Computational Characterization of the Intermixing of Iron Triade (Fe, Co, and Ni) Surfaces and Sub-nanometric Clusters with Atomic Gold

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ABSTRACT: Dispersion-corrected density functional theory (DFT-D3) is applied to model iron triade (Fe, Co, and Ni) surfaces upon exchange of surface atoms with atomic gold. One first goal is to analyze the contact problem at the triade surface−Au interface and to correlate our findings with recent observations on iron triade nanoparticles (with diameters of around 5 nm) passivated by a few layers of gold. For this purpose, we analyze: (1) the energies of substitution; (2) the restructuring of the iron triade surfaces upon the atomic exchange; (3) the density of the orbitals bearing the largest projection on d(Au) atomic orbitals and, particularly, their overlap with orbitals from neighboring atoms of the triade surfaces; (4) the modification of the electronic density of states; and (5) the redistribution of the electronic density upon intermixing of Au and triade atoms. Inspite of the similarities between Ni, Co, and Fe in the condensed phase, significant differences are found in the features characterizing the exchange process. In particular, we find a better integration of the Au atom on the substitutional site of the Ni(001) surface than on those of the Fe(001) and Co(001) surfaces. This is in agreement with the fact that the electronic density of states is almost indistinguishable before and after Ni−Au intermixing. This outcome is correlated with the experimental observation on the allowing transition of Ni−Au core−shell nanoparticles before reaching the melting temperature. Our second objective is to explore the Au−triade atom intermixing process in sub-nanometric clusters, finding that it is energetically more favored than at solid surfaces yet endothermic at 0 K. This feature is explained as the result of the structural fluxionality characterizing clusters at the sub-nanometer scale. Entropy contributions make mixed Au−Ni clusters more stable than the unmixed counterpart already at 650 K while unmixed Co clusters remain energetically more favored up to 1295 K and iron clusters are predicted to be stable against intermixing over the experimentally relevant range of temperatures (up to 1100 °C). Remarkably, the net charge donated from the three triade atoms to atomic gold upon intermixing is similar in triade sub-nanometric clusters and at extended triade surfaces. Gold clusters are prone to host Fe, Co, and Ni atoms at the center of their structures and the exchange process is predicted to be exothermic at 0 K even for a small cluster made of 13 atoms. More generally, our work highlights the importance of the polarity of the chemical bond between unlike metal atoms in alloys.

1. INTRODUCTION

Nanostructured bimetallic core–shell systems are being intensively studied due to both their unexpected physical behavior and wide range of applications in biomedicine1−5 as well as in optics,6−9 heterogeneous catalysis,9−12 electrochemistry,13 and electronics.13,14 For instance, it is known that the catalytic and photocatalytic properties of gold nanoparticles can be tuned with the insertion of a magnetic core made of Ni atoms.15 Remarkably, external fields have been successfully applied on magnetic nanoparticles for diagnosis, isolation, and photothermal destruction of cancer cells.8

Modern methods for the controlled synthesis of mixed-metallic nanoparticles with a core–shell structure include the employment of superfluid helium nanodroplets. The droplets...
not only provide an ultracold, very clean, solvent-free, and inert environment for their successful synthesis at the sub-10 nm scale\textsuperscript{16} (see, e.g., ref 17 for a comprehensive review) but also for their soft-landing deposition on any substrate in an ultrahigh vacuum environment.\textsuperscript{18–23} The droplets are sequentially doped when passing through two pickup cells, first with the atoms forming the core and then with those creating the shell, which allows us to build the desired onion-type structures. Next, the doped droplets are soft-landed on a heated transmission electron microscopy (TEM) grid,\textsuperscript{24} with the helium droplet absorbing the collision energy and evaporating (see, e.g., ref 23 for details).

Previous works using the helium droplet-mediated synthesis and soft-deposition technique have shown how bimetallic clusters (with diameters of around 5 nm) made of iron triade (Fe, Co, and Ni) cores protected by gold shells experience thermal-induced restructuring.\textsuperscript{24,25} Although the core atoms have similar interaction energies and bond lengths in the condensed phase, their thermodynamical behavior differs significantly. Clusters with a centralized core experience a transition toward an energetically more stable configuration at temperatures around 400 °C. Upon heating, atomic mobility is enhanced, and Co–Au clusters suffer a modification from a centralized core–shell configuration to a decentralized structure. The Fe–Au clusters also undergo a transition toward a decentralized configuration when the temperature increases, but in this case, the core is fragmented into several iron pieces which remain below the protective layer of gold. Finally, Ni–Au core–shell nanoparticles exhibit an alloying transition before reaching the melting temperature.

