# Single Impurity Effect on the Melting of Nanoclusters

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We show by molecular dynamics simulations that the melting temperature of clusters can be tuned by selective doping. In fact, a single Ni or Cu impurity in Ag icosahedral clusters considerably increases the melting temperature even for sizes of more than a hundred atoms. The upward shift is correlated to the strain relaxation induced by a small central impurity in icosahedral clusters.

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The melting properties of nanometer-sized clusters were the subject of considerable interest about 30 years ago when the reduction of their melting point at decreasing particle size, predicted since 1871 by Thomson [1], was measured in gold clusters [2]. This has been followed by several experiments on different metals [3–5]. All the experiments confirmed the so-called "Pawlow law" [6] predicting a regular linear decrease of the melting temperature with the inverse of the cluster radius. Such a description, based on macroscopic thermodynamic arguments, becomes questionable, however, for cluster sizes of the order of 2 nm (~100 atoms), in which most of the atoms belong to the surface and the interior atoms do not necessarily have the bulk structure. In fact, experiments on sodium clusters [7,8] have shown that the melting temperature of sodium clusters does not evolve monotonically with cluster size, but displays evident peaks and minima in a size range from 70 to 200 atoms. Changing the size of sodium clusters by just a few atoms can change their melting temperature by more than 10%. Usually, the melting temperature remains lower than the bulk melting temperature. Recent experiments on tin [9] and gallium [10] clusters of less than 40 atoms have shown that the melting transition could occur significantly above the bulk melting temperature. This has been attributed in such cases to a substantial change in the atomic structure linked with pure covalent bonding in the clusters in contrast with the covalent-metallic bonding in the bulk [11].

In this Letter, we show that, besides the size effect, there is an *alloying* effect which can considerably increase the melting temperature even by the introduction of a *single impurity* in clusters of more than a hundred atoms.

The substitution of one atom in a pure cluster with an atom of a different chemical species creates a chemical defect which may be associated with a decrease of the melting temperature, as shown by Aguado *et al.* for Li and Cs-doped sodium clusters [12]. On the contrary, we find that, in icosahedral silver clusters, a single impurity can increase the melting temperature. This upward shift is obtained when the impurity atom is smaller than Ag atoms and has a strong tendency to be incorporated inside the cluster. The increase is due to a combination of geometric and chemical effects. The geometric effects derive from the following fact. It is well known that, for small sizes, the icosahedral structure is more stable than crystalline structures, because it optimizes the surface energy exposing only compact (111) facets instead of both (100) and (111) facets (as happens in the bulklike structure). The price to pay is a distortion of the lattice (intershell atomic distances are contracted by 5% as compared to intrashell atomic distances). Such strain causes an important compression at the center of the icosahedron. The icosahedral strain accommodation depends on the material, specifically on the stiffness of its interatomic potential [13,14] and on its surface stress relaxation [15]. Many-body effects in transition metals lead to an inward relaxation of interatomic distances at the surface (due to the bond order/bond length correlation), which is antagonistic with the surface bonds expansion in the icosahedral geometry. Introducing a vacancy at the central site of the icosahedron, in order to relax the maximal stress located in the core, can help the contraction of surface bonds, thus causing a general release of the stress. Indeed, single-metal and Lennard-Jones icosahedrons with a central vacancy were found as new magic clusters [16,17]. However, these clusters do not melt at a higher temperature than pure complete icosahedrons. Here we show that introducing a small impurity atom at the center of an icosahedron has a much stronger effect on the stability of the structure.

Our energetic model is derived from the second moment approximation in the tight binding scheme [18] extended to the description of alloys [19]. This model has proved to be effective in describing Ag-Ni and Ag-Cu nanoclusters, in agreement with density-functional calculations [20]. The form and parameters of the potential can be found in Refs. [21,22] with the exception of Ag-Au [23]. This model allows a detailed study of the melting process even for large clusters (more than 500 atoms) on very long time scales by molecular dynamics simulations. Very long time scales are necessary to obtain a sufficient statistical sampling in the melting temperature range [24,25]. Our simulations start at 400 K from a solid cluster.

