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Generalizing segregation and chemical ordering in bimetallic nanoclusters through atomistic view points

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We predict general trends for surface segregation in binary metal clusters based on the difference between the atomic properties of the constituent elements. The energetically most favorable site for a guest atom on a pure metal cluster is determined considering the attractive and repulsive contributions of the cohesive energy of an atom in the cluster. It is predicted that for adjacent elements in a period of the periodic table, the bimetallic system would be more stable if the component with smallest valence electron density is placed on the surface. On the other hand, in bimetallic clusters built with elements of only one group, the trend to be in the volume (of the atomic component with smaller core density) will be higher for that cluster with atomic components most separated in the group. Such chemical ordering trends in the lowest energy configurations of Pt-Au, Pt-Pd, and Pt-Ni binary alloy clusters are verified for their 561 atom systems through a simulated annealing process. Some of our atomistic predictions are verified through quantum mechanical calculations.

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Surface segregation mechanism in nanoalloy clusters is of great importance for controlling their morphology, composition, and catalytic activities. Though current understanding of this phenomenon based on some theoretical calculations[1–10] and discrete experimental observations[11–14] highlights the general trend of this process in some particular systems, there exist no generalized convention and physical explanation to suit for all the binary systems until now.

Understanding of surface segregation in alloy systems based on the properties of component elements and composition has been addressed in the pioneer works of Friedel.[1] For bulk alloys, several groups[2–6] at different theory levels have confirmed the otherwise intuitively general physical trend that surface segregation energy in a transition metal (TM) alloy is given by the difference in the surface energies of the pure alloy components.[7] The present understanding of this phenomenon is based on empirical and thermodynamic models, although there have been attempts to predict both the surface alloy extent[2,3] and crystalline structure of an alloy from quantum mechanical perspectives.[8]

Motivated by practical applications in heterogeneous catalysis, surface segregation process has also been addressed in metallic nanoparticles (NPs). Baletto *et al.*[10] explored the idea of atomic size mismatch between the components to shed light on the core-shell structure formation of different TM alloys, where the size mismatch between the atoms is one of the driving forces for the formation of such structures. On the other hand, Bozzolo *et al.*[7] adapted a simple semiempirical method based on the concept that energy of formation of a given atomic configuration is the sum of strain and chemical energies of the individual atoms in the cluster, to calculate the heat of formation of binary alloys. However, though these criteria highlight the general trends of surface segregation, they do not give any physical explanation of the phenomenon.

In general, the cohesive energy of an atom in a cluster is the sum of the energies corresponding to its attractive and repulsive interactions with the other atoms of the system: $U_{\mathrm{coh}}=U_{\mathrm{atr}}+U_{\mathrm{rep}}$.[15] Also, the interaction of an atom with the others of the system is mainly determined by its nearest neighbors. Thus, the magnitudes (absolute values) of the changes ΔU_{atr} and ΔU_{rep} at a site of a pure cluster induced by the replacement of the original atom at that site with a guest one (guest-replacement), fundamentally depend on the coordination number of the site. The magnitudes of both the changes reach their minima when the guest-replacement is done at a cluster surface and maxima when the replacement site is inside the cluster. Because the values of U_{atr} and U_{rep} are negative and positive, respectively, the most energetically favored site for the guest-replacement process is the replacement site in which both ΔU_{atr} and ΔU_{rep} reach their minimum values.

Now, the cohesive energy can be changed only by three ways: (i) only one of its contributions changes, (ii) both of them increase or decrease, and (iii) one contribution increases and the other decreases. According to the above described relation between these energy changes and the coordination number, in the cases (i) and (ii), the best replacement site for the change of one contribution is also the best for the change of the other. On the contrary, for the situation (iii), the change in attractive contribution reaches its minimum value at the same site at which the repulsive one reaches its maximum. The best site for the change in one contribution is the worst for the change in the other. Therefore, while the most energetically favored replacement site by the guest-host replacement process can be *a priori* determined in cases (i) and (ii), it is not possible in the case (iii) and the changes in the cohesive energy contributions must be calculated.

