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Low-temperature caloric behavior of a free sodium nanoparticle

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We report on accurate temperature control of size-selected sodium cluster cations by buffer gas thermalization in a temperature variable dodecapole radio frequency trap, which permits measurements of the cluster caloric behavior down to a temperature of $T = 6$ K. For $\mathrm{Na}_{139}{}^{+}$, a fit to the caloric curve obtained yields a Debye temperature of 163.5 ± 10 K, which compares well to the value of bulk sodium (158 K), and indicates that the overall vibrational density of states of the cluster is similar to that of the bulk. An estimate based on this finding shows that at $T = 6$ K the majority of the clusters are in their vibrational ground state.

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In principle the finite size of nanoparticles results in three major differences in their vibrational density of states (VDOS) as compared to bulk systems. First, because of the finite number of constituents, the VDOS is discrete; consequently there exists a cutoff at low frequencies. Second, surface vibrational modes can lead to an enhancement of the VDOS at low frequencies. Third, due to the strong influence of the surface, nanoparticles often have crystalline structures different from that of the bulk, as well as experience internal strain. This can again modify the shape of the VDOS. Nanoparticles therefore should exhibit thermodynamic properties different from those of the bulk;[1] the question is how pronounced these deviations are. Despite a large number of theoretical and experimental studies this question is not fully answered yet.

Experimentally the VDOS of nanoparticles has been measured by inelastic neutron[2,3] or x-ray scattering[4,5] applied to nanocrystalline films. The results show a rather strong enhancement of the VDOS at low as well as at the highest frequencies. In direct measurements of the heat capacity of small particles[6,7] an enhancement at low temperatures was observed, which also hints at an enhanced VDOS at low frequencies and can be described by a lowering of the Debye temperature θ_D. For instance, for 22-Å lead particles (consisting of about 184 atoms) in porous glass a lowering of θ_D by about 10% with respect to the bulk value was found.[6] For 22-Å indium particles (about 214 atoms) in porous glass the lowering was about 20%[6]. For 84-Å palladium particles (about 21000 atoms) pressed to a bulk material a lowering of θ_D by 17% was observed.[7] Extended x-ray absorption fine structure measurements have also been used to determine Debye temperatures; here a densely packed single layer of 20-Å (248 atom) gold nanoparticles on a mylar film showed a lowering of θ_D by 15%.[8] A similar effect has been seen for thin films: Kästle *et al.* showed by temperature-dependent resistivity measurements that in a gold film with a thickness of 2.1 nm θ_D is reduced by 30%.[9] So in general rather strong deviations from bulk behavior have been observed. On the theoretical side, in earlier studies the VDOS of nanoparticles was treated by spherical continuum models,[10,11] while more recent work has employed atomistic modeling of the particles.[12,13] The results show that nanoparticles indeed exhibit a modified VDOS, which can cause a certain lowering of θ_D, but that the strong effects seen in the experiments are probably caused by vibrational modes of the nanoparticle-nanoparticle or nanoparticle-matrix interface regions,[12] which is in agreement with recent x-ray-scattering results.[5] Nevertheless, a corroboration of these statements by measurements on isolated, unperturbed particles is needed.

In this Brief Report we describe low-temperature caloric experiments on free, size-selected sodium nanoparticles with 139 atoms (corresponding to a diameter of 2.2 nm). For the thermalization of the ions a radio frequency (rf) trap was used, which has become a standard technique in low-temperature experiments on free, charged particles.[14–17] Usually, however, considerably smaller particles are investigated; we are not aware of a demonstration of full thermalization of particles as large as the sodium cluster studied here (the clarity of the absorption spectra of a 150-atom polypeptide in a 10-K trap does hint at a very low vibrational excitation of the molecule, though[18]). The first part of this Brief Report is therefore dedicated to experiments which show that 139-atom clusters can indeed be reliably thermalized in a rf trap. After this the results of the low-temperature caloric measurements will be described.

In the experiment, positively charged sodium clusters were produced by a gas aggregation source. The clusters were transferred to a 12-pole rf trap by an ion guide. Inside the ion trap, which is encased in a copper block in contact with a closed cycle refrigerator (see inset in Fig. 1), the clusters were thermalized by collisions with helium atoms at temperatures adjustable between 6 K and 350 K. After thermalization, bunches of ions were extracted from the trap and injected into a double-reflectron time-of-flight (TOF) mass spectrometer, where the mass-selected clusters were irradiated by a nanosecond laser pulse (308 nm). The absorption of several photons from the laser pulse leads to a heating of the clusters, and subsequent thermal evaporation of atoms. The second half of the double-reflectron TOF mass spectrometer was used to analyze the resulting photofragments. The recorded fragment mass spectra are sensitive to the inner energy of the thermalized clusters, which allows one to link temperature and energy. By measuring fragment distributions as a function of temperature, therefore, caloric curves can be obtained, as has been described earlier.[19]

