Melting of Isolated Tin Nanoparticles

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The melting of isolated neutral tin cluster distributions with mean sizes of about 500 atoms has been investigated in a molecular beam experiment by calorimetrically measuring the clusters' formation energies as a function of their internal temperature. For this purpose the possibility to adjust the temperature of the clusters' internal degrees of freedom by means of the temperature of the cluster source's nozzle was exploited. The melting point of the investigated tin clusters was found to be lowered by 125 K and the latent heat of fusion per atom is reduced by 35% compared to bulk tin. The melting behavior of the isolated tin clusters is discussed with respect to the occurrence of surface premelting.

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The phenomenon of particle size dependent melting point depression, as first reported by Pawlow [1], is a result of the size dependent chemical potential of the atoms in finite systems [2]. Such a size dependence of the melting point is expected to be especially pronounced for particles in the nanometer size range because of their strongly enhanced ratio of surface to volume atoms. For example, the melting point T_m of supported nanometer-sized gold particles is lowered by 300 K in comparison with the bulk value, which was observed by transmission electron microscopy (TEM) [3].

There exist several phenomenological models addressing the melting point depression of small metal particles [1,3,4]. However, as Lai *et al.* [5] have pointed out, for a more comprehensive understanding of the thermodynamics of finite material systems it is imperative not only to investigate the size dependence of the melting point depression but also the dependence of the heat exchange associated with the melting process on the particle size. Since TEM investigations merely allow the recognition of structural transformations, Lai *et al.* [5] developed a novel experimental technique to calorimetrically investigate the melting process of supported tin clusters with radii ranging from 5 to 50 nm. In these experiments, it was found that the melting point $T_m(R)$ depends nonlinearly on the inverse of the cluster radius R, which is in contrast to the traditional description of the melting behavior of small particles [1,3,4]. Additionally, the latent heat of fusion Δu^{ls} was found to be reduced for the nanometer-sized particles. Both effects can be explained by taking the phenomenon of surface premelting for the finite particles into account [6]. The significance of surface premelting for small particles has first been reported by Kofman *et al.* [7] in an electron microscope study of lead particles and was theoretically described by Beaglehole [8] and Sakai [9]. The theoretical description of the surface melting of small particles can be treated by analogy with the description of planar surfaces [10,11]. The formation of a liquid skin on a planar or curved solid surface at a temperature below the bulk (volume) melting point becomes energetically favorable if the sum of the surface energies of the liquid-solid and the liquid-vapor interfaces (σ^{ls} and σ^{lv}) is smaller than the surface energy of the solid-vapor interface σ^{sv}, because in this case the formation of the liquid film results in a reduction of the surface free energy. The thickness δ of the liquid skin is balanced by two opposing effects: On one hand, the surface energy is lowered due to the formation of the liquid layer; on the other hand, the energy, which is necessary to generate the undercooled liquid film, has to be invested. Therefore the thickness δ of such a liquid skin turns out to be only on the order of some monolayers and the macroscopic solid-liquid surface energy has to be modified for the description of the thermodynamic properties of a particle consisting of a solid core covered with a molten skin. For metallic systems, one can introduce a characteristic length ξ, which allows a consideration of influences on the interatomic interaction of the metal atoms at the interface caused by the finite thickness of the liquid film and leads to the definition of a thickness dependent interfacial energy $\sigma^{\mathrm{ls}}(\delta)$. Then, with the assumption of a spherical geometry for a finite particle consisting of N atoms in an incompressible volume V, it is possible to obtain the total free energy F of the particle as a function of the number of atoms N^1 in the liquid layer [7]:

$$F = (N - N^1)\mu^{\mathrm{s}} + N^1\mu^1 + 4\pi R^2 \times \left[\sigma^{\mathrm{ls}}\left(\frac{(R-\delta)}{R}\right)^2 + \sigma^{\mathrm{lv}} + S'\exp(-\delta/\xi)\right], \quad (1)$$

with

$$S' = \sigma^{\mathrm{sv}} - \left[\sigma^{\mathrm{lv}} + \sigma^{\mathrm{ls}}\left(\frac{(r-\delta)}{R}\right)^2\right], \quad (2)$$

wherein R is the total particle radius, and μ^{s} and μ^1 are the bulk chemical potentials of the atoms in the solid and the liquid phases. The thickness δ of the liquid layer is