In addition, the differences between the properties of the guest atom and those of the host atoms define the values of ΔU_{atr} and ΔU_{rep} at the replacement site. In a first approximation, the core and the valence electron charge densities of the atoms determine the extent of their repulsive and attractive interactions, respectively. If we assume that the electron charge transfer between the atoms inside the cluster is practically negligible, the extent of the energy changes induced at a given site can be *a priori* determined only from the core and valence electron densities of the neutral host and guest atoms. Besides, if the stress energy induced by the replacement is also negligible, the cohesive energy change provides just the cohesive energy of the host-guest system respect to the host system. Independently, each of the two electron charge densities of the guest atom can be less, equal or higher than the corresponding one of the host atom. When the guest and the host atoms have adjacent locations in a row on the periodic table, their core electron charge densities are similar, thus $\Delta U_{\mathrm{rep}} \approx 0$, and due to the difference between their valence charge densities, $\Delta U_{\mathrm{atr}} \neq 0$. Thus, this situation belongs to case (i). The more energetically favored site for the guest-replacement will be a surface site if the valence electron density of the guest atom is lower, and it will be a core site if the valence electron density is the higher. On the contrary, if the guest and the host atoms are far enough away in a column on the periodic table, the difference between their core electron charge densities will be more important than the difference between their valence electron charge densities, i.e., $|\Delta U_{\mathrm{rep}}| > |\Delta U_{\mathrm{atr}}|$. Then, in this special situation of case (iii), the more energetically favored site for the replacement will be a surface site if the core electron density of the guest atom is the higher one, and will be a volume site if it is the smaller one. The analysis assumes that the interaction between the cluster and its surrounding is weaker than the interaction between the cluster atoms.

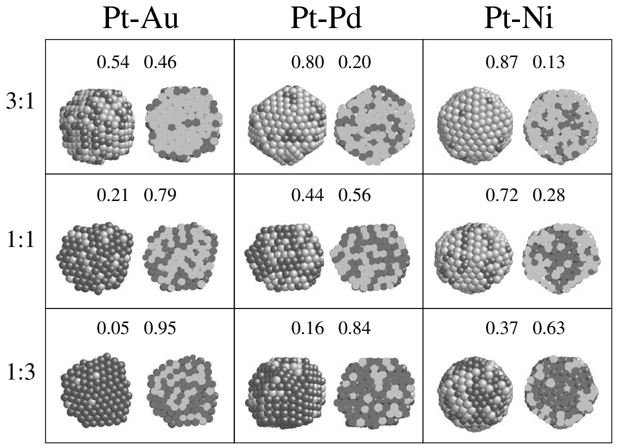

FIG. 1. Candidates for the lowest energy structures of each binary system (columns), at the 3:1, 1:1, and 1:3 global compositions (rows). The superficial and cross sectional views of a particular cluster are shown in each block. Lighter spheres represent platinum atoms. The values presented in each block are the superficial compositions of the clusters.

