Melting-Point Depression by Insoluble Impurities: A Finite Size Effect

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Melting-point depression by soluble impurities is an entropy-driven phenomenon. Studying partially oxidized free sodium nanoparticles, we found an additional mechanism, which is caused by insoluble impurities. Oxidization of sodium clusters with 135–192 atoms by a single oxygen molecule causes a melting-point depression of 17 ± 6 K; additional oxygen amplifies the effect. This is in contrast to the behavior of bulk sodium, where the melting point does not change upon partial oxidization. First-principles density functional theory calculations reveal the interaction between the pure and the oxidized part of the cluster to be responsible for the effect. There is more structural freedom in a liquid cluster to optimize the interface between the two parts. This stabilizes the liquid phase and causes the observed, cluster-specific melting-point depression.

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Salt is used for deicing. Brine is even synonymous with antifreeze protection. It is the entropy that causes this well-known freezing- (or melting-) point depression of solutions: upon freezing, the impurities are concentrated in the liquid phase, while the solid phase is purified. This costs entropy. The liquid phase becomes more favorable; its chemical potential is reduced and it thus occupies a larger temperature range in the phase diagram.

Such effects should occur in nanoparticles as well, and have indeed been examined both in experimental [1,2] and theoretical studies [2–6] of binary and ternary metal nanoalloys. Some of them show phase separation in the solid phase, but mixing when they are liquid [4]. This corresponds to the above-mentioned classical dissolution and typically causes entropy-driven melting-point depressions. Other studied systems form alloys, which blend in the solid *as* in the liquid phase [5]. Analogous to the bulk, the melting points of alloy nanoparticles can be depressed or enhanced, depending on the system and the conditions.

In this Letter we describe an additional, impurity-driven effect that systematically reduces melting points of the host material even *without* dissolution. It is an interface-driven effect and therefore characteristic of small particles. We noticed it when studying the thermodynamic properties of free oxidized sodium clusters $\mathrm{Na_nO_m}^+$ ($n = 135$–195, $m = 0$–6). The corresponding bulk-sodium/oxygen system does not show a melting-point depression. Here the reaction with similar relative quantities of oxygen leads to the formation of sodium oxide Na_2O. Liquid sodium is a very bad solvent for its oxide; the saturation concentration of Na_2O is only 6 wt-ppm at 400 K [7]. The crystalline oxide therefore drops out of the liquid sodium and forms a separate phase. The melting point of the remaining, almost pure sodium, consequently, is not changed by the oxidation [8]. In small particles such a formation of two, practically noninteracting phases is not possible; it was therefore an interesting question how the presence of oxygen in sodium clusters would influence their melting behavior.

In the experiment we produce the partially oxidized sodium clusters by injecting O_2 into the helium buffer gas of a gas aggregation cluster source close to its exit, prior to the thermalization of the gas and the clusters in a variable temperature tube. After transfer to high vacuum and mass selection, the internal energies E of the clusters are measured by a photofragmentation technique [9,10]. The resulting caloric curves $E(T)$ yield the melting points T_m and latent heats q of the clusters. These are shown in Fig. 1 as a function of cluster size and degree of oxidization, together with older data of pure sodium clusters.

Oxygen in the free sodium clusters obviously reduces both the melting points and the latent heats. The reduction of the two quantities correlates with the amount of oxygen, which is demonstrated for $\mathrm{Na_{144}}^+$ oxidized with up to 3 oxygen molecules. In the studied size range the melting points and latent heats of the $\mathrm{Na_nO_2}^+$ are depressed by 17 ± 6 K and 3.2 ± 1.4 meV per sodium atom, respectively.

One conclusion can be directly drawn. We have shown earlier that the characteristic size dependence of the cluster melting points has its origin in the geometrical structure of the clusters; more precisely it stems from a strongly compensating interplay between the energies and the entropies of the different geometries [11–13]. Figure 1 shows that the pure and the partially oxidized clusters exhibit a very similar size dependence of the melting points. This suggests that the geometries of the sodium clusters are not fundamentally changed by the presence of the two oxygen atoms, meaning that the optimal atomic configurations of $\mathrm{Na_nO_2}^+$ run through essentially the same size-dependent sequence as those of the pure sodium clusters.