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given by the minimum of the free energy for fixed T, V, and N, where T is the temperature. Using the relation $(\mu^{l} - \mu^{s}) = \Delta u^{ls}(T_m(\infty) - T_m(N))/T_m(\infty)$, which is valid for temperatures close to the bulk melting point, the minimization leads to the following formula:

$$\frac{T_m(\infty) - T_m(N)}{T_m(\infty)} = \frac{2\sigma^{ls}\upsilon}{\Delta u^{ls}} \frac{[1 - \exp(-\delta/\xi)]}{(R - \delta)} + \frac{S'\upsilon}{\xi \Delta u^{ls}} \frac{R^2 \exp(-\delta/\xi)}{(R - \delta)^2}, \quad (3)$$

wherein $\upsilon = 4\pi R^3/(3N)$ is the atomic volume of bulk tin. This formula allows one to calculate the thickness of the liquid layer for a given temperature T and cluster radius R numerically. However, one has to point out that the temperature and size dependence of the interfacial energies, the atomic volume, and the latent heat of fusion have been neglected in the derivation of Eq. (3). Nevertheless, this formula is a reasonable basis for discussing the size dependence of the melting behavior of finite particles. For large clusters, the model predicts that at a critical temperature T_c the surface melting process is initiated. An increasing temperature causes the thickness of the liquid skin to continuously increase until the melting point of the cluster is reached. Here, the remaining solid core of the cluster discontinuously turns into the liquid phase. For clusters smaller than a critical radius R_c, the melting point will drop below the critical temperature T_c, at which the surface melting starts. Under these circumstances, the cluster will directly transform from the totally solid to the liquid state at the melting temperature. This predicted change of the melting behavior has a strong influence, not only on the size dependence of the melting temperature [9] but also on the latent heat of fusion.

In this Letter, we focus on the influence of the cluster size on the melting behavior by investigating the thermodynamic properties of isolated tin clusters. The investigation of isolated clusters has two major advantages relative to the experiments on supported particles: The influence of the substrate on the melting process can be completely eliminated, and the molecular beam experiments allow one to investigate the thermal behavior of very small clusters, i.e., clusters smaller than the theoretically predicted critical cluster size with the radius R_c.

For this purpose, we used a molecular beam apparatus [12], which allows the generation of intensive, neutral tin cluster beams. With a nanocalorimeter based on a pyroelectric foil as a temperature sensor [13,14], it is possible to measure the heat, which is released during the condensation of narrow size distributions of tin clusters on a solid tin surface. The measured released heats then allow a determination of the formation energies of the isolated clusters. The internal temperature of the clusters is controlled through the temperature of the nozzle at the cluster source, which is assumed to be in thermal equilibrium with the carrier gas helium. A similar technique was also used for measurements of the magnetic moments of superparamagnetic iron clusters in Stern-Gerlach experiments [15]. These experiments indicate that, for nozzle temperatures above 300 K and under low stagnation pressures, the internal (vibrational) temperatures deviate only by less than 10–20 K from the nozzle temperature since adiabatic expansion into vacuum then has a negligible effect. It is assumed that the similarly designed cluster source, which was used for this experiment, behaves in a similar fashion. The results, which will be shown in the following, clearly show that it is possible to tune the clusters' internal temperature, although the absolute temperature scale remains somewhat uncertain.

In Fig. 1(a), the temperature dependence of the internal energy of isolated tin clusters with a mean size of $N = 430$ is shown together with the behavior of bulk tin [16], for which the internal energy at 298 K is set to zero. The temperature dependence of the internal energy of the clusters clearly shows a distinctly stronger increase in the temperature interval from 340 to 420 K compared to the two ranges below 340 K and above 420 K, which exhibit a linearly growing energy with increasing temperature with a slope of approximately $3k_B$, i.e., the Dulong-Petit behavior. This behavior can be interpreted as the melting transition of the isolated size distribution of tin clusters. In comparison to the bulk values, the melting point of the cluster distribution is reduced by about 125 K and the latent heat of fusion amounts to (40 ± 10) meV per atom instead of 73 meV for bulk tin [16]. In a second experiment, we investigated tin clusters with a mean size of $N = 520$ finding a similar value for the melting temperature but a latent heat of fusion of (54 ± 10) meV. As can be seen in the temperature dependence of the specific heat capacity in Fig. 1(b), the melting transition takes place over a temperature range of about 80 K. However, this phenomenon cannot exclusively be attributed to a broadening of the phase transition due to finite size effects [17] because the molecular beam consists of a distribution of different cluster sizes between $N \approx 100$ and $N \approx 900$. This interpretation is supported by investigations of Schmidt *et al.* [18] on the melting behavior of isolated sodium cluster cations, for which irregular variations of the melting temperature over the range of 60 K have been found for cluster sizes between $N = 70$ and 200 atoms.