The temperature is raised up to 900 K in steps of 5 K each 7 ns, so that the heating rate is close to the experimentally relevant ones [25]. For each cluster and size, ten independent simulations are performed (with the exception of size 561, at which three simulations are made), and the results are averaged.

Let us now concentrate on the melting of silver icosahedrons. We compare pure clusters to clusters with a central impurity. Four different impurities are considered: Ni, Cu, Pd, and Au, which display a decreasing misfit with Ag, from 14% to almost no misfit. Selected snapshots from simulations for $Ag_{55}$, $Ag_{54}Ni_1$, and $Ag_{54}Pd_1$ are shown in Fig. 1. $Ag_{55}$ and $Ag_{54}Pd_1$ are clearly liquid at 600 K, while $Ag_{54}Ni_1$ is still a solid cluster. Caloric curves are shown in Fig. 2 for 55- and 147-atom size icosahedrons, which are stable at 0 K compared to other structures [13] (these sizes represent, respectively, two and three atomic shells around the central atom). In all clusters, the solid-liquid transition is not sharp as in bulk systems, but takes place in a finite temperature range [26–28], whose width decreases as the cluster size increases. We single out the melting range by looking at changes in the slope of the caloric curves. Let us consider size 55. The melting range of pure $Ag_{55}$ is centered at 570 K. There is a considerable upward shift for $Ag_{54}Ni_1$, of about 70 K, and a still important one for $Ag_{54}Cu_1$ (about 40 K), while for $Ag_{54}Pd_1$ the shift is small (10 K or so). Finally, for $Ag_{54}Au_1$ there is no shift at all. At size 147, the melting point of Ag is centered at 660 K, while the ranges of $Ag_{146}Ni_1$ and $Ag_{146}Cu_1$ are shifted by 50 and 30 K, respectively. For Ni impurities, non-negligible effects are found even for larger clusters (see Fig. 3) with shifts of 30 and 20 K for the 309- and 561-atom icosahedrons, respectively.

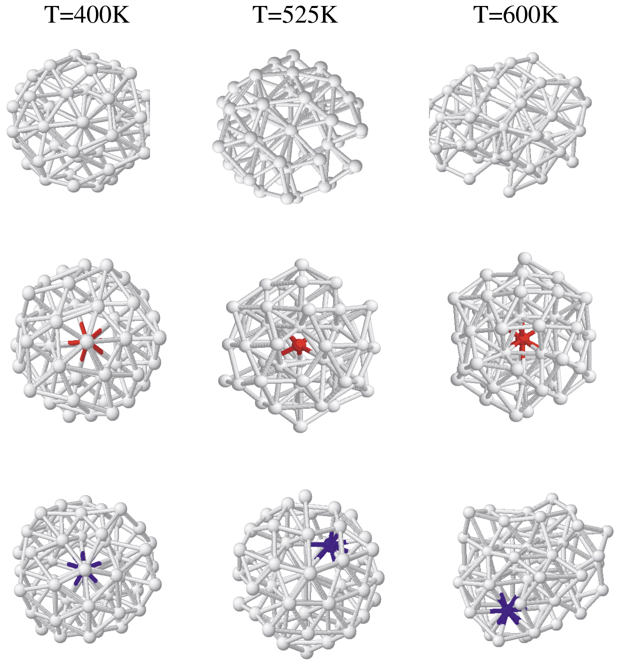

FIG. 1 (color online). Snapshots from the melting simulations: pure $Ag_{55}$ (top row), $Ag_{54}Ni_1$ (middle row), and $Ag_{54}Pd_1$ (bottom row). At 600 K, $Ag_{54}Ni_1$ is still icosahedral, while $Ag_{55}$ and $Ag_{54}Pd_1$ are already melted. In $Ag_{54}Pd_1$, the central impurity migrates to the intermediate icosahedral shell before melting. In $Ag_{55}$ at 525 K, a rosette structure is shown, with a distorted hexagonal ring on its surface.