As noticed earlier [12–14], the entropy variations cause slight deviations between the maxima in melting points

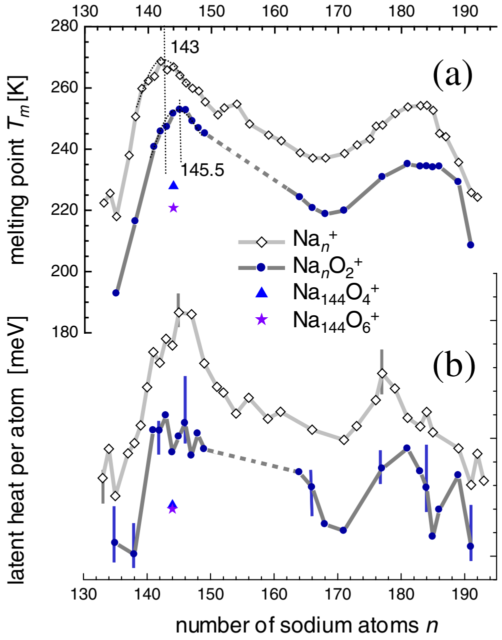

FIG. 1 (color online). (a) Melting points of pure and oxidized sodium cluster cations as a function of cluster size, showing systematically lower values for the oxidized clusters. The characteristic size dependence of $T_m(n)$ is governed by geometrical effects. It is conserved upon oxidation, indicating that the geometries are not principally changed by the presence of oxides. (b) Latent heat of melting for pure and oxidized clusters. Again the values are reduced by the oxidation. Higher concentration of oxygen in the cluster enhances both effects, as shown for $Na_{144}O_4{}^+$ and $Na_{144}O_6{}^+$. The vertical, dotted lines visualize a slight shift between the maxima of pure and oxidized clusters that is discussed in the text.

and those in the stability of the clusters. For example, the maximum in the melting points of the pure clusters in Fig. 1(a) is located at about $n = 143$, although the enhanced melting points in this region are caused by the icosahedral shell closing at $n = 147$ [11,15]. The corresponding maximum of the oxidized clusters is found at $n = 145.5$. Most likely the smaller offset to $n = 147$ is due to a somewhat weaker compensation between entropy and latent heat and does not necessarily indicate structural differences between the pure and oxidized species in this size range.

Our experiments show that the presence of oxygen atoms in sodium clusters causes a melting-point depression. This indicates that the chemical potential of the liquid is lowered with respect to that of the solid upon oxidation. In other words, a liquid sodium cluster reacts more strongly with oxygen than a solid one. This gain in free energy could be due to entropy, as is the case for the classical melting-point depression in solutions. Since bulk sodium does not dissolve Na_2O, however, an energetic reason seems to be more probable.

In order to understand the microscopic aspects of these phenomena, we calculated the ground state structures and the thermal behavior of two sample systems, $Na_{55}O_2$ and $Na_{145}O_2$. Kohn-Sham density functional theory, as implemented in the SIESTA code [16], were employed both to optimize the structure of the solid clusters and to perform *ab initio* molecular dynamics simulations at selected finite temperatures up to 500 K. Exchange and correlation effects were described within the spin-polarized generalized gradient approximation [17]. All necessary tests involving the choice of basis set, pseudopotential generation, etc., were performed to assess the convergence and accuracy of the results. Finite temperature simulations, each of 80 ps length, were performed in the isokinetic ensemble with a time step of 3 fs.

The calculations show that the oxygen molecule dissociates in contact with the surfaces of the sodium clusters. As known for the bulk [18], the oxygen atoms penetrate the surface in order to increase the coordination to the sodium atoms. The icosahedral structures of sodium clusters [11,15] contain octahedral interstices [19] of an appropriate size to house oxygen atoms. Our calculations demonstrate that the oxygen atoms tend to occupy these interstices, where they can attain the highest possible coordination without damaging the host structure (Fig. 2). This conservation of the geometries of the host icosahedra is in agreement with the observation of the conserved size-dependence in T_m as mentioned above. Nevertheless the oxygen atoms do have an influence onto the structure: the ionic Na_6O octahedra are slightly smaller than a normal Na_6 octahedron around an empty interstice in a pure cluster. This causes a certain distortion of the whole cluster.