The experimentally determined size dependence of the melting point T_m for the isolated and supported tin clusters is shown in Fig. 2 together with the predicted behavior determined from the model of surface melting of finite particles. The theoretically expected melting behavior was analyzed by numerically calculating the temperature $T = T_m(R)$ for a given cluster size R at the limiting case $\delta/R \rightarrow 1$ from Eq. (3). The result is displayed in the solid line in Fig. 2. The interfacial energies relevant for Eq. (3) amount to [5,11] $\sigma^{sv} = 660$ mJ/m^2, $\sigma^{lv} = 550$ mJ/m^2, and $\sigma^{ls} = 55$ mJ/m^2. We did not find an experimental value for the characteristic length ξ of liquid tin. In order

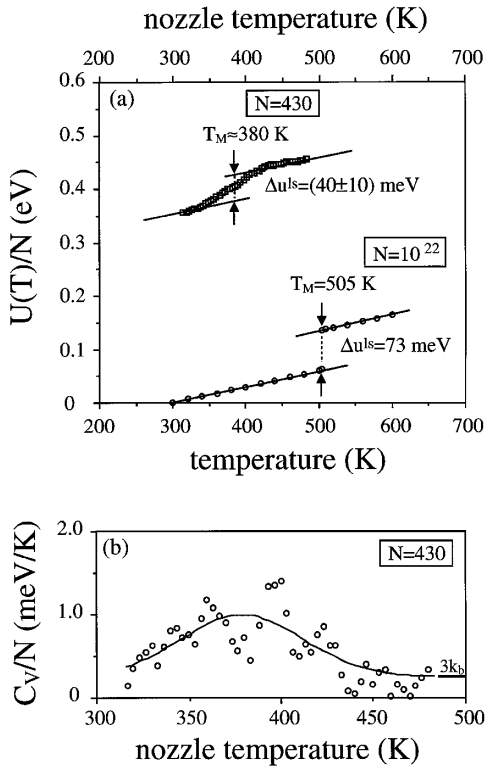

FIG. 1. (a) The internal energy per atom $U(T)/N$ of isolated tin clusters (squares) and bulk tin (circles) as a function of the temperature. The mean cluster size of the investigated tin cluster distribution is $N = 430$ atoms per cluster. The melting transition takes place at a nozzle temperature of about 380 K compared to 505 K for bulk tin. The corresponding latent heat of fusion of (40 ± 10) meV is lowered by 33 meV compared to the value of macroscopic tin. In a second experiment, we found a value of (54 ± 10) meV for the latent heat of fusion for clusters consisting of 520 atoms on average. (b) The heat capacity $C_V(T)/N$ of isolated tin clusters with $N = 430$. For nozzle temperatures above the melting transition, the value of the heat capacity is close to the classical value of $3k_B$ per atom. The melting transition takes place over a temperature range of about 80 K, which essentially is a result of the fact that a size distribution of tin clusters is investigated. The solid lines in (a) and the Gaussian in (b) are shown only as guides to the eye.

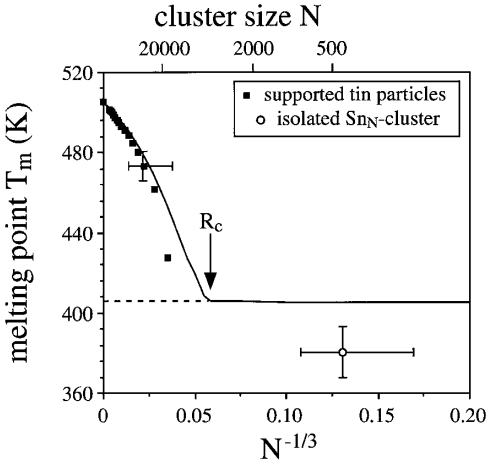

FIG. 2. The melting point of tin clusters as a function of the inverse cluster radius. The full squares were obtained for supported tin particles investigated by Lai *et al.* [5]. The open circle was achieved by the thermal investigation of the isolated tin clusters. The solid line is the prediction of the size dependent melting temperature from the surface premelting model. The dashed line corresponds to the critical temperature T_c, at which the surface melting starts. The critical cluster radius R_c is reached when the melting temperatures of the clusters become smaller than the surface melting temperature T_c. Here, the cluster melting process changes, which strongly affects the size dependence of the melting point depression as predicted from the surface premelting model. The melting temperatures of the supported tin clusters, which have radii larger than the critical radius, follow the nonlinear dependence on the inverse cluster radius predicted from Eq. (3). The change in the size dependence of the melting temperature for the isolated tin clusters, which have a radius smaller than the critical one, is clearly observable.

