P H Y S I C A L   R E V I E W   L E T T E R S

Melting of Sodium Clusters: Where Do the Magic Numbers Come from?

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Melting temperatures of Na clusters show size-dependent fluctuations that have resisted interpretation so far. Here we discuss that these temperatures, in fact, cannot be expected to exhibit an easily understandable behavior. The energy and entropy differences between the liquid and the solid clusters turn out to be much more relevant parameters. They exhibit pronounced maxima that correlate well with *geometrical* shell closings, demonstrating the importance of geometric structure for the melting process. Icosahedral symmetry dominates, a conclusion corroborated by new photoelectron spectra measured on cold cluster anions. In the vicinity of the geometrical shell closings the measured entropy change upon melting is in good agreement with a simple combinatorial model.

Melting is an ubiquitous phenomenon and a paradigm of a first order phase transition. Melting studies in finite systems have recently been undertaken with renewed interest, both theoretically [1–9] and experimentally [10–14]. These studies have shown that melting in finite systems can, indeed, be considered as the finite size analogue of the macroscopic thermodynamic phase transition [1,2].

Sodium is the prototype of a ''simple'' metal and has played a special role in the development of cluster science [15–17]. It was the first element for which magic numbers of *electronic* origin were identified [17]. Many properties of not too small sodium clusters can be understood in the context of free electron models, which totally neglect geometric structure [1,15,16]. Melting, on the other hand, is a process connected with the structure and dynamics of the atomic lattice. A study of this process in sodium clusters can therefore be expected to help to disentangle the intricate interplay between electronic and geometric structures.

The calorimetric experiment has been discussed in detail [12,13,18]. Briefly, positively charged sodium clusters are thermalized in a heat bath of temperature T, mass selected, and the internal energy E of the clusters is measured. This allows one to construct the caloric curve, $E = E(T)$, from which the melting temperature (T_{melt}) and latent heat of fusion (q) can be extracted. The melting temperatures shown in Fig. 1 have been published earlier [12,13]. The q values have been reevaluated as described in Ref. [19], giving data with considerably smaller error bars.

In the heat bath the ensemble of clusters acquires a canonical energy distribution [12,19]. This canonical ensemble undergoes melting in the bath when the free energies ($E - TS$) of the solid (sol) and the liquid (liq) are equal, with E, T, and S being energy, temperature, and entropy, respectively. This gives $E_{sol} - T_{melt}S_{sol} = E_{liq} - T_{melt}S_{liq}$ or

$$T_{melt} = \frac{E_{liq} - E_{sol}}{S_{liq} - S_{sol}} = \frac{\Delta E}{\Delta S} = \frac{q}{\Delta s}, \qquad (1)$$

where $q = \Delta E/N$ and $\Delta s = \Delta S/N$ are the energy and entropy differences per atom at the melting temperature (N being the number of atoms in the cluster). It is shown below that the variables q and Δs yield much more specific information about the system than their ratio T_{melt}.

Three data sets are given in Fig. 1: T_{melt} and q have been obtained directly from the experiment; Δs has been calculated from these using Eq. (1). In the size range $135 < N < 360$, T_{melt} and Δs are reduced by roughly 35% with respect to the bulk; q is even reduced by about 58%. Note the extreme increase in q by about a factor of 3 between $N = 100$ and 140, which had been attributed to the completion of a third atomic shell earlier [11,13,19]. None of the maxima in Fig. 1 can be identified with electronic shell closings, which dominate most known properties of metal clusters [1,15–17]. On second thought this is not so surprising, as the number of electrons stays constant upon melting. Here the effect of the electronic shell structure should be limited to the preference of certain (size-dependent) cluster deformations, which might influence the energetics of atomic rearrangements.

Additionally, photoelectron spectra (PES) of negatively charged, cold ($T \sim 100$ K) sodium clusters have been measured. The experimental setup was almost the same as used earlier [20]; only a liquid nitrogen cooled thermalization stage has been added. Figure 2 shows some typical results. To a good approximation, PES are a map of the electronic density of states. A spherical outer shape of the cluster and/or a high symmetry of the atomic packing lead to highly degenerate states, and thus large level separations.