To investigate the origin of this upward shift, we calculate the local stress in the clusters and their energetic relative stability after local energy optimization by quenched molecular dynamics. The local stress $\sigma_n$ at the atomic site $n$ (equal to the trace of the stress tensor $\underline{\sigma}_n$) can be written as

$$\sigma_n = \frac{1}{3}\sum_{i=1}^{3} \sigma_n^{ii} = \frac{1}{3}\sum_{m} \frac{dE_n(r_{nm})}{dr_{nm}} r_{nm},$$

where $E_n(r_{nm})$ is the energy at site $n$, as described in Refs. [21,22]. Then we evaluate the impurity solution energy of one impurity in silver clusters of $N$ atoms as

$$\Delta E_{\text{imp}} = E(\text{Ag}_{N-1}M) - E(\text{Ag}_N) + \frac{1}{N}[E(\text{Ag}_N) - E(M_N)],$$

where $E(\text{Ag}_{N-1}M)$, $E(\text{Ag}_N)$, and $E(M_N)$ are the total en-

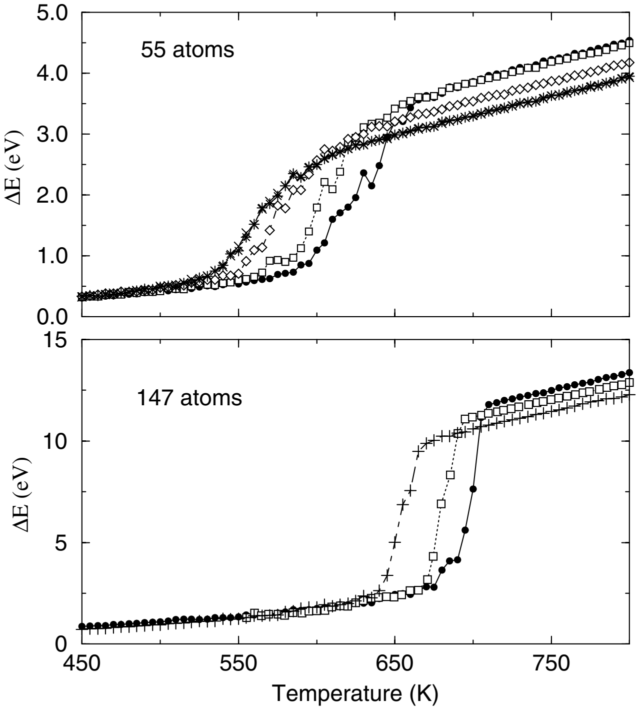

FIG. 2. Caloric curves. The quantity plotted is $\delta E = E(T) - E(O) - 3(N-1)k_BT$, where $E(T)$ is the total cluster energy, $E(0)$ is the minimum energy at 0 K, and $3(N-1)k_BT$ is the harmonic part of the energy. In the upper panel, size 55 is considered and all systems are shown. In the lower panel, size 147 is considered and only pure Ag, Ag-Cu, and Ag-Ni are shown. Crosses (+) refer to pure Ag, solid circles (●) to Ag-Ni, squares (□) to Ag-Cu, diamonds (◇) to Ag-Pd, and asterisks (*) to Ag-Au.