to apply a reasonable ξ value for liquid tin, we used the value for liquid lead of 6 Å [11], since lead is the heavier homologous element of tin. With these parameters, the latent heat of fusion for bulk tin of 73 meV per atoms [16] and the atomic volume [5] of 27.76 Å^3, the critical temperature T_c, at which the surface premelting starts, can be evaluated to $T_c = 406$ K and is shown in Fig. 2 as a dashed line. This temperature belongs to a critical cluster radius of $R_c = 35$ Å. Hence, for tin particles with a radius smaller than the critical radius, the melting point $T_m(R)$ lies below the surface melting temperature T_c leading to a suppression of the surface premelting effect and, consequently, to a significant change in the size dependence of the melting temperature, as can be seen in Fig. 2. The supported clusters, which have radii larger than R_c, follow the behavior predicted by the surface premelting model. Clearly, the nonlinear dependence of the melting temperature on the inverse cluster radius can be observed as expected theoretically. The experimentally determined melting temperature of the isolated tin cluster distribution with a mean size smaller than the critical radius R_c clearly shows that a deviation in the size evolution of the melting temperatures occurs, when the cluster radius crosses R_c. The relatively poor agreement between the measured melting temperature of the isolated tin cluster distribution and the theoretically predicted dependence may be caused by the insufficient knowledge of the parameters taken into account for the evaluation of Eq. (3). Specifically, the values of the different interfacial energies might be incorrect, because, at temperatures where the wetting of the solid surface by a quasiliquid film occurs, the solid-liquid, solid-vapor, and liquid-vapor interfaces are in fact unstable. Hence, one is forced to estimate values by extrapolating the experimentally determined interfacial energies to the relevant temperature range [11].

In order to confirm the applicability of the model of surface premelting to describe the variation in the melting process of clusters smaller than the critical radius R_c, the calorimetrically measured values of the latent heat of fusion Δu^{ls} of the larger supported and the isolated

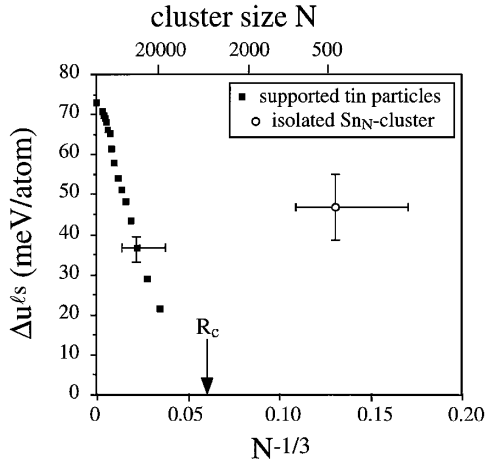

FIG. 3. The latent heat of fusion as a function of the inverse cluster radius. The full squares correspond to the supported tin particles investigated by Lai *et al.* [5]. The open circle was obtained by measurements on isolated tin clusters. When the particles approach the critical cluster size, the effective latent heat of fusion is strongly reduced for the cluster sizes examined by Lai *et al.,* due to the effect that for a given temperature below the melting point the remaining solid core of the tin clusters becomes smaller. The experimentally found enhanced latent heat of fusion of the isolated tin clusters compared to the much larger supported tin particles indicates the change in the melting process for particles, which are smaller than the critical size R_c.

tin particles are very useful. This is related to the effect that, for particles whose size approaches the critical cluster size, the remaining solid core, which melts discontinuously at $T = T_m(R)$, vanishes. Therefore the effective heat of fusion, i.e., the fraction of the latent heat of fusion corresponding to the phase transition of the solid cluster core, which actually agrees with the calorimetrically measured heat, disappears for clusters approaching the critical size. This behavior has been observed for the supported tin clusters [5], which is shown in Fig. 3. If the tin clusters smaller than the critical size melt as a whole, then it could be expected that the effective latent heat of fusion for these clusters should be significantly enhanced compared to the larger clusters with $R > R_c$. Exactly this behavior is observed in the thermal investigation of the isolated tin clusters, as can be seen in Fig. 3. Hence, the influence of the cluster size on the latent heat of fusion clearly supports the validity of the surface premelting model describing the change in the melting process for tin particles with $R < R_c$. Although the application of the premelting model to clusters merely consisting of a few hundreds of atoms should be treated with care, because of the crude assumptions, which have been made in the derivation of Eq. (3), the experimentally determined values of the melting temperature and the latent heat of fusion demonstrate the importance of surface premelting effects for the phase behavior of very small metal particles.

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