In Fig. 2 one can observe deep modulations of the spectra for $N = 147$ and 309; these clusters must therefore be close to spherical and highly symmetric. The spectrum of $N = 298$ does not exhibit such a pronounced modulation, but still has well defined sharp features; this cluster is probably less spherical, but should have a rather symmetrical geometric structure. For $N = 164$, on the other hand, one observes only a broad, smeared out spectrum, indicat-
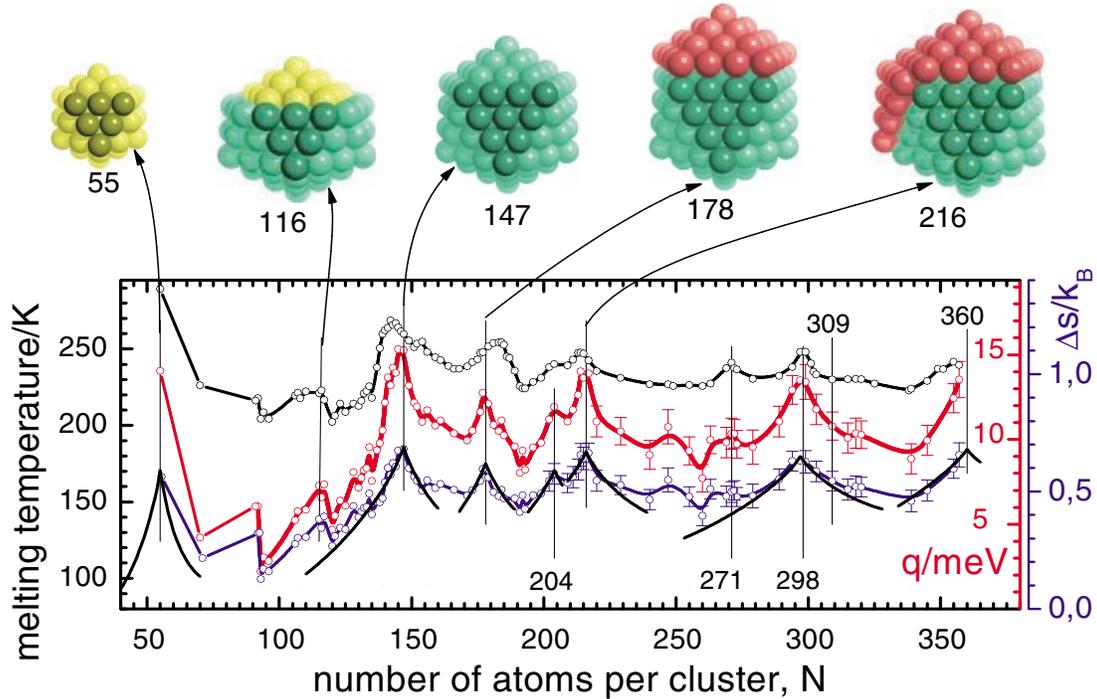
FIG. 1 (color).   Upper panel: Clusters of icosahedral growth pattern. The 2nd, 3rd, and 4th layers are given in yellow, green, and red, respectively. One of the 20 triangular faces is colored in a deeper shade. Only the structure of the closed shell icosahedra at $N = 55$ and 147 has been confirmed so far, and for the other sizes different outer layers are possible [22,25]. Lower panel: Size dependence of the melting temperature (T_{melt}, black), the latent heat of fusion per atom (q, red), and the entropy change upon melting per atom (Δs, blue). The data, given by the open circles, are joined (for $N > 92$) by splines. Error bars are given only for N above 200, in order to avoid cluttering the figure. The error bars for T_{melt} have about the size of the symbol used. The data for Δs and q have their maxima at the same N, while those for T_{melt} can be shifted. The cluster sizes are indicated for some peaks. The N values are given above the data if the cluster geometry is known or can be guessed. The black solid lines, overlapping partially with the blue line, give the calculated entropy change upon melting. The simple hard sphere model gives a surprisingly good fit of the peak shapes.
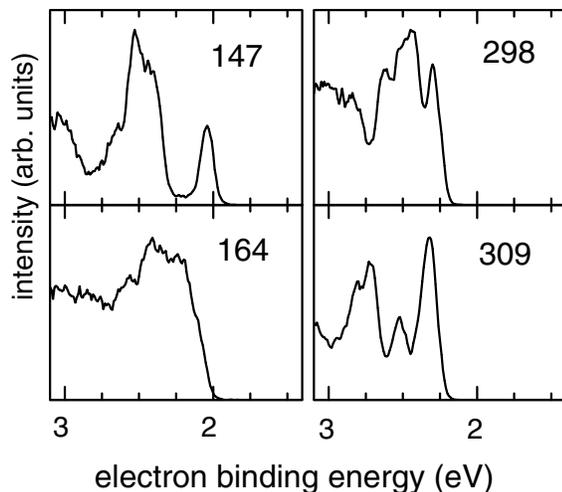

FIG. 2.   Photoelectron spectra for cold, negatively charged sodium clusters. The $N = 147$ and 309 atom clusters are of icosahedral symmetry; the spectra agree well with theoretical results [22]. The geometry for $N = 298$ is unknown. These three spectra are well modulated giving a large modulation (see text). The $N = 164$ cluster has such a low symmetry that the electronic bands overlap, giving a low modulation.

ing that this cluster is probably nonspherical and of low symmetry. Furthermore, probably several isomers are present, which again indicates that no preferred closed packed atomic structure exists for this size.

