their thermal motion [2,5]. 2) The latent heat of fusion is reduced, which is also due to a surface effect, and 3) the finite number of particles causes the phase transition to be spread out over a finite temperature range. It has recently become possible to study the solid to liquid phase transition in mass selected, free clusters [6,7,10–13].

## 2 Experiment and data

Figure 1 shows the basic idea of the experiment. Clusters are prepared with a temperature $T$ and their internal energy $U$ is measured as explained below. The curve

$$U = U(T)$$

is called the caloric curve and its derivative, $c(T) = \partial U/\partial T$, the heat capacity. In order to determine $U$, a cluster of temperature $T_1$ is mass selected and irradiated with photons of energy $\hbar\omega$ (see Fig. 2). The cluster absorbs several photons, say $j$, and as a consequence emits on the average $x$ atoms. The process studied is thus:

$$Na_n^+(T_1) + j\hbar\omega \longrightarrow Na_{n-x}^+(T_{\text{evap}}) + x\text{Na}\,. \qquad (1)$$

The temperature after the fragmentation is that of the evaporative ensemble [14], which does not depend on $T_1$ and $j$. Energy conservation applied to (1) gives:

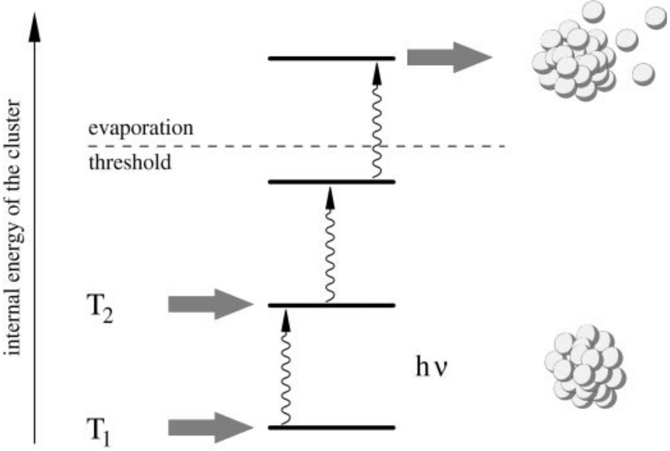

**Fig. 1.** Basic idea of the experiment. A cluster of known size and temperature $T_1$ absorbs three photons until it starts to evaporate atoms. Then the cluster is heated to temperature $T_2$, which is so determined that the cluster needs only two photons to give the same photo fragmentation mass spectrum. This allows to construct the heat capacity as discussed in the text.

$$U_n(T_1) + j\hbar\omega = U_{n-x}(T_{\text{evap}}) + \sum_{i=1}^{x} D_i + \sum_{i=1}^{x} \epsilon_i \qquad (2)$$

where $D_i$ and $\epsilon_i$ are the dissociation energies and kinetic recoil energies, respectively. In principle, this equation is sufficient to determine $U_n(T_1)$, if all the energies on the right hand side (rhs) would be known with good accuracy. As this is not the case, we employ a differential procedure where most of uncertainties cancel. The clusters are heated to a higher temperature $T_2$ so that only $(j-1)$ photons are

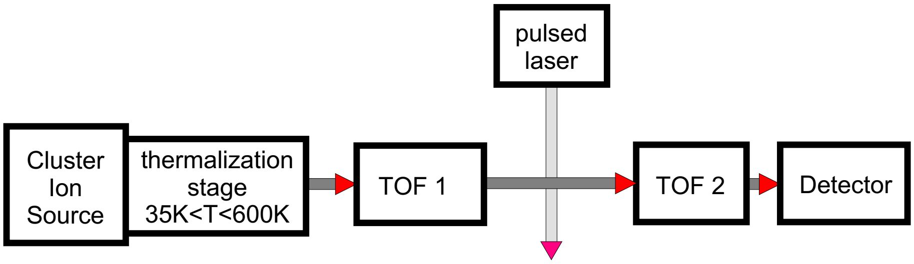

**Fig. 2.** Schematic of the experimental set-up. Clusters are produced in a cluster ion source, thermalized, and mass selected in a time–of–flight (TOF) mass spectrometer. They are irradiated by photons from a pulsed dye laser, and the resultant mass spectrum is measured in a second TOF. Mass spectra are measured every one to two degrees of cluster temperature, and the heat capacity constructed via (6).