As mentioned earlier, bulk sodium is a bad solvent for its oxide, which causes a separation between the oxide and the metal. Analogously, the oxygen atoms in the cluster prefer to be close to each other. The oxidized clusters can thus be seen as an ionically bonded molecule [20] embedded into a

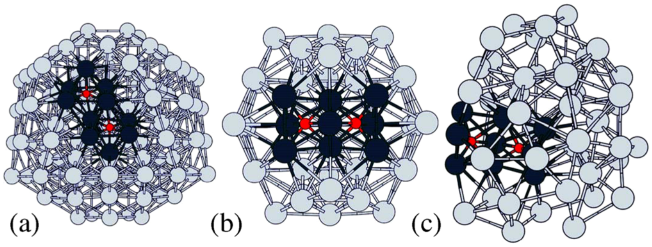

FIG. 2 (color online). The structures of (a) $Na_{145}O_2$ at 0 K and of $Na_{55}O_2$ at (b) 0 K and at (c) 340 K: Large and small spheres stand for sodium and oxygen, respectively. Light gray spheres represent metallic sodium atoms while the dark ones are part of the oxide molecule. In the solid phase, the oxygen atoms occupy neighboring octahedral interstices of the metal cluster. This causes a certain structural distortion of the host icosahedron, which is released upon melting (c). The resulting reduction of the interfacial energy between oxide and metal causes the observed melting-point reduction and improves the wetting of the sodium on the oxide. The impurity therefore occupies a more internal position within the liquid metal cluster.

metal matrix. This molecule is Na_9O_2 for $n = 55$ (two Na_6O octahedra sharing one triangular face) and $Na_{10}O_2$ for $n = 145$ (two edge-sharing octahedra, see Fig. 2). The octahedra are firmly linked. In the following these nonasodium-dioxide and decasodium-dioxide molecules will be termed ‘‘oxide’’ for shortness. In fact, the oxygen and the ‘‘bridging’’ sodium atoms exhibit Mulliken charges and bond lengths that are very close to those occurring in the bulk-Na_2O crystal. The main difference to the bulk oxide is the coordination of the oxygen atoms. In the Na_2O-crystal each oxygen is coordinated to 8 sodium atoms, while in the cluster an *octahedral* coordination is preferred (see Fig. 2), similar to structures that have been found for free sodium oxide molecules [21].

Apart from this slight structural difference, which is probably mostly due to the smallness of the oxide molecule, the cluster and bulk behavior is very similar. This is even more apparent at higher temperatures. Bulk sodium oxide has a much higher melting point (1403 K) than bulk sodium (371 K). In a large temperature range above 371 K, partly oxidized sodium separates into a liquid, metallic phase and the solid oxide [8]. Our findings for $Na_{55}O_2$ and $Na_{145}O_2$ are similar: At 400 K the metallic part of the cluster is liquid, while the oxidized part stays essentially intact. The number of Na-O bonds is strictly conserved and the Na_6O octahedral units are never separated (dissolved) at the studied temperatures up to 500 K.

Nevertheless, the sodium oxide molecule is not completely rigid: different atomic configurations dynamically coexist even at temperatures only slightly above the melting point of the metallic part. They are related to variations in the connectivity of the two octahedra: The oxide molecule thus fluctuates in time between Na_9O_2 (face-sharing octahedra), $Na_{10}O_2$ (edge-sharing) and $Na_{11}O_2$ (vertex-sharing). Through this concerted mechanism, which modifies the number of Na atoms bridging the two octahedra, the oxide occasionally exchanges sodium atoms with the metallic part of the cluster.

In the liquid as well as in the solid clusters the oxide molecules prefer to reside at the cluster surface. They are therefore only partly covered by the pure metal; i.e., the metal atoms are only partially wetting the oxide.

In spite of the big size difference, the theoretical results for $Na_{55}O_2$ and $Na_{145}O_2$ are very similar. This indicates that the findings should be quite general.

So what is the origin of the melting-point depression? As mentioned above, the oxidized part of the solid cluster shrinks under the reaction and puts the metallic part under tension. In the simulations of $Na_{55}O_2$ the oxide (Na_9O_2) contracts by 42.6 Å^3 [22]. The volume of the whole cluster also decreases, but only by 22.5 Å^3. The reduced density of the metallic part indicates a tensile stress in its lattice, which engages the whole cluster. Even $Na_{145}O_2$ cannot entirely compensate the shrinking of its oxide (43.9 Å^3) by elastic deformations. The cluster shrinks less than $Na_{55}O_2$, but still by 8.5 Å^3. Like in the bulk, the oxide is about a factor of 10 stiffer than the solid metal. In consequence, it is the metal that deforms and adapts to the oxide and not contrariwise. The related deformation energy is dominantly stored in the metal.