To quantify this, a modulation of the PES, called mod(PES), is defined, which is high if the spectrum is well structured and low if otherwise. To calculate mod(PES), the PES were Fourier transformed, the squares of the Fourier coefficients were added up, and these were normalized to the highest value at $N = 268$. The result is given by the black line in Fig. 3. It is again a strongly modulated curve, which exhibits a strong correlation with the curves of q (and Δs).

PES are influenced by both electronic and geometric shell closings. A spherical shape induced by electronic shell closing leads to a highly modulated spectrum even in cases of low symmetry atomic ordering. Indeed, in the mod(PES) curve two peaks appear (138 and 268) which coincide with electronic shell closings [1,15–17]. As these are the only ones occurring in the size range shown here, all other peaks must be due to geometrical effects. Indeed, almost all of the maxima of q, Δs, and mod(PES) can be interpreted as being due to *geometric* shell closings
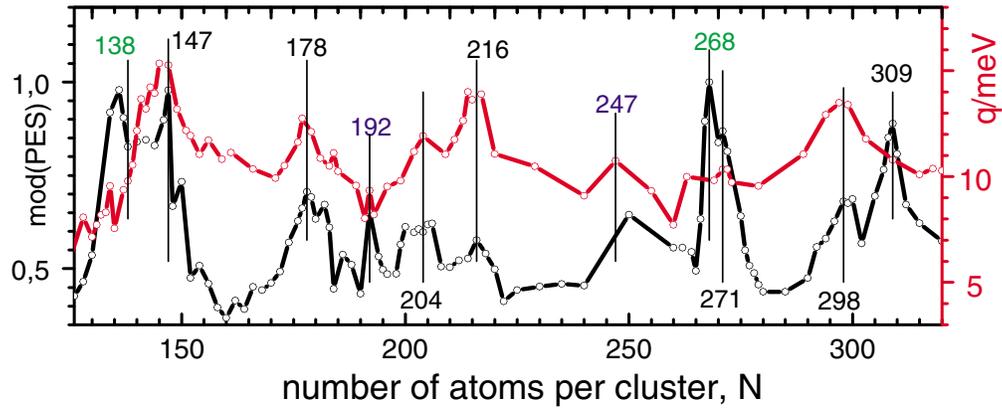
FIG. 3 (color). Comparison of the latent heat (red) with the modulation of the photoelectron spectra (black). There are six peaks (at $N = 147$, 178, 192, 216, 271, and 298) where the maxima occur at the same N in both curves. The code for placing N values is the same as in Fig. 1. The N values are in black if the cluster has icosahedral symmetry. Blue N values indicate possible Marks decahedra [4]. The modulation spectrum also shows electronic shell closings (138, 268) marked in green. Note that the PES have been measured for negatively charged clusters while the melting experiment used positively charged ones. Nevertheless, maxima occur at the same N, indicating that geometrical and not electronic shell closings are important in most cases.

[21]. Comparison of the measured PES spectra with the calculated density of states [9,22] shows that the clusters with $N = 55$, 147, and 309 are closed shell icosahedra. The maxima at 116, 178, and 216 can likewise be attributed to icosahedra with "caps" added or subtracted [1,3,23,24] (but other geometries are possible as well [25]). Several minor peaks (127, 156, 192, 247) could be due to Marks-decahedral symmetry [1,4,10]. All identifications (save those for 55, 147, and 309) must await the confirmation by theoretical results. No structures yet could be attributed to $N = 204$, 271, and 298. One obvious assignment for the latter, the 309 atom icosahedron minus the 12 vertex atoms (making 297 the true magic number) can be safely excluded due to the strong differences in the PES.