necessary to give the same mass spectrum.

$$\mathrm{Na}_n^+(T_2) + (j-1)\hbar\omega \longrightarrow \text{same as rhs of (1)}\,. \qquad (3)$$

Energy conservation gives as above:

$$U_n(T_2) + (j-1)\hbar\omega = \text{same as rhs of (2)}\,. \qquad (4)$$

Subtracting (4) from (2) one has

$$U(T_1) + \hbar\omega = U(T_2)\,. \qquad (5)$$

Rewriting this equation in terms of energy and temperature increments one obtains

$$U(T_1) + \delta U = U(T_1 + \delta T)$$

from which one can obtain a finite difference approximation to the heat capacity:

$$c(T) = \frac{\partial U}{\partial T} \approx \frac{\delta U}{\delta T} = \frac{\hbar\omega}{T_2 - T_1}\,. \qquad (6)$$

The photon energies used are in the three to four electron Volt range. The binding energy of a sodium atom is about 1 eV, so that per photon typically three to four atoms are evaporated. This leads to oscillatory structure in the mass spectra, as discussed earlier [10], from which it is easy to read the values for $\delta U$ and $\delta T$.

Below $\sim 70$ atoms this data treatment becomes unsatisfactory. Also, the oscillatory structure becomes perturbed by magic number effects, so that an alternative way of extracting the information from the mass spectra was developed. Using the ideas presented above, one can calibrate the mass scale of the photo fragment spectra in terms of the total internal energy [i.e. the lhs of (2)]. This allows to construct the caloric curve and obtain the heat capacity by differentiation. Both methods give the same melting points and heat capacities.

The validity of (5) and (6) was checked for sodium clusters by measuring the heat capacity of $\mathrm{Na}_{139}^+$ using four different photon energies. The results for the melting points, latent heat of fusion and width of the phase transition agree within experimental accuracy [15].

These procedures cannot be applied to clusters where direct, photo–induced processes are important, as e.g. for the alkali-halides. For direct process, the kinetic energies $\epsilon_i$ in (2) and (4) do depend on the photon energies, and do not cancel on subtraction. For sodium clusters on the other hand, the electronic energy supplied by the photons seems to be completely converted to internal energy. Only after this process has been completed, atoms start to boil off. Thus it is unimportant how energy is supplied to the cluster, thermally or by photons, which is the message of (5).

Another check was done on this basic assumption: different sodium clusters where photo excited and the kinetic energies of the emitted atoms measured. Independent of the degree of excitation – by a nano-second laser – only thermal emission of atoms was seen, proving that no direct photo emission processes occur for sodium [15]. This is in agreement with data for sodium surfaces.

The machine for these experiments has been used earlier to measure optical data for sodium clusters [16]. It consists of a cluster ion source (see Fig. 2), a thermalization stage, two time of flight mass spectrometers one after the other, and an excimer pumped dye laser. The only innovative part is the thermalization stage for the clusters, where they make $10^5$ to $10^6$ collisions with a helium gas, whose temperature can be controlled from the outside. After less than $10^4$ collisions, the cluster ensemble does not exchange energy any longer with the gas, which gives by definition a *canonical* energy distribution for the clusters. Once the clusters have left the thermalization stage, they do not make any collisions and have to be treated microcanonically.

Figure 3 shows the results for the heat capacity of $\mathrm{Na}_{139}^+$. The $\delta$-function of the bulk result has become a broad maximum, shifted to a lower temperature by 104 K. Aside from the maximum, the data agree with the bulk result. Note, that an absolute value is obtained for the heat capacity, without using any adjustable parameters. Three data can be read off this curve:

1. the melting point, as given by the maximum of the curve,
2. the latent heat of fusion, as given by the integral under the maximum, and
3. the width of the phase transition.

The results of the first two sets of data are plotted in Figs. 4 to 6. The width will be discussed elsewhere [15].