In contrast to the solid one, the liquid cluster can follow the contraction of its oxide [Fig. 3(b)]; it shrinks by a similar amount as the oxide. Thus the density of the liquid metallic part is not changed by the oxidation and the liquid metal is not under tension. Melting therefore releases the immanent stress of the solid, oxidized cluster, which enhances the exothermic character of the oxidation. This thermodynamically promotes the liquid, which therefore occupies a larger temperature range in the phase diagram and causes the observed melting-point reduction. The calculated energy gain upon oxidation for Na_{55} is 4 meV/atom smaller for the solid at 0 K than for the liquid at 340 K. This fits well to the measured latent heat depressions [Fig. 1(b)].

For sufficiently large clusters the lattice deformation by the two oxygen atoms should become a local effect and the total deformation energy size independent. The depression of melting point and latent heat per atom should then scale with the reciprocal cluster size. The clusters studied in this work are obviously not big enough for this scaling (see Fig. 1). As mentioned above, the clusters shrink as a whole under the oxidation, what confirms a global perturbation. In the studied size range the deformation energy and thus the energy gain under melting still increase with cluster size.

In principle, the observed melting-point depression is a surface effect. Even though the whole cluster is involved,

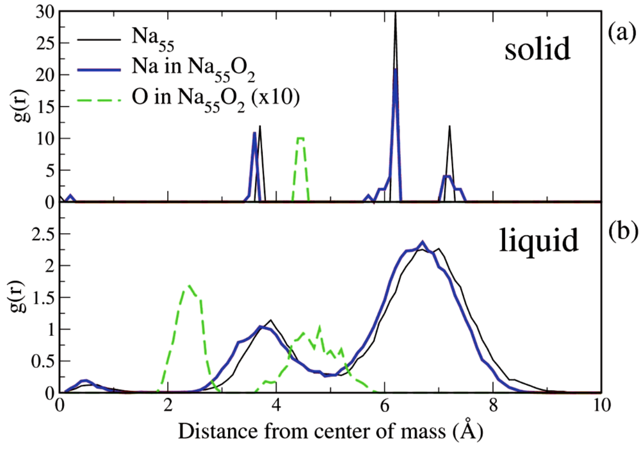

FIG. 3 (color online). The deformation of the solid and the shrinking of the liquid cluster under oxidation: Atomic radial distribution function $g(r)$, giving the average number of Na or O atoms at a given distance from the center of mass of the sodium atoms, is shown for Na_{55} and $Na_{55}O_2$. (a) solid cluster at 0 K; (b) liquid cluster at 340 K. While the oxidation puts the solid cluster under tension, the liquid metal can follow the contraction of the oxide and avoids the mechanical stress. Because of a better wetting of the oxide, the oxygen atoms occupy more internal positions in the liquid cluster (cf. Fig. 2).

the process can be seen as driven by the oxide-metal interface. Because of the different lattices of the pure metal and the oxide, the interfacial energy is *larger* when the whole cluster is solid. This leads to the observed melting-point depression.

This point of view is supported by a second observation. In bulklike samples reduced interface tensions lead to a better wetting. We observed a related behavior of the cluster: Under melting the interfacial energy decreases. In consequence, the oxide penetrates deeper into the liquid host than into the solid, as it is typical for a better wetting (see Figs. 2 and 3).

Impurities typically *perturb* the lattice of a host cluster. However, in some cases, especially for small clusters and specific cluster sizes, small impurities might also *ameliorate* the structure of the host and invert the effect [3]. However, the bigger host and impurity become, the less probable are such exceptions. For mesoscopic particles and impurities, the interface-driven melting-point depression should therefore become a general rule. It should occur for all nanoparticles containing an insoluble impurity, provided that there is a lattice mismatch between the cluster material and the impurity.

The effect should also play a role in the melting of pure clusters and nanoparticles deposited or grown on surfaces of a different material. It is known since long that the melting points of such particles are depressed [23,24]. Like for the free clusters this is caused by the cluster surface, but it has been noticed that the cluster-substrate interface has an influence as well. The interface-driven melting-point depression should lead to an enhanced decrease of the melting points with decreasing cluster size. The observation of this effect might, however, be difficult, because supported clusters can be strongly, lenticularly flattened by the contact to the surface, and it has been shown that such deformations can systematically *increase* the melting points [25].

In summary, our experiments and calculations show that the insoluble oxide molecule in a sodium cluster causes a cluster-specific depression of melting point and latent heat. The observed effect is due to the interface between the impurity and the cluster. The related surface energy decreases under melting. This stabilizes the liquid phase, hinders the freezing, and therefore depresses the melting points. The effect should be a general phenomenon for nanoparticles with insoluble impurities.