What makes it so difficult to interpret the magic numbers in T_{melt}? It had already earlier been noted that q and Δs have almost the same size dependence [19]. Plotting q and Δs against each other, one observes that all our sodium data fall into a narrow band, bounded by two straight lines given by $\Delta s_k = a_k q$, with $a_{1,2} = (47 \pm 5) k_B/eV$. Equation (1) shows that for $a_1 = a_2$ one would have no size dependence of T_{melt} at all. The small variations in a lead to small variations in T_{melt}, about $\pm 12\%$ for N between 100 and 200 and about $\pm 6\%$ for $200 < N < 360$. A similar behavior can be extracted from simulations on Lennard-Jones clusters [26]. Thus both q and Δs can show large, physically motivated fluctuations, while T_{melt} changes only slowly.

In order to gain further insight into the melting process, the entropy in the vicinity of the geometrical shell closings has been calculated from a simple model. The results, given by the black lines overlapping the blue ones in Fig. 1, show a remarkably good agreement with the data. It was assumed that the entropy of the liquid clusters S_{liq}/N [see Eq. (1)] does not vary much with size. For the solid

clusters we employ a simple hard sphere model to estimate the configurational part of the entropy. One atom outside the $N = 147$ closed shell icosahedron can occupy $\sigma = 180$ possible sites (nine triply coordinated sites per triangular face). For the next atoms one has two possible choices. At a low temperature, the number of bonds is maximized, meaning that the next atoms are always positioned next to the atoms already on the surface. The configurational entropy of this arrangement is very small, in complete disagreement with the experimental result. If one assumes the atoms on the surface to be mobile, however, they can roam about all remaining places. In this case the standard enumeration of multiplicities gives for m atoms outside (or missing from) a cluster containing a magic number (MN) of atoms the binomial expression

$$\Omega(MN \pm m) = \binom{\sigma}{m}. \tag{2}$$

Although the number of possible places σ is 9 per empty face, one can put only a total of 6 atoms on one face, and 120 on all 20 faces. As the results are rather insensitive to the value of σ, an average value of $\sigma = 150$ was used. For N below 147 one has a maximum of $\sigma = 147 - 55 = 92$ possible places. The entropy is calculated from the standard expression $S = k_B \ln\Omega$, where k_B is the Boltzmann constant. The result is plotted as the black line peaking at 147 in Fig. 1. The calculated curve (black) has been shifted vertically so that it agrees with the measured Δs curve (blue) at $N = 147$, in order to account for the contribution of the liquid. A surprisingly good fit is obtained. Similarly, the black lines peaking at $N = 178$, 204, 216, and 298 have been obtained, using a constant $\sigma = 150$. For $N = 360$ a value of $\sigma = 250$ had to be employed, indicating that two outer layers are mobile for this cluster. Note that the calculated and measured entropy values agree *absolutely* with each other, except for an additional constant.

Mobile atoms in the outer layers of an otherwise still solid cluster are a sure sign of "premelting," a phenomenon that had been found in many simulations [1–3,5,8,9,26]. The related increase in the heat capacity seems to be so small that it was not detected in our measurements of the caloric curves [12,13]. The good agreement between the experimental and the calculated entropy changes is the first indication of its ubiquitous occurrence also in sodium clusters.

One has a closed shell icosahedron also at $N = 309$. So why do the thermodynamic data show no structure there at all, while the mod(PES) data give a pronounced peak? In a preliminary experiment, the temperature dependence of the $N = 309$ photoelectron spectrum was measured. At a low temperature the data indicate an icosahedral structure, but this seems to change to a new geometry in a solid to solid transition at about 40 K below T_{melt}. The $N = 309$ cluster thus no longer has an icosahedral shape near T_{melt}. A related behavior has been calculated for larger icosahedra bound by a Morse potential [27].

In summary, the size dependence of thermal and electronic properties of mass selected sodium clusters has been discussed. Maxima in three properties (energy and entropy change upon melting, modulation of the photoelectron spectra) can be interpreted as being due to geometrical shell closings. The maxima in the melting temperatures are shifted to different sizes if the curves of q and Δs have slightly different slopes in the vicinity of the closed shell size. This result suggests that the intensive variable melting temperature is physically less relevant compared to extensive variables like entropy and energy change. The $N = 309$ cluster displays icosahedral symmetry at low temperatures, which changes in a solid to solid transition at higher T. The entropy change of melting, as calculated from a simple hard sphere model, is in good agreement with the experimental data. The model assumes that atoms in incomplete outer layers are mobile, at least down to 20 to 30 K below the melting temperature. Sodium clusters do show magic numbers of electronic origin in general, but the thermodynamic properties near T_{melt} seem to be governed by geometric shell closings. Sodium clusters thus show two completely different kinds of magic numbers, depending on which property is studied.

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