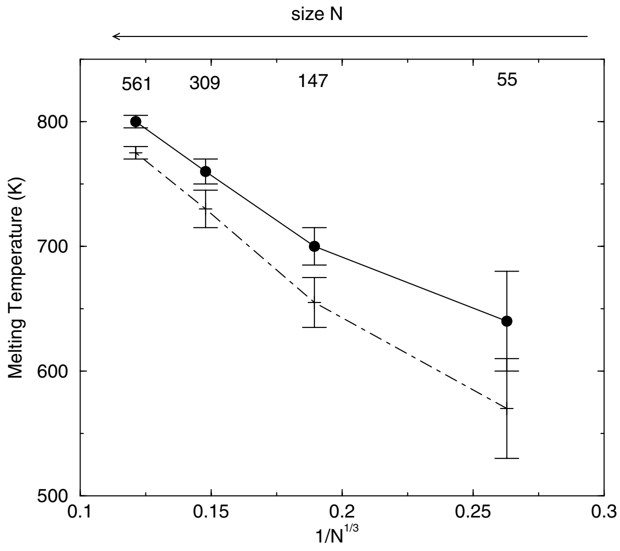

FIG. 3. Melting temperatures and melting ranges for pure Ag clusters (crosses) and clusters with Ni impurity (dots). The error bars indicate the amplitudes of the melting ranges, and the symbols its center. A linear behavior of the melting temperature with $N^{-1/3}$ (namely, with the inverse cluster radius) is found, in qualitative agreement with Pawlow's law.

ergies of mixed and pure clusters, with $M$ representing the element of the impurity. The values of the atomic stress on the central site $\sigma_{\rm core}$ and of $\Delta E_{\rm imp}$ are reported in Fig. 4. It appears clearly that $\sigma_{\rm core}$ is well correlated with the misfit: the larger the misfit, the smaller the core stress. Putting a small atom (Ni or Cu) at the central site of the Ag icosahedron considerably decreases its core stress. On the contrary, central Au or Pd atoms slightly increase the stress. Let us now consider solution energies. As a first indication, the negative sign in each case means that it is favorable to substitute the central silver atom by a different one, even in the case of immiscible systems as Ag-Cu and Ag-Ni. This negative solution energy for Cu and Ni impurities represents the energetic gain due to the strain release by substituting the central atom by a smaller one, and it is specific to the icosahedral structure. Indeed, in fcc cluster structures, we recover a positive solution energy for Ni and Cu, as happens in the bulk phase. Both the atomic stress and the solution energy indicate that Ni is the most effective impurity, which is well correlated with the fact that the Ni impurity causes the largest upward shift in the melting temperature. Cu is the second most effective impurity, and Au (with almost no misfit) the least effective. Pd is in between: its solution energy in cluster is better than the one in the bulk, but (as Au) it causes a slight increase of the atomic stress in the central site. A note about Pd and Au impurities is necessary: For these atoms, the best sites are not the central ones, but those of the intermediate icosahedral shells. However, these intermediate sites are close in energy with the central site. As can be seen in Fig. 1, when a melting simulation for $\rm Ag_{54}Pd_1$ is started with Pd in the central site, the Pd atom migrates to the intermediate shell before the cluster melts. In this case, the intermediate site is lower in energy than the central site by 0.05 eV.

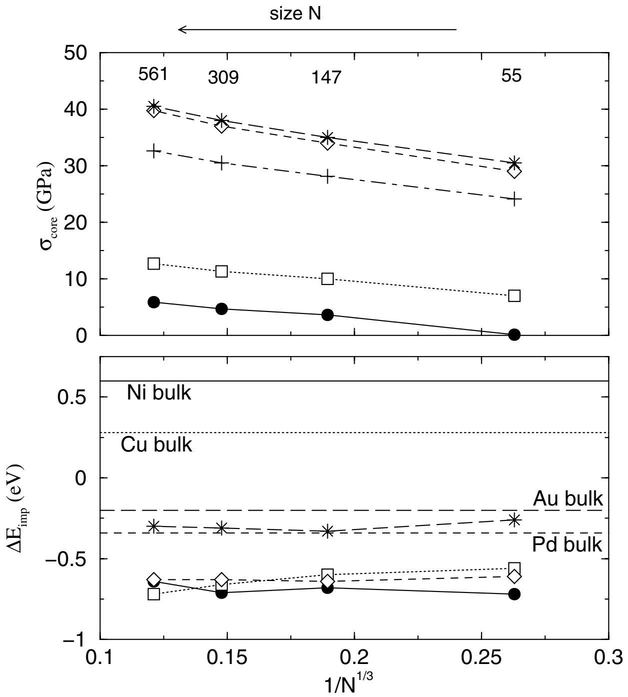

FIG. 4. Atomic stress on the central site $\sigma_{\rm core}$ and impurity solution energy $\Delta E_{\rm imp}$ for icosahedral clusters of different sizes. Symbols are the same as in Fig. 2. The impurity solution energy in bulk phases [34] is reported.