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[1] C. M. Neal, A. K. Starace, and M. F. Jarrold, J. Phys. Chem. A **111**, 8056 (2007); W. A. Jesser, R. Z. Shneck, and W. W. Gile, Phys. Rev. B **69**, 144121 (2004).

[2] R. Ferrando, J. Jellinek, and R. L. Johnston, Chem. Rev. **108**, 845 (2008), and references therein.

[3] C. Mottet, G. Rossi, F. Baletto, and R. Ferrando, Phys. Rev. Lett. **95**, 035501 (2005).

[4] A. Aguado and J. M. López, J. Chem. Theory Comput. **1**, 299 (2005); Phys. Rev. B **71**, 075415 (2005); **72**, 205420 (2005).

[5] F. Calvo, E. Cottancin, and M. Broyer, Phys. Rev. B **77**, 121406(R) (2008).

[6] A. Aguado, L. E. González, and J. M. López, J. Phys. Chem. B **108**, 11 722 (2004); F. Y. Chen, B. C. Curley, G. Rossi, and R. L. Johnston, J. Phys. Chem. C **111**, 9157 (2007).

[7] H. U. Borgstedt, H. Schneider, and G. Wittig, Atomwirtschaft-Atomtechnik **17**, 157 (1972).

[8] B. Predel in 54 Na-*X Binary Systems*, edited by O. Madelung, Landolt-Börnstein, Group IV, Physical Chemistry: Vol. 5H, p. 246 (Springer-Verlag, Berlin, 2006).

[9] M. Schmidt, R. Kusche, and W. Kronmüller *et al.*, Phys. Rev. Lett. **79**, 99 (1997).

[10] M. Schmidt, R. Kusche, and B. v. Issendorff *et al.*, Nature (London) **393**, 238 (1998).

[11] H. Haberland, T. Hippler, and J. Donges *et al.*, Phys. Rev. Lett. **94**, 035701 (2005).

[12] M. Schmidt, J. Donges, and Th. Hippler *et al.*, Phys. Rev. Lett. **90**, 103401 (2003).

[13] A. Aguado and J. M. López, Phys. Rev. Lett. **94**, 233401 (2005); A. Aguado, J. Phys. Chem. B **109**, 13 043 (2005).

[14] C. M. Neal, A. K. Starace, and M. F. Jarrold, Phys. Rev. B **76**, 054113 (2007).

[15] O. Kostko, B. Huber, M. Moseler, and B. v. Issendorff, Phys. Rev. Lett. **98**, 043401 (2007).

[16] J. M. Soler, E. Artacho, and J. D. Gale, J. Phys. Condens. Matter **14**, 2745 (2002).

[17] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[18] B. Woratschek, G. Ertl, and J. Kuppers *et al.*, Phys. Rev. Lett. **57**, 1484 (1986); A. Bottcher, R. Grobecker, and T. Greber, Surf. Sci. **280**, 170 (1993).

[19] J. P. K. Doye and D. J. Wales, J. Chem. Soc., Faraday Trans. **93**, 4233 (1997); U. Müller, *Inorganic Structural Chemistry* (John Wiley & Sons, New York, 2006).

[20] S. D. Elliott and R. Ahlrichs, J. Chem. Phys. **109**, 4267 (1998).

[21] S. D. Elliott, and R. Ahlrichs, Phys. Chem. Chem. Phys. **2**, 313 (2000).

[22] The choice of volume definition [S. E. Baltazar, A. H. Romero, and J. L. Rodriguez-Lopez *et al.*, Comput. Mater. Sci. **37**, 526 (2006)] causes an uncertainty of about 1 Å in the volume differences.

[23] P. Pawlow, Z. Phys. Chem. **65**, 1 (1909); Ph. Buffat and J-P. Borel, Phys. Rev. A **13**, 2287 (1976).

[24] O. A. Yeshchenko, I. M. Dmitruk, and A. A. Alexeenko *et al.*, Phys. Rev. B **75**, 085434 (2007); F. Ding, A. Rosen, S. Curtarolo, and K. Bolton, Appl. Phys. Lett. **88**, 133110 (2006); M. Dippel, A. Maier, and V. Gimple *et al.*, Phys. Rev. Lett. **87**, 095505 (2001).

[25] F. Ding, A. Rosen, and S. Curtarolo *et al.*, Appl. Phys. Lett. **88**, 133110 (2006).