The experimental observations were explained using the embedded atom model (EAM) method on mixed and unmixed configurations along with an approach delivering their Helmholtz free energies as a function of temperature.\textsuperscript{24} The adequacy of the EAM method was supported by density functional theory (DFT) calculations on vacancy formation energies using slab models composed by 256 atoms. The correlation of the free energies with the configurational entropy nicely explained the experimentally observed (thermal-induced) phase transitions on the core–shell nanoparticles.

In this work, we analyze the impact of atomic exchange with gold on iron triade surfaces and sub-nanometric clusters. We are first aimed at a better understanding into the reasons for the different structural rearrangements of core–shell nanoparticles depending on the nature of the triade atom. For this purpose, supercell slab models composed of 500 atoms of one of the triade metals, with one of the triade atoms replaced by Au, have been created in a first step. Next, the exchange of one triade atom with atomic gold has been examined in the iron triade surfaces by applying dispersion-corrected DFT. This way, the propensity of iron triade (Fe, Co, and Ni) surface atoms to intermix with atomic gold has been evaluated. Besides delivering vacancy formation and energies of substitution,\textsuperscript{24} the application of DFT has allowed us to analyze the redistribution of electronic density upon intermixing, the variation of the electronic density of states upon the atomic substitution, as well as the most relevant orbitals at the interface between the triade surfaces and atomic gold. More generally, we have been aimed to analyze the polarity of the chemical bond between unlike (Au and triade) metal atoms at extended surfaces and in sub-nanometric clusters.

The same atomic intermixing process is analyzed in sub-nanometric clusters made of iron triade (Fe, Co, and Ni) and gold atoms. On the one hand, solid triade surfaces and sub-nanometer clusters represent two extreme cases when modeling nanoparticles of 5 nm size. On the other hand, sub-nanometric metal clusters have recently emerged as a new generation of quantum materials with exceptional properties. For instance, it has been recently demonstrated that the smallest metal clusters are highly stable\textsuperscript{26–30} and possess special chemical and physical properties, making them innovative materials for numerous applications in, for example, energy conversion, catalysis,\textsuperscript{31–35} and photocatalysis.\textsuperscript{36,37} For instance, it has been shown that the deposition of Cu\textsubscript{5} and Ag\textsubscript{5} clusters onto TiO\textsubscript{2} surfaces can be useful for the creation of novel visible-light photoactive materials,\textsuperscript{36,37} potential photocatalysts for CO\textsubscript{2} reduction and elimination from the atmosphere,\textsuperscript{38} and two-dimensional (2D) polaronic materials.\textsuperscript{39,40}

The properties of sub-nanometric clusters, more generally atomically precise clusters,\textsuperscript{41} are determined by an interplay between their shape, size, and composition and, in particular, much effort is being dedicated to the synthesis of bimetallic clusters in the quest of bifunctional catalysts. Very recently, a new technique to dope small thiolate protected gold clusters has been experimentally probed by exchanging the gold atoms with surface silver, copper, and cadmium atoms.\textsuperscript{42} Moreover, it has been shown both experimentally and theoretically how small thiolate-protected silver and gold clusters undergo spontaneous exchange of metal atoms in solution under ambient conditions.\textsuperscript{43} In this work, in order to evaluate the likelihood of triade sub-nanometric clusters to intermix with atomic gold as a function of temperature, the restructuring of the pure cluster upon the atomic exchange, the corresponding charge transfer, and the Gibbs free energies are analyzed. Our findings are linked to the thermal-induced restructuring of core–shell nanoparticles as well.\textsuperscript{24}

The article is structured as follows. A discussion of the results is provided in Section 3 for the iron triade surfaces, including test calculations on the formation of vacancies, a detailed description of the exchange of one triade surface atom with atomic gold, and the exploration of the same substitution reaction in small clusters composed of a few Fe, Co, Ni, and Au atoms. Our findings are summarized in Section 3. Finally, in Section 2, we provide a detailed description of the computational methods.

2. RESULTS AND DISCUSSION

2.1. Vacancy Formation Energies. The formation of surface and inner vacancies is a key factor to be considered for evaluating the likelihood for core–shell exchange of atoms on nanoparticles.\textsuperscript{24} We have considered surface, inner, and bulk vacancies (see Figure 1). The vacancy formation energies are presented in Table 1 along with those reported in ref 24 using 4 × 4 × 4 (10 × 10 × 10) supercell models in DFT (EAM) calculations. Theoretical and experimental values of cohesive energies are also shown. It can be observed that the bulk vacancy formation energies ($E_V$) using 5 × 5 × 5 and 4 × 4 × 4 supercell models are similar (to within 0.2 eV) with the exception of bulk cobalt for which the enlargement of the unit cell size causes a significant reduction of the $E_V$ value (by 25%), making it closer to the EAM-based value. As a result, the ranking of bulk vacancy formation energies is also modified and, particularly, iron (i.e., instead of cobalt) holds the largest
The surface vacancy formation energies differ very little (0.16 eV). It can be seen from Table 2, when the structures are optimized, lower kinetic energy cutoff and SW values have been considered to calculate the energies of substitution in the case of the Ni(001) surface. The charge acquired by the Au atom is also indicated (referred to as “Bader”) as well as the difference between the mean X–Au distance (X = Fe, Co, and Ni) and the X–X distance in the bare triade surface (referred to as “d–d”, see the “Methods section” for the definition). The geometries of all atoms have been relaxed. The geometries of all atoms have been fixed.