The different behavior of icosahedral $\rm Na_{54}Li_1$ [12,29] with respect to $\rm Ag_{54}Ni_1$ and $\rm Ag_{54}Cu_1$ may be due to the fact that silver is much more stiff than sodium [30]. Sodium accommodates icosahedral strain much better, in agreement with experimental observations of icosahedrons of very large sizes [31]. Therefore, strain relaxation due to a small central impurity should be much less relevant in sodium than in silver, so that the factors causing the upward shift of the melting temperature could be overcome by other effects.

From a thermodynamic point of view, as shown recently in experiments on sodium clusters [8], high cluster melting temperatures arise by a subtle combination of energetic and entropic effects. Usually, one may expect that a cluster melts at higher temperatures if its global minimum is well separated in energy from its higher isomers. This is an important factor, but it is not the only one, since the statistical weight of higher isomers may be crucially influenced by entropic factors. This is what happens when comparing, for example, $\rm Ag_{55}$ with $\rm Ag_{54}Ni_1$. In $\rm Ag_{55}$, the second isomer is separated from the global minimum by 0.52 eV. In this second isomer, one of the vertex atoms of the icosahedron is placed on the cluster surface, leaving a vacancy at the vertex. However, this second isomer does not have a leading role in the melting process. In fact, there is another isomer (separated from the global minimum by 0.58 eV) of the *rosette* type [32], which is much more likely to be observed during simulations. In the rosette isomer (see Fig. 1), a vertex atom is pushed inside the surface to form a hexagonal ring around the vertex (see [32]). This rosette minimum has a very high entropy (namely, soft vibrational modes on average), much higher than the global minimum and the second isomer, as we have verified by means of harmonic thermodynamics calculations [33]. In $Ag_{54}Ni_1$, the second isomer is the one with the Ni impurity in the second shell (see Fig. 1) and is separated from the global minimum by 0.51 eV. However, this second isomer has a low entropy, so that it is not likely to be found in comparison with the global minimum, and it does not play a relevant role in the melting transition. The minima which play a role in initiating the melting process are those related to the disordering of the surface, in analogy with $Ag_{55}$. These minima, in the $Ag_{54}Ni_1$ case, are separated from the global minimum by at least 0.57 eV and are not of the rosette type but display a missing vertex with pentagonal symmetry, plus an adatom on the surface. Therefore, they do not present an especially favorable entropy. Rosette structures do not play any role in the melting process of doped clusters, and there is an indication that they are not even local minima (as happens for nonstiff pure metal clusters, as pure Cu [32]).

The combination of thermodynamics and stress relief arguments leads to the conclusion that the small central impurity, by releasing the core stress as detailed before, allows the cluster surface to better contract (without surface disordering as it is the case in rosette-type structures), thus becoming more stable against disordering. Indeed, the surface stress in the $Ag_{54}Ni_1$ is reduced by 14% as compared to $Ag_{55}$ and by 10% in $Ag_{54}Cu_1$, which is a direct consequence of the central site stress relief since the global stress of the free particle is zero and intermediate shell stress varies only by 3%. Comparing Cu and Ni impurities, we note that they have almost the same size mismatch with Ag (driving to almost same surface stress); however, a Ni impurity is clearly more effective than a Cu one. This is due also to the fact that Ni is more cohesive than Cu (with a higher melting point), and its interaction with Ag is stronger, so that clusters with Ni impurity are better stabilized than those with Cu impurities.

In conclusion, we have shown that a single impurity can considerably shift the melting temperature of icosahedral silver clusters of several tens or hundreds of atoms. A small central impurity causes a better relaxation of the strained icosahedral structure, which becomes more stable against thermal disordering. Our results thus show the possibility of tuning the melting temperature of clusters by selective doping.

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