Therefore, with respect to the relative location of the component atoms in the periodic table, there are two situations at which the more stable chemical ordering in a binary metal cluster alloy can be *a priori* determined. When they have adjacent locations in a period, the component with smaller valence electron density will be on the surface. On the other hand, in bimetallic clusters built with elements of only one group, the trend to be in the volume (of the atomic component with smaller core density) will be higher for that cluster with atomic components most separated in the group. While the first prediction refers to only one cluster, the second concerns to all the bimetallic clusters built with a set of elements of a column. Both predictions constitute a useful rule to determine the most stable chemical ordering in bimetallic clusters. As immediate consequence of these results, stable Pt-Au clusters have Au enriched surfaces, and the tendency of the Ni atoms to be located in the core is higher in the Pt-Ni alloy than for Pd atoms in the Pt-Pd alloy. In order to support these predicted results, the chemical ordering in Pt-Au, Pt-Pd and Pt-Ni alloy clusters of 561 atoms are investigated. The atomic interaction in the alloy nanoclusters is modeled by the many body Rafii-Tabar and Sutton potential that is based on the second moment approximation of a tight binding Hamiltonian.[16] The simulated annealing method was implemented with constant energy molecular dynamics (MD) simulations using the model potential.[17] The used time steps of 2, 3, and 4 fs for the Pt-Ni, Pt-Pd, and Pt-Au clusters, respectively, provided total energy conservation within $\pm 0.002\%$ for trajectories of 1×10^6 steps. From a icosahedral geometry, the clusters were heated to their liquidlike states. The final temperature of each of the clusters was so high that the cluster loses its initial structure. For cooling, the final liquidlike state was simulated by a dynamic trajectory of 20×10^6 steps. Five microstates were selected arbitrarily from this trajectory (extracting each every 4×10^6 steps). From these microstates, the liquidlike cluster was cooled down to room temperature ($\sim$300 K) in 20×10^6 steps; which corresponds to an average cooling rate of $\sim$20 K/ns. The final configurations were the candidates for global minimum (see Fig. 1). Although various morphologies were found like icosahedral, Mark's decahedral and cuboctahedral species distributions are practically the same for the five homotops. For a uniform species distribution, the surface and global (the system as a whole) compositions should be the same. Thus, according to our atomistic prediction, the values of the superficial composition for Au in Pt-Au must be greater than the global composition value. In addition, the superficial concentration of Ni in Pt-Ni must be less than that of Pd in Pt-Pd. The superficial composition values of Au, Pd and Ni for the most stable structures of Pt-Au, Pt-Pd, and Pt-Ni alloy nanoclusters were found to confirm the predicted results. For the Pt-Au clusters, the values of the superficial composition of Au: 0.46, 0.79, and 0.95, are greater than their corresponding global concentration values: 0.25, 0.50, and 0.75 (see the values in the Fig. 1). In addition, for the Pt-Ni system the superficial composition values of Ni: 0.13, 0.28, and 0.63, are less than the ones corresponding to Pd in Pt-Pd system: 0.20, 0.56, and 0.84 (see the values in the second and third columns of Fig. 1). Thus, the theoretical predictions are completely supported by the model potential used to describe these three nanoalloy systems. However, the final proof of our predictions comes from the reported experimental results. Recently, using several experimental techniques, Yang *et al.*[14] have shown that Pt-Au nanoparticles with core-shell structure can be obtained only when nanoparticles of Pt are used as seeds. On the contrary, only monometallic nanoparticles of each constituent metal are produced

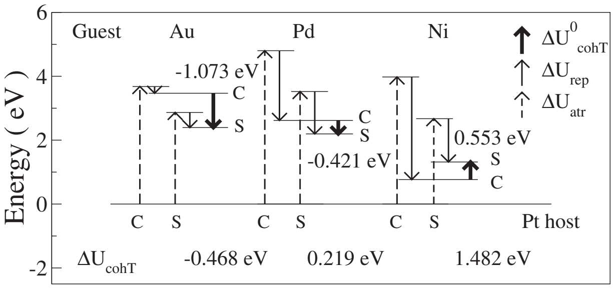

FIG. 2. Energy changes at a site of a Pt cluster, induced by the replacement of its original atom with a guest one. The changes are calculated at the center (C) and a surface (S) site. The horizontal line represents the original energy of the site, the dashed arrow corresponds to ΔU_{atr} and the following continuous arrow to ΔU_{rep}. The term $\Delta U^0_{\mathrm{coh}T}$ (see the text) is represented by the bold arrow. Note that the sign of this term is the same as that of $\Delta U_{\mathrm{coh}T}$ (see the text) for Pt-Au and Pt-Ni.

when the synthesis order is reversed using Au nanoparticles as seeds.[14] Though there are experimental evidences of existing stable Pt-Pd clusters with Pd enriched surfaces[12] and also the stable Pt-Ni alloys with Pt enriched extended surface,[13] the nanostructures were grown through low temperature synthesis processes, where a complete thermodynamic equilibrium is not achieved.