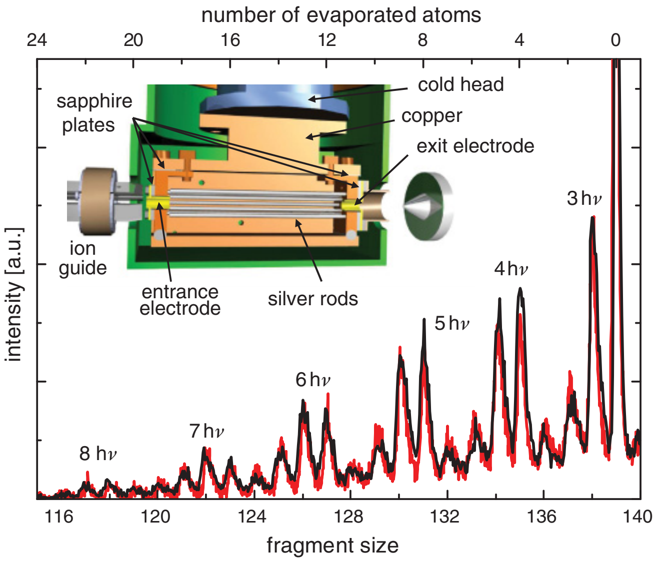

FIG. 1. (Color online) Comparison of photofragmentation spectra of $Na_{139}{}^+$ obtained for two different thermalization methods, employing a flow tube (red or gray curve) or a rf trap (black curve). Both spectra were recorded at $T = 204 \pm 0.7$ K using a photon energy of 4.02 eV. For each fragment group the number of photons absorbed by the parent cluster is indicated. The inset shows a sectional view of the 12-pole rf trap.

The design of the ion trap closely follows the work of Gerlich,[14] but some modifications were necessary to achieve an ion temperature close to that of the trap enclosure. Not only the ac electrodes but also the entrance and exit apertures were thermally connected by sapphire plates to the copper block surrounding the rf trap (see Fig. 1). Thin indium foil layers proved to be indispensable for a good thermal contact between the sapphire plates and the copper parts. Furthermore, silver rods (12 rods with a diameter of 2 mm and a length of 80 mm, mounted on an 11-mm diameter circle) have been used as rf electrodes. The very good heat conductivity of silver results in a fast thermalization of the rods, which is necessary as during experiments the trap temperature is ramped with about 1 K per minute. Direct temperature measurements showed that the temperature differences between all elements of the trap is $\leqslant 1$ K at all temperatures.

In order to investigate the thermalization of the clusters in the rf trap, photofragmentation spectra recorded at a given temperature were compared to the results of earlier experiments.[20] In these earlier studies a flow tube has been used for the cluster thermalization. The flow tube is a temperature-controlled copper tube attached to the cluster source, through which all of the helium used in the source is flowing. Extensive test measurements have demonstrated that under typical conditions (helium pressure 0.5 mbar, cluster residence time in the tube about 10 ms) the clusters can be reliably thermalized to the tube temperature. Photofragmentation spectra measured at a temperature of 204 K are presented in Fig. 1. The black line indicates the result obtained using the rf trap, while the red (gray) line shows the one for the flow tube. In the spectra the size-selected parent clusters (the cropped peak at size 139) are visible as well as fragments down to size 115. The fragment mass distribution exhibits an intensity envelope with a periodic structure. This envelope separates the photofragments into groups that originate from clusters having absorbed a different number of photons;[19] the photon numbers are indicated. A change of the initial cluster temperature leads to a shift of the envelope function; for the cluster $Na_{139}{}^+$ at $T = 200$ K a temperature change of about 26 K will shift the position of a fragment group by one atom. The very good agreement between the two spectra shows that the temperature difference between the clusters thermalized with the two methods is at least one order of magnitude smaller than this value. The almost identical width of the fragment groups additionally shows that not only the average internal energy, but also the width of the energy distribution of the clusters is very similar for both methods.