Table 2. Exchange Energies (Eexch) for Fe(001), Co(001), and Ni(001) Surfaces (See eq 2)\(^a\)

| atom | E_{sub}–SW (eV) | E_{exch} | Bader | d–d (Å) |
|------|----------------|----------|-------|---------|
| Ni   | 270–0.42       | 1.43\(^b\) | −0.41 | 0.16    |
| Ni   | 370–0.42       | 1.46\(^b\) | −0.44 | 0.17    |
| Ni   | 400–0.20       | 1.64\(^c\) | −0.46 | 0.17    |
| Ni   | 700–0.20       | 1.64\(^c\) | −0.46 | 0.17    |
| Ni   | 800–0.20       | 1.64\(^c\) | −0.46 | 0.17    |
| Fe   | 700–0.20       | 1.29\(^c\) | −0.73 | 0.17    |
| Co   | 700–0.20       | 1.70\(^c\) | −0.48 | 0.31    |

\(^a\)Different kinetic energy cutoff (E_{cut}) and the SW values have been considered. E_{exch} was calculated using a 500-atom unit cell model and the same DFT-D3 ansatz. Therefore, our test calculations using a 500-atom unit cell allow us to confirm previous findings using a smaller (256-atom) unit cell.\(^b\)In particular, note that the cobalt surface is the most reluctant to lose one of its atoms while the gold surface is the most prone to host a vacancy. Likewise,\(^c\) among the triade elements (Fe, Co, and Ni), Fe has the lowest energy for vacancy formation in the surface (top layer) and the largest energy for vacancy formation in the bulk. For the sake of accuracy, the 500-atom unit cell model has been used in the calculations of energies of substitution presented below.

2.2. Iron Triade Surfaces upon Exchange with Atomic Gold. As described in the Methods section, iron triade (Fe, Co, and Ni) surfaces [(001) facet] upon exchange with atomic gold have been modeled with 500-atom unit cells. First, we have analyzed the influence of the values for the kinetic energy cutoff and SW parameters for the Ni(001) surface. As can be seen from Table 2, when the structures are optimized, lower kinetic energy cutoff and larger SW values result in smaller exchange energies. If the SW value is fixed to a stringent value of 0.2 eV, there is no further increase in the energy of substitution upon augmenting the kinetic energy cutoff from 400 to 800 eV.

Based on these test calculations, the geometries of all atoms of the three triade surfaces (before and after intermixing with atomic gold) were optimized in a first step using kinetic energy cutoff and SW values of 270 and 0.42 eV, respectively. The resulting optimized geometries were kept fixed in follow-up calculations using kinetic energy cutoff and SW values of 700 and 0.2 eV instead. We also mention that the energies of substitution calculated with the 256-atom unit cell model differed by less than 0.05 eV from those obtained with the 500-atom unit cell.

2.2.1. Fe(001) Surface. First, we have analyzed the restructuring of the Fe(001) surface when one surface atom is exchanged by atomic gold. Panel a of Figure 2 shows that due to its relatively large atomic radius, the Au atom does not perfectly fit in the position of the hole left after removing one surface Fe atom: its location is therefore slightly shifted upward along the z direction compared with the original position of the exchanged Fe atom. The electronic density of the orbitals with the maximum projection onto atomic 5d(Au) orbitals

Figure 1. Considered surface vacancy positions. (a) Inner vacancy position. (b) Surface vacancy position.

Table 1. Cohesive (E_{c}) and Vacancy Formation Energies (E_{fi}) Using the DFT-D3 Scheme\(^a\)

| E_{c} (eV/atom) | Fe | Co | Ni | Au |
|-----------------|----|----|----|----|
| bulk 5 × 5 × 5  | 4.75 | 5.12 | 4.28 | 3.68 |
| Experiment      | 4.28 | 4.39 | 4.44 | 3.78 |

\(^a\)The values with entries “bulk 4×4×4” and “bulk EAM” have been reported in ref 24 using kinetic energy cutoff and smearing values of 270 and 0.42 eV, respectively. Using kinetic energy cutoff and SW values of 700 and 0.2 eV, respectively. Experimental values of cohesive energies are quoted in brackets (from ref 44).
indicates a “poor” overlap with orbitals of neighboring Fe atoms located at the surface (see panels b and c of Figure 2).

Note also that the electronic density of states of the Fe(001) surface (see Figure 5) is slightly modified upon intermixing. As can be seen from Table 2, there is a net charge donation from the Fe(001) surface to the gold atom of about $-0.73\,\text{e}$, clearly indicating the formation of a polar local bond at the interface between atomic gold and the iron surface.

As occurs with the surface vacancy formation energy, it can be seen in Table 2 that the energy necessary to exchange Fe to Au (1.29 eV) is the smallest among those of the triade surfaces. In stark contrast, the energy penalty to form a vacancy in bulk Fe is the largest (see Table 2). This behavior along with the imperfect Fe–Au lattice mismatch on the Fe(001) surface, and the evidence for the occurrence of ionic (local) displacement upon Au–Fe intermixing can be linked to the tendency of the Fe core of Fe–Au nanoparticles to be fragmented upon heating.\textsuperscript{24} On the one hand, the large energy penalties to create vacancies at the bulk of the material explain why it is not experimentally observed the exchange of all core iron atoms by atomic gold.\textsuperscript{24} On the other hand, interactions implying polar bonding are typically steeply repulsive at short distances and might cause rebounding upon the collision of shell Au atoms by the surfaces of the Fe cores. Evidently, this effect should be more pronounced upon increasing the temperature as the collision energy of the shell Au atoms becomes larger. In the experiment on nanoparticles,\textsuperscript{24} the fragmentation is observed at temperatures as low as 400 °C.

2.2.2. Co(001) Surface. Moving to the case of the Co(001) surface, it can be observed from Figure 3 that the surface restructuring upon exchange with atomic gold is more pronounced than for the Fe(001) counterpart: the gold atom is shifted upward from the position of the removed Co atom, reaching a location above the top-most layer of the Co(001) surface. Furthermore, the Co–Au bonds are about 0.31 Å longer than the Co–Co bonds in the bare Co(001) surface (see Table 2). However, the overlap of Au orbitals with either surface or subsurface Co atoms is larger than in the case of the Fe(001) surface (see panels b and c of Figure 3). The Bader decomposition analysis shows a partial charge donation of $-0.5\,\text{e}$ from the Co atoms to atomic gold. The Co(001) surface stands out also for having the major energy necessary for the intermixing (1.70 eV). The modification of the electronic density of states upon the exchange is small yet non-negligible (see Figure 5). The experimentally observed resistance of Co cores to intermix with the Au shell on core–shell nanoparticles\textsuperscript{25} can be explained by the more pronounced restructuring of the Co(001) surface upon the exchange with atomic gold when compared with their triade counterparts (see Table 2) and their larger energy penalties to host vacancies in the surface (i.e., as compared with the Fe(001) and Co(001) surfaces). Actually, for all three metals (Co, Fe, and Ni), the rather high values of the energies of substitution suggest their
resistance to alloy with Au (as also known from bulk binary phase diagrams), which is consistent with their large mismatch in atomic size. However, nickel can alloy with gold at high temperature. Moreover, the temperature at which the two metal species start mixing is lower in the case of nanoparticles compared to bulk,\(^4^5\) which is consistent with the experimental observations on core–shell nanoparticles.\(^2^4\)

2.2.3. Ni(001) Surface. As compared with Fe(001) and Co(001) surfaces, the features characterizing the exchange on the Ni(001) surface are much more conclusive. The analysis of the restructuring upon exchange, the most relevant orbitals at the Au–Ni interface, and the electronic density of states highlights the differences between the triade surfaces. On the one hand, as can be seen from panel a of Figure 4, there is an almost perfect integration of the Au atom on the Ni surface, becoming shifted by just 0.005 Å along the z direction from the original Ni position. Moreover, the Ni–Au bonds are elongated on average by just 0.12 Å as compared with the Ni–Ni bonds in the original structures (see Table 2). On the other hand, the density of orbitals with the maximum projection onto atomic Au(5d) orbitals signals a more favored overlap with Ni surface atoms than with Fe and Co atoms (see panels b and c of Figure 4). Specifically, in contrast with either the Fe(001) or the Co(001) surface, the density of the orbitals at the Au–Ni interface extends toward both surface and subsurface atoms. Similar to the Co–Au system, the Bader decomposition shows the donation of charge from the triade surface to the Au atoms (about −0.46 e\(_\text{f}\), see Table 2), also indicating a polar interaction at the Ni–Au interface. Finally, notice that the electronic density of states for the Ni(001) surface is almost indistinguishable from that calculated when one Ni atom is replaced by atomic gold (see Figure 5). This outcome indicates the better mismatch of the Au atom on the substitutional site of the Ni(001) surface than on those of the Fe(001) and Co(001) surfaces, hardly disturbing the electronic layout of the nickel surface.

Taken together, our findings on the Ni(001) surface can be linked with the experimentally proved tendency of core nickel atoms to be alloyed with shell gold atoms in core–shell Ni–Au nanoparticles.\(^2^4\) In stark contrast with both the Fe–Au and Co–Au cases, the experimental observations indicate that all core Ni atoms become exchangeable upon heating, even below the melting temperature. Furthermore, using a \((5\sqrt{2} \times 5\sqrt{2})\) R45° unit cell and a 10-layer-thick slab to model the Au(001) surface, we have calculated the energy necessary for the inverse process (the exchange of one Au surface atom with atomic nickel). The value of the energy of substitution (1.59 eV) is very similar to that obtained for the exchange of one surface Ni atom with atomic gold (1.64 eV). As expected from the smaller size of the Ni atom, when one gold surface atom is replaced by Ni, the Ni–Au bonds become shorter than the Au–Au bonds in the bare Au(001) surface.

Finally, it should be stressed that the atomic \([\text{Xe}]5d^{10}6s^1\) configuration of gold is much perturbed upon intermixing with triade surface atoms. This way, the binding mechanism cannot be simply explained as the donation of one electron from the iron triade surfaces to atomic gold so that the Au(6 s) orbital becomes double-occupied. The comparison with the free Au atom case clearly shows that s- and p-type orbitals of atomic gold gain population upon intermixing while the opposite holds true for d-type orbitals. The charge donated to s- and p-type orbitals is roughly twice as large that lost by d-type orbitals. Therefore, it is apparent that s-, p- and d-derived orbitals are participating in the binding mechanism between atomic gold and the three iron triade surfaces. In particular, the hybridization of s and p orbitals eases the accommodation of atomic gold onto the substitutional sites of the triade lattices. This outcome is in stark contrast with a spectroscopic study of the Ni–Au dimer (see ref 46) for which a low degree of participation of d-orbitals in the Ni–Au chemical bond was identified.

2.3. Sub-nanometric Iron Triade and Gold Clusters. We have analyzed the exchange of sub-nanometric triade clusters of six atoms with atomic gold as well. Panel a of Figure 6 shows the transition from octahedral unmixed clusters made of six identical triade atoms to mixed clusters bearing five Fe, Co, or Ni atoms and one Au atom. In all cases, the X–Au bonds (X = Fe, Co, and Ni) become just slightly elongated as compared with the X–X counterparts in the unmixed clusters. Thus, almost no structural changes are distinguished in iron and cobalt clusters having a pentagonal bipyramidal structure (see Figure 6). The nickel cluster experiences a more noticeable structural rearrangement: the Ni5 fragment acquires a trigonal bipyramidal structure to maximize the Ni–Au interaction, with the intruder gold atom lying on the hollow.

![Figure 4](image-url)
position of one of the bipyramid faces. However, compared with the restructuring of the triade surfaces upon the exchange, the modification in the shape of the Ni₆ cluster upon intermixing is remarkable.

Regarding the clusters, the energies of substitution (see Table 3) are smaller than those calculated at the triade surfaces. In contrast to what is observed for the surface, the substitution of one Ni atom by atomic gold is the most favorable process yet endothermic at 0 K. However, due to the increase in the entropy contribution, the mixed Ni−Au cluster is predicted to be stable at 650 K (see Figure 7). Intermixed phases in (initially) centralized core−shell Ni−Au nanoparticles were predicted (observed) to become favorable at 662 K (570−670 K). The entropy contribution, and in particular the configurational entropy, is also responsible for the reduction of the gap between the free energies of Fe₆ and Fe₅−Au clusters. However, the larger weight of the electronic energy contribution in the case of iron (see Figure 7) makes that the mixed cluster be less stable than the pure one in the experimentally relevant temperature range (up to about 1100 °C). Free energies of Au−Fe core−shell nanoparticles were also found to be dominated by the energy contribution and no local minimum was identified for the mixed states. Finally, the intermixed Co₅−Au cluster is predicted to become more stable at 1295 K. This outcome is in accordance with the experimental findings showing that decentralized Co cores were observed to remain intact without any tendency toward alloying up to the melting temperature (1100 °C).

Figure 5. Electronic density of states (EDOS) of Fe(001), Co(001), and Ni(001) surfaces, using (5√2 × 5√2)R45° unit cells and a 10-layer-thick slab, before (green curve) and after exchange (blue curve) of one of the surface atoms with atomic gold. Also, the projected density of states of orbitals with the maximum projection onto atomic orbitals of the exchanged Au atom are represented (referred to as Au(x200), shown in red). The zero of energy corresponds to the Fermi energy, defined as the energy of the highest occupied level at 0 K. The most intense peaks indicate the energy positions of the orbitals shown in Figures 2−4.
The Au₆/Au₅ Clusters

Atom Replaces Fe, Co, or Ni (Au) Atoms in Triade (Gold)

pressure have been estimated to be Gibbs free energies under ambient conditions of temperature and "atomic gold is provided as well (referred to as exchanged with atomic gold is presented. The charge donated to Au₁₃ cluster to Au₁₂ clusters; (b) from the Au₆ cluster to Au₅ clusters; and (c) from the Au₁₃ cluster to Au₁₆−X clusters.

Table 3. Exchange Energy (E_exch) When One Au (Triade) Atom Replaces Fe, Co, or Ni (Au) Atoms in Triade (Gold) Clusters

| system | E_{exch} | Bader | d−d (Å) |
|--------|----------|-------|---------|
| Fe₆ → Fe₅−Au | 0.99 | −0.56 | 0.072 |
| Co₆ → Co₅−Au | 0.43 | −0.47 | 0.097 |
| Ni₆ → Ni₅−Au | 0.19 | −0.38 | 0.022 |
| Au₆ → Au₅−Ni | −1.13 | −0.80 |         |
| Au₆ → Au₅−Co | −1.13 | −0.61 |         |
| Au₆ → Au₁−Fe | 0.63 | −0.54 |         |
| Au₁₃ → Au₁₂−Ni | −2.48 | −0.89 |         |
| Au₁₃ → Au₁₂−Co | −1.83 | −0.65 |         |
| Au₁₃ → Au₁₂−Fe | −1.85 | −0.58 |         |

"The lowest energy spin state has been selected for each structure. Also, the increase in the mean distance (referred to as "d−d") (see Methods for the definition) when one triade cluster atom is exchanged with atomic gold is presented. The charge donated to atomic gold is provided as well (referred to as "Bader"). Relative Gibbs free energies under ambient conditions of temperature and pressure have been estimated to be −1.16, −0.64, and −0.62 when for the Au₆/Au₅−X (X = Fe, Co, and Ni) substitutional process.

An analysis of the charge distribution using the Bader scheme indicates that the intruder atom always acquires charge from the clusters (see Table 3) so that polar metallic X−Au bonds (X = Fe, Co, and Ni) are formed. The charge donated by triade clusters and extended triade surfaces differ just a little (less than 0.15 lel, see Table 3), with the former being just slightly smaller. Correlating with Pauling’s electronegativity differences, the charge acquired by atomic gold in iron clusters and surfaces is the largest, whereas the opposite holds true for nickel counterparts.

The opposite transition (i.e., from a six-atom gold cluster to clusters composed by five gold atoms and one triade atom) has also been analyzed. Our selection is based on previous experimental measurements on the catalytic activity of Auₙ clusters (with n in between 3 and 10) for the oxidation of thiophenol, showing that the Auₙ cluster holds the best performance. Interestingly, the converged structures, which are shown in Panel b of Figure 6, indicate a very pronounced geometry transformation upon atomic exchange. They evolve from a planar triangular-like structure to planar pentagon-like arrangements, hosting the triade atoms at the center of the clusters. The structure of the Au₆−Fe bimetallic clusters is completely planar while, in Au₅−Co and Au₅−Ni clusters, Co and Ni atoms are slightly shifted out from the plane of the gold atoms. Remarkably, the substitutional reactions with Fe and Ni atoms are exothermic in six-atom gold clusters even at 0 K, as opposed to the case of atomic nickel as well as the triade surface counterparts. Taken together, our findings reveal the major structural fluxionality of triade clusters compared with extended surfaces. As shown on a study of the oxidation quenching of Cuₙ clusters, when the cluster size is reduced to a very small number of atoms, a sub-nanometer network of discrete molecule-like d orbitals centered on the metal atoms is formed. The special structures of these molecular orbitals favor that the metal atoms become cooperatively active in the given (e.g., substitution) process.

In order to confirm the tendency of triade atoms to be hosted in central positions of gold clusters, the exchange process has been explored in a 13-atom cluster as well. Panel c of Figure 6 illustrates the noteworthy structural rearrangements experienced by the gold cluster when one of its atoms is replaced by either Fe, Co, or Ni. The intruding atom remains in a central position inside a coverage of gold atoms, which takes out a little more electronic charge from the triade atom than the smaller six-cluster atom. Curiously, as opposed to the
case of triade surfaces, the exchange of atomic gold with a Fe atom is the most favorable process, with the Fe atom residing at the core of a gold icosahedral structure (see panel c of Figure 6). The isodensity surface of the highest-energy single-occupied molecular orbital (see Figure 8) also indicates that the hybridization between Fe and Au orbitals is stronger than in the cases of Co and Ni. The formation of a core formed by one triade atom inside the gold cage process is thus favorable. Our results are consistent with a recent work showing that core–shell clusters can be formed from pairs of metals (Co and Ag) that do not form macroscopic alloys. Similarly, we have found that the replacement of atomic gold by a Ni atom is highly endothermic at extended gold surfaces (1.59 eV), whereas it becomes exothermic for all triade atoms in 13-atom gold clusters (see Table 3).

3. CONCLUSIONS

In this work, we have modeled the Fe(001), Co(001), and Ni(001) triade surfaces with 500-atom unit cells. Vacancy formation energies have been calculated confirming previous findings using smaller 256-atom unit cells. Although bulk iron is the more reluctant to host bulk vacancies, the Fe(001) surface stands out over their triade counterparts due to its smaller surface vacancy formation energy while the energy required to form a vacancy at the Co(001) surface is the largest.

In a second step, a surface triade atom has been replaced by atomic gold. The values of the energies of substitution (from 1.3 to 1.7 eV) depend on the particular triade atom constituting the surface. The restructuring of the triade surfaces changes depending on the particular material as well: while atomic gold occupies a position very close to that left by a Ni atom when the vacancy is formed, it stays on top of the substitutional site of the Co(001) surface. The better integration of the Au atom at the vacancy left by the Ni atom is evident when noticing that the electronic density of states of the Ni(001) surface is hardly modified when one Ni atom is replaced by atomic gold. Additionally, Bader charges and orbitals indicate the polarity of the interaction between atomic gold and the substitutional sites of the three triade surface, specially for the case of the Fe(001) surface. These findings correlate well with the experimental observations on core–shell nanoparticles, showing that the Co core is the most reluctant to be mixed with the Au shell while the opposite holds true for the Ni counterpart. The anomalous observed propensity of Fe cores to be fragmented upon heating can be related with a pronounced ionic displacement at the Fe–Au interface, the imperfect Fe–Au mismatch on the Fe(001) surface and, as previously reported, and the large energies necessary to create vacancies in the bulk of the material.

We have also analyzed the exchange process in sub-nanometric iron triade and gold clusters, showing that the scenario changes significantly in the sub-nanometer range. For instance, the restructuring of Ni clusters is much more pronounced upon exchange with atomic gold than at the Ni(001) surface. Most importantly, although the exchange process is predicted to be endothermic, the energies necessary for the atomic exchange are significantly smaller in the case of the clusters (0.2–1 eV) than on the surfaces (1.3–1.7 eV). We explain both outcomes as the result of the structural fluxionality of sub-nanometric clusters. The intermixing of atomic gold with nickel clusters is energetically more favorable than with the other triade atoms. In addition, the entropy contributions are also highly favorable to the exchange so that the bimetallic Ni–Au cluster is predicted to be more stable than the pure cluster already at 650 K. This value compares well with the predicted (observed) intermixing temperature of 662 K (570–670 K) on Ni–Au nanoparticles. Interestingly, the thermodynamics predicted for sub-nanometric clusters closely follows that simulated in much larger core–shell nanoparticles. Remarkably, the net charge donated by triade atoms to atomic gold upon intermixing is very similar at extended surfaces and in sub-nanometric clusters, highlighting the importance of the polar nature of chemical bonding in alloys. Finally, we have provided evidence that gold clusters made of 6 and 13 atoms are prone to host Fe, Co, and Ni at the center of their structures, with the substitutional process being exothermic for the Au13 cluster for all triade atoms even at 0 K.

4. METHODS

4.1. Periodic Calculations. Periodic electronic structure calculations were carried out with the Vienna Ab initio Simulation Package (VASP 5.4.4), following a similar computational approach to that reported in previous works on Ag, TiO2 (110) interactions as well as iron triade surfaces. Specifically, we used a dispersion-corrected DFT-D3 ansatz giving its excellent performance in describing the adsorption of sub-nanometer silver and copper clusters on oxide surfaces. Structural optimizations and the calculation of interaction energies were carried out using the Perdew–Burke–Ernzerhof (PBE) density functional and the Becke-Johnson (BJ) damping for the D3 dispersion correction.

Electron-ion interactions were described by the projector augmented-wave method, using PAW–PBE pseudopotentials as implemented in the program. The electrons of the Fe(3d, 4s), Co(3d, 4s), Ni(3d, 4s), and Au(5d, 6s) species were treated explicitly as valence electrons. Plane-wave basis sets with kinetic energy cutoffs ranging from 270 to 700 eV were used. The first-order Methfessel and Paxton scheme was applied to account for partial orbital occupations, with SW values of 0.2 and 0.42 eV. All the atoms from the supercells were optimized using a low kinetic energy cutoff of 270 eV and a force threshold of 0.02 eV/Å. Unless otherwise noticed, the resulting converged geometries were kept frozen in follow-up calculations using kinetic energy cutoff and SWs values of 700 and 0.2 eV. The Brillouin zone was sampled at the Γ point. The energy convergence criterion was fixed to a value of $10^{-4}$ eV in the self-consistent electronic minimizations. All calculations were spin-polarized.

The bulk of the models was created by building 5 × 5 × 5 face-centered-cubic (fcc) unit cells of 500 atoms. The (001)
facets of the surfaces were modeled through the introduction of a vacuum region in the direction perpendicular to the surface, using a $(5\sqrt{2} \times 5\sqrt{2})$R45° unit cell and a 10-layer-thick slab (in between 17 and 18 Å). In a first step, calculations on vacancy formation energies ($E_v$) were carried out as in ref 24 but using our larger 500-atom unit cell

$$E_t = E_v - \frac{N - 1}{N} E_b$$  \hspace{1cm} (1)

where $E_b$ ($E_v$) is the energy of the periodic supercell before and after removing one of its $N$ atoms ($N = 500$ in our case). Vacancy formation energies were calculated similarly for the bulk, inner, and surface slab positions. Bulk vacancies were located at the center of the $5 \times 5 \times 5$ fcc supercell of 500 atoms with periodicity in three dimensions. Inner surface vacancies were located inside the 500-atom unit cells modeling the surfaces, as shown in Figure 1. These test calculations were aimed to evaluate the convergence of the relative energies with the unit cell size. Energies of substitution (also referred to as exchange energies$^{59}$ as in ref 24) were calculated in a second step by replacing one triade atom on one side of the supercell models with the intruding gold atom using the expression

$$E_{\text{exch}} = E_{\text{(Au)in(Fe,Co,Ni)slab}} + E_{\text{(Fe,Co,Ni)atom}} - E_{\text{(Fe,Co,Ni)slab}}$$  \hspace{1cm} (2)

where $E_{\text{(Au)in(Fe,Co,Ni)slab}}$ is the energy of the Fe, Co, or Ni surface bearing one surface atom replaced by Au, $E_{\text{(Fe,Co,Ni)atom}}$ stands for the energy of the Fe, Co, or Ni atoms, $E_{\text{(Fe,Co,Ni)slab}}$ denotes the energy of the pure Fe, Co, or Ni surface, and $E_{\text{(Au)atom}}$ is the energy of atomic gold.$^{60}$ The energies of isolated atoms were chosen for the purpose of better comparison with the energies of substitution calculated in sub-nanometric clusters below. An analysis of the atomic charges was carried out using the Bader decomposition scheme as well.$^{66}$ The mean distance between the gold atom and the nearest-neighbor triade atoms, located either in the top surface layer or in the first subsurface layer, was also calculated and compared with its equivalent on the unmodified triade surface. The increase in the mean distance upon exchange with atomic gold is referred to as “d–d.”

4.2. Cluster Model Calculations. Cluster model calculations of 6- and 13-atom systems were carried out with the ORCA$^{61}$ suite of programs (version 4.0.1.2), using the PBE density functional and the D3 Becke-Johnson damping (BJ) for the dispersion correction as in the periodic calculations. A balanced polarized triple-zeta basis set (def2-TZVPP) was used.$^{62}$ Geometry and energy convergence were reached by allowing all the atoms to relax, choosing the lowest-energy spin states. Similar to the case of the triade surfaces, the exchange energy ($E_{\text{exch}}$) was calculated as

$$E_{\text{exch}} = E_{\text{(Au)–(Fe,Co,Ni)cluster}} + E_{\text{(Fe,Co,Ni)atom}} - E_{\text{(Fe,Co,Ni)cluster}} - E_{\text{(Au)atom}}$$  \hspace{1cm} (3)

where $E_{\text{(Au)–(Fe,Co,Ni)cluster}}$ is the energy of the Fe, Co, or Ni cluster with one atom exchanged by atomic gold, $E_{\text{(Fe,Co,Ni)atom}}$ stands for the energy of the Fe, Co, or Ni atom, $E_{\text{(Fe,Co,Ni)cluster}}$ denotes the energy of the bare Fe, Co, or Ni