A quantitative description of the analysis presented here can be given through the energy changes shown in the Fig. 2. The change $\Delta U_{\mathrm{coh}T}$ represents the difference in cohesive energy of the surface homotop (with a guest atom at the surface) of an icosahedral Pt cluster with respect to its central homotop (with the guest atom at the volume). According to the sign of $\Delta U_{\mathrm{coh}T}$, the most stable homotop is the central one for Pd and Ni guest atoms, and the surface one for Au. This is why the superficial compositions of Pd and Ni atoms are less than 0.25, and that of the Au is higher than 0.25 for the Pt-Pd, Pt-Ni, and Pt-Au nanoclusters with global atomic compositions 3:1, respectively (see the values presented in the first row of Fig. 1). The expression of $\Delta U_{\mathrm{coh}T}$ as the sum of the cohesive energy changes at all the sites of the cluster; the replacement sites, the nearest sites to the replacement sites and so on, can be used to determine the sign of $\Delta U_{\mathrm{coh}T}$.[17] The first term of this sum is given by $\Delta U^0_{\mathrm{coh}T} = \Delta U_{\mathrm{coh}}(S) - \Delta U_{\mathrm{coh}}(C)$, where $\Delta U_{\mathrm{coh}}(i)$ is the change in the cohesive energy induced at the replacement site i through the guest-replacement; S and C denote the surface site and the center site, respectively.

The approximation $\Delta U_{\mathrm{coh}T} \approx \Delta U^0_{\mathrm{coh}T}$ is enough to obtain the sign of $\Delta U_{\mathrm{coh}T}$ for Au and Ni, but for Pd it is insufficient (compare the values of $\Delta U_{\mathrm{coh}T}$ at the bottom of the Fig. 2 with those of $\Delta U^0_{\mathrm{coh}T}$ at the top). Thus, for this guest, the next term must be added. The calculated changes in the repulsive and attractive energy contributions as well as the term $\Delta U^0_{\mathrm{coh}}$ are represented in the Fig. 2, by the continuous, dashed, and bold arrows, respectively. The Fig. 3 shows the same quantities described in the Fig. 2, but now for three pure icosahedral hosts of 561 Au, Pd, or Ni atoms with a single Pt guest atom. This figure shows that Pt is more stable at the center of the Au and at surface of the Ni hosts. The fact that $\Delta U_{\mathrm{coh}T} \sim 0$ for Pd means that the changes $\Delta U_{\mathrm{atr}T}$ and $\Delta U_{\mathrm{rep}T}$ almost cancel each other for this situation of case (iii). Thus, for the most stable chemical ordering of Pt-Pd nanoclusters, the species distribution will be nearly homogeneous and the surface and global compositions must be similar (note that the superficial composition values of the column Pt-Pd in the Fig. 1 are close to the global composition values). We had tested these predictions in $\mathrm{Pt}_{54}\mathrm{Au}_1$ and $\mathrm{Pt}_{54}\mathrm{Ni}_1$ by density functional theory (DFT) calculations. Three homotops (those with the guest atom at the center, at the corner, and on one edge) of these host-guest systems were optimized using the VASP package.[17] The DFT calculations were performed at the local density approximation (LDA) level using the projector-augmented wave method (PAW).[17] According to the DFT binding energies values shown in Table I, The maximum binding is reached when the Au and Ni atoms are on the surface and inside the volume of the, respectively, $\mathrm{Pt}_{54}\mathrm{Au}_1$ and $\mathrm{Pt}_{54}\mathrm{Ni}_1$ clusters; just as is predicted by our atomistic considerations.