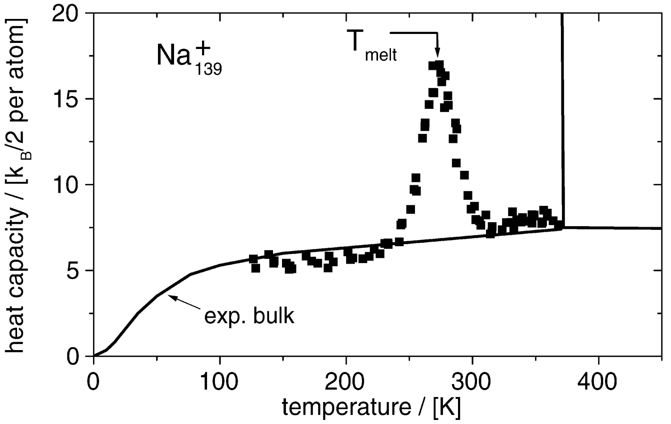

**Fig. 3.** The heat capacity of $Na^+_{139}$ is plotted against the temperature of the cluster thermalization stage. The experimental value for bulk sodium has a $\delta$-function at the melting point of 371 K. The squares give the experimental results. The $\delta$-function has become a broad peak, whose maximum is taken to be the melting point. Away from the maximum, the data agree surprisingly well with the bulk result.

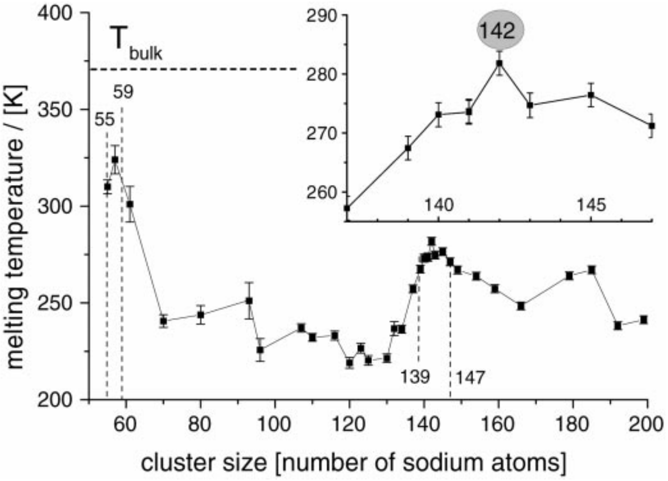

**Fig. 4.** Melting points as a function of cluster size. One obtains an irregular variation with large fluctuations. The vertical dashed lines indicate the icosahedral and electronic shell closings. When two of them are near to each other, the melting temperature is high. The inset shows the data around 142 on an expanded scale.

## 3 Discussion

The reduction in the melting point had been studied intensively for small particles and clusters on a surface. One typically observes a linear reduction of the melting point as a function of the inverse cluster radius [1–3, 8]. The data presented here show also a reduction of the melting point, typically by about 30% compared to the bulk value. The actual size variation, on the other hand, shows a very different behaviour. One sees large variations of up to ±50 K, with maxima and minima whose positions do not correlate well with any known number of special stability or instability. Figure 4 shows the size variations of the melting points, $T_{\mathrm{melt}}$. The insert shows the data on an expanded scale around the 142 atom maximum, in whose surrounding every single cluster size was studied. The error is typically ±2 K for $n \geq 100$ atoms. It becomes larger for smaller cluster sizes, as indicated in Fig. 4.

There are two pronounced maxima, one near 57, the other at 142 atoms per cluster. One is tempted to correlate these numbers with shell closings, where the energetic difference between the ground state and the first excited state is largest [7, 17]. Icosahedral shell closings occur at 13, 55, 147, 309 … atoms, while electronic shell closings happen for positively charged sodium clusters for … 41, 59, 93, 139, 199, 255, 339 … atoms. For none of these values, there is a maximum in the melting point. But, both maxima in $T_{\mathrm{melt}}$ are bracketed by an electronic *and* an icosahedral shell closing, as indicated in Fig. 4. So far, we have only two maxima of $T_{\mathrm{melt}}$ which fall into this class. A third one can be expected between 310 and 340 atoms, a region which will be studied in the future.

Icosahedral shell closings are known to occur for clusters, which can be described by geometrical ball stackings, like e.g. the rare gases. It would be surprising, if sodium with its soft interaction potential would fall into this class.

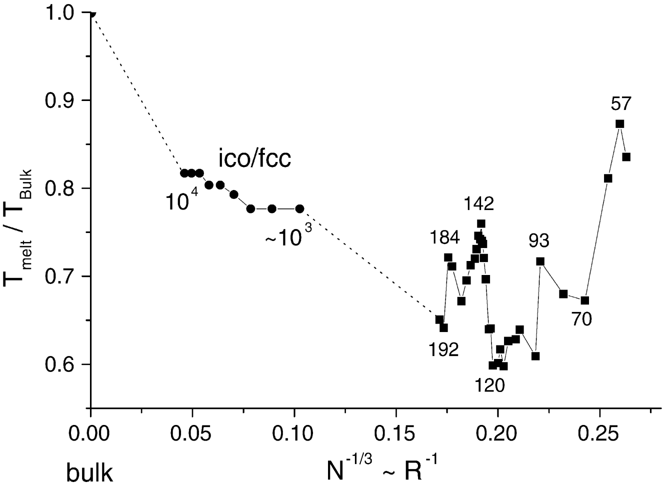

**Fig. 5.** Melting points as a function of the inverse cluster radius. The data from [7] for larger clusters are included. The behaviour is far from the expected from many studies on supported clusters, which all find a linear decrease from the bulk value in such a plot.

A possible way around this problem can be found in [18], where an icosahedral precursor was calculated in the melting of gold clusters, although the ground state has a different symmetry.

Figure 5 shows the variation of $T_{\mathrm{melt}}$ as a function of $n^{-1/3}$, a value which is proportional to the inverse cluster radius. The data for the larger clusters ($10^3$ to $10^4$ atoms) have been obtained from the Stuttgart group [7]. From structure visible in mass spectra of thermalized sodium clusters, these authors deduce, that large Na-clusters have either icosahedral or fcc symmetry. Bulk sodium is bcc,

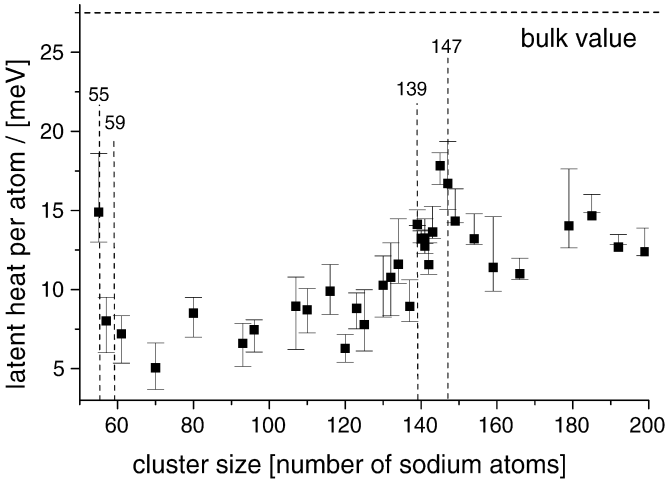

**Fig. 6.** Latent heat per degree of freedom as a function of cluster size. There is a weak correlation of the maxima with those of the melting points. Shell closings are again indicated by vertical lines.

on the other hand, so that a structural phase transition must occur between $n = 10^4$ and the bulk. An alternative interpretation would be: large sodium clusters near their melting point show the same icosahedral precursor as calculated in [18] for gold clusters. In this case the ground state could already be bcc-like.

The cluster sizes 55, 57, and 61 have a higher melting temperature than those in the $10^3$ to $10^4$ range. This is a totally unexpected and not understood result. In fact, it seems that the mean cluster melting temperature increases with decreasing cluster size for $n$ below $\sim$ 90 atoms.

Figure 6 shows the variation of the latent heat. Classically this is the integral over the $\delta$-function, and gives the energy to destroy the crystalline lattice at $T_{\mathrm{melt}}$. The maxima occur near, but not at the same masses as for $T_{\mathrm{melt}}$, i.e. for 145 atoms (max. of $T_{\mathrm{melt}}$ at 142), and at 55 or below (57). Thus, the peaks in the latent heat seem to be shifted in both cases from that of $T_{\mathrm{melt}}$ in the direction of the icosahedral shell closing.

## 4 Conclusions

Heat capacities have been measured for free sodium cluster ions $\mathrm{Na}_n^+$, with $55 \leq n \leq 199$ atoms. The melting points are lower by about 30% than the bulk one at 371 K. They also show large irregular fluctuations of up to ±50 K. Maxima in the melting point and the latent heat of fusion seem to occur if an electronic shell closing is near to an icosahedral one.

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