Further tests have been done in order to characterize the trap performance. The most important parameter for an estimate of the cluster thermalization is the number of collisions with the buffer gas atoms. During measurements the ion trap is permanently loaded with ions from the continuous cluster ion source; a slightly repulsive potential on the entrance aperture allows the ions to enter the trap, but keeps them from exiting again because in the trap the ions lose kinetic energy by collisions with the buffer gas. The extraction of the ions from the trap is pulsed, and removes only a small portion (less than 10%) of the trap filling. At a repetition rate of 100 Hz this leads to an average residence time of the ions in the trap of about 100 ms. The buffer gas pressure in the trap is determined by the pressure in the surrounding chamber (usually no additional gas is introduced into the trap). The chamber pressure of 10^{-3} mbar translates into a helium atom density in the trap of $n = 2.7 \times 10^{13}$ cm^{-3} at a trap temperature of 300 K and $n = 1.9 \times 10^{14}$ cm^{-3} at 6 K. Under these conditions the number of collisions between a stored cluster and the helium atoms is temperature independent; for $Na_{139}{}^+$ one calculates a value of about 1.3×10^4 collisions during the 100-ms residence time. In view of molecular dynamics simulation of palladium clusters in rare gas atmospheres[21] this is sufficient for a complete thermalization, especially if taking into account that the energy transfer between the sodium and helium atoms is much more efficient than between palladium and helium atoms, and that the sodium clusters already have a temperature of about 100 K when leaving the cluster source. In fact even fewer collisions are actually necessary, as neither the increase of the extraction frequency to 300 Hz (a reduction of the residence time by a factor of three) nor a decrease of the buffer gas density by a factor of three leads to discernible changes in the photofragment distributions. Finally, we checked whether radio frequency heating of the clusters plays a role. Decreasing the radio frequency amplitude (usually $U_{pp} = 260$ V, at $f = 670$ kHz) by a factor of two did not have any visible effect, which means that under these conditions rf-induced heating obviously is negligible.

The final and most sensitive test of the thermalization in the trap is the measurement of a caloric curve in the vicinity of a phase transition. In Fig. 2 two such experimental caloric curves measured in the temperature range of the melting transition of $Na_{139}{}^+$ are presented. One was recorded with the dodecapole rf trap, the other one using the flow tube. The absolute energy scale was obtained by extrapolating the experimental data

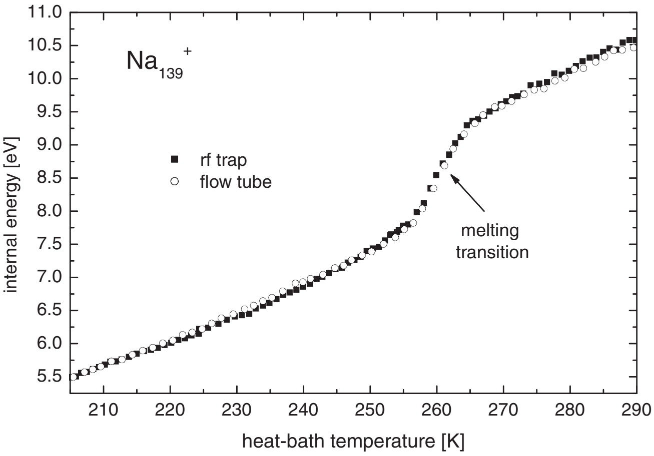

FIG. 2. Comparison of experimental caloric curves of $Na_{139}{}^+$ in the vicinity of the melting transition recorded using two different thermalization methods.

to 0 K using the bulk caloric curve.[22,23] In both curves one can observe the characteristic softened step indicating the melting. The difference of the evaluated melting temperatures is less than 0.5 K, which is actually smaller than the specified accuracy of the sensors measuring the temperature of the trap or the flow tube. This result again demonstrates the very reliable cluster thermalization in the rf trap, which allows us to extend the caloric measurements on sodium clusters to much lower temperatures than were studied before. Using the flow tube, cluster intensities sufficient for caloric measurements could only be obtained for temperatures above about 60 K. With the present trap experiments measurements are instead possible down to temperatures of 6 K.

Figure 3 shows the result, the experimental low-temperature caloric curve of $Na_{139}{}^+$. We want to emphasize that no input parameter except the photon energy has been used to obtain this curve; the only uncertainty is the zero of the energy scale, which is obtained by extrapolating the curve to $T = 0$ K. One can clearly see a flattening of the caloric curve toward lower temperatures, which indicates the freezing out of the vibrational modes of the system. For comparison two bulk curves are shown in Fig. 3. One is the experimental isobaric thermal energy of the bulk (the integrated isobaric heat capacity per atom from Refs. 22, 23 scaled by $(3n-6)/3$ to match the number of degrees of freedom in the cluster). The cluster and bulk data almost coincide, which demonstrates that the thermal behavior of sodium clusters of this size is already very close to that of the bulk. The second curve is the isochoric thermal energy of the bulk in the simple Debye model, again scaled to the number of degrees of freedom of the cluster

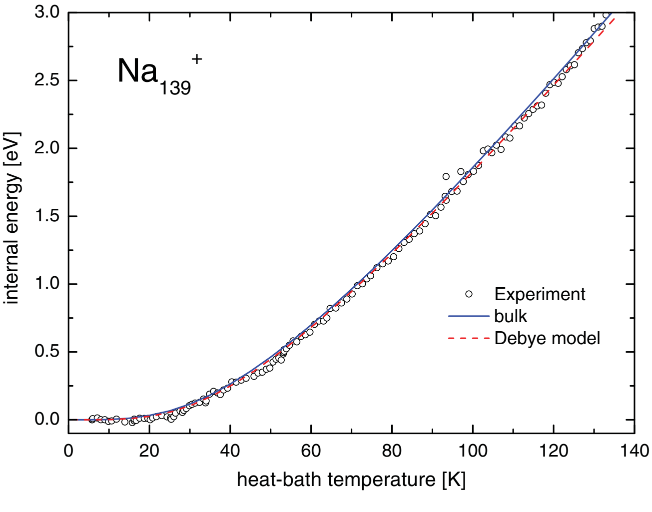

FIG. 3. (Color online) Experimental caloric curve of $Na_{139}{}^+$ at low temperatures (○). The blue (dark) line shows the isobaric thermal energy of the bulk,[22,23] scaled to the number of degrees of freedom of the cluster. The dashed red (gray) line is a fit to the experimental data, using the Debye model [Eq. (1)]. A Debye temperature of $\theta_D = 163.5 \pm 10$ K has been extracted from the fit.

$$E = 3(3n-6)k_BT\left(\frac{T}{\theta_D}\right)^3\int_0^{\theta_D/T}\frac{x^3}{e^x-1}dx. \qquad (1)$$

The Debye temperature θ_D is the only free parameter of this model. The best fit to our data is obtained for $\theta_D = 163.5 \pm 10$ K, which compares well to the Debye temperature of 158 K of bulk sodium.[24] Note that here an isochoric model has been used to fit cluster data measured at constant pressure. This is justified, as in most of the temperature range discussed the isochoric and isobaric thermal energy is practically identical. Nevertheless the slight deviation between the cluster data and the fit above about 125 K already indicates that this is not a valid assumption anymore for temperatures higher than that. The very similar behavior of the clusters and the bulk shows that the overall vibrational density of states of a $Na_{139}{}^+$ cluster must be similar to that of the bulk. The results seem to indicate a weak increase of the cluster Debye temperature with respect to that of the bulk, but also a value a few percent below that of the bulk one would be consistent with our results. What we can certainly exclude are such strong deviations from the bulk value as mentioned in the introduction. This shows that an isolated particle indeed behaves more bulklike than nanocrystalline material. In fact the practically unchanged Debye temperature is in agreement with a simple continuum model, which for a sodium cluster of this size predicts a depression of θ_D by only 2.5%.[25] A full atomistic simulation of the low-temperature heat capacity of sodium clusters of this size unfortunately is not available. We hope that our results will stimulate efforts in this direction.

One should mention that bulklike caloric curves of free clusters have been observed earlier, for example for systems like gallium[26] or aluminum.[27] But as these experiments were done at temperatures above or not far below the Debye temperature of the corresponding bulk systems, Debye temperatures of the particles have not been determined. Our group has observed bulklike caloric curves of $(H_2O)_n{}^-$ clusters at low temperatures.[28] Water, however, exhibits a rather complex caloric behavior, which cannot be described within a simple Debye model.

Finally we want to discuss another consequence of our results. For high-resolution spectroscopy on molecules or clusters it is highly advantageous if the vibrational temperature of the studied particle is as low as possible. In order to estimate the vibrational excitation of the $Na_{139}{}^+$ clusters, their VDOS has been calculated using a simple lattice model which reproduces the known phonon dispersion relation of bulk sodium.[29] For 137 k vectors equally spaced in the first Brillouin zone the frequencies of the three possible vibrational modes have been calculated, meaning that the cluster was treated as a small piece of matter cut out of the bulk crystal. The 411 frequencies obtained form a discrete VDOS, which exhibits a cutoff at 0.39 THz (corresponding to a temperature of $T = 19$ K). Using this VDOS the temperature-dependent total vibrational excitation of the clusters has been calculated. It turns out that at 6 K, the lowest temperature reached in the experiment, about 85% of the clusters are in their vibrational ground state. Although the true VDOS of the real cluster will be somewhat different, we do not expect a fundamentally different result for the low-temperature vibrational excitation. This expectation is based on the fact that the measured caloric curve indicates a rather strong similarity between the overall VDOS of the cluster and the bulk, and that both spherical continuum models[10] and atomistic simulations of clusters[13,30] obtain cutoff frequencies close to the one given above. It should therefore be a safe statement that at 6 K the majority of the clusters are in their vibrational ground state.

Summarizing, we have demonstrated that a cluster as large as $\mathrm{Na}_{139}{}^{+}$ can be efficiently thermalized in a rf trap by collisions with helium buffer gas. The caloric curve measured down to a temperature of 6 K shows the close to complete freezing out of the vibrational degrees of freedom of the cluster. A Debye temperature of $\theta_D = 163.5 \pm 10$ K has been obtained from a fit to the data, indicating that the finite size effect onto the Debye temperature of sodium nanoparticles is weak.

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