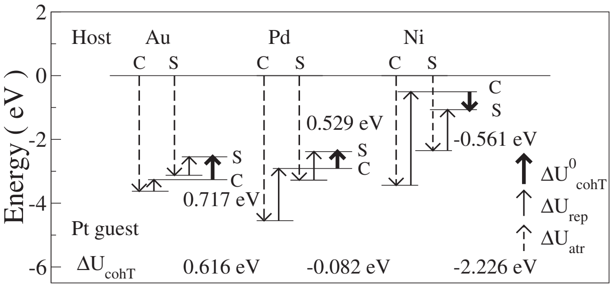

FIG. 3. Energy changes at a site of a pure Au, Pd, and Pt cluster induced by the replacement of its original atom with a Pt guest atom. The same quantities as in Fig. 3, but now for three pure icosahedral hosts of 561 Au, Pd, or Ni atoms and a Pt guest atom. Again the sign of $\Delta U^0_{\mathrm{coh}T}$ is the same of $\Delta U_{\mathrm{coh}T}$ for Pt-Au and Pt-Ni.

The deduced rule to determine *a priori* the most stable chemical ordering is additionally supported by reported studies of many bimetallic systems. Its first part is confirmed for binary systems in 4th (Ti-V, V-Cr, Fe-Co, Co-Ni, and Ni-Cu), 5th (Zr-Nb, Nb-Mo, Ru-Rh, Rh-Pd, and Pd-Ag), and 6th (Hf-Ta, Ta-W, Os-Ir, Ir-Pt, and Pt-Au) periods by the data of Ruban *et al.*[3] For instance, they found strong segregation of Ti in a V host; just as is predicted the Ti tends to be on the surface of a Ti-V system (the valence density of Ti atom is lower than that of the V atom). Its second part is confirmed for alloys in 4, 5, 6, 7, 9, 10, and 11 groups also by this data.

TABLE I. DFT binding energies of three homotops of $\mathrm{Pt}_{54}\mathrm{Au}_1$ and $\mathrm{Pt}_{54}\mathrm{Ni}_1$ icosahedral clusters. $\mathrm{Pt}_{54}\mathrm{Au}_1$ is most stable when the Au guest atom is on its surface. On the contrary, $\mathrm{Pt}_{54}\mathrm{Ni}_1$ is most stable when the Ni guest atom is inside its volume.

	Binding energies (eV)	
Guest site	$\mathrm{Pt}_{54}\mathrm{Au}_1$	$\mathrm{Pt}_{54}\mathrm{Ni}_1$
Center	−273.15139	−278.04946
Corner	−273.76343	−275.91019
Edge	−273.94529	−275.78156

For example, for the alloys in the 11 group it is found no segregation of Ag in a Au host and strong antisegregation of Cu in a Au host; just as is predicted by the rule the tendency to be located in the volume of a Au host is bigger for Cu atoms than for Ag atoms. On the other hand, Aguado and López[18] confirm the rule for bimetallics in the first group. By means of DFT molecular dynamics calculations they found a complete segregation of Cs in a $Na_{13}Cs_{42}$ cluster, and a partial segregation of Na in a $Li_{13}Na_{42}$ cluster. As is predicted by the rule, the tendency of Na atoms to be located inside the Cs-Na cluster is bigger than the tendency of Li atoms to be located within the Na-Li cluster. We confirmed ourselves the rule for the alloys in the second group and for the Na-Mg system.[17]

In summary, two predictions were presented in this Rapid Communication. One refers to any binary system whose atomic components have adjacent locations on a period of the periodic table. The other concerns binary systems whose atomic components are elements of only one group of the periodic table. Both predictions were supported by reported results and by our own MD and DFT calculations.

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[17] See EPAPS Document No. E-PRBMDO-80-R29940 for the details of the constant energy molecular dynamics simulations for optimizing Pt-Au, Pt-Pd, and Pt-Ni clusters. The document also presents an approximation for the cohesive energy difference between the surface and central homotop, and a description of the DFT binding energies calculations for the host-guest systems Pt-Au, Pt-Ni, Mg-Ca, Mg-Ba, and Na-Mg which support our general predictions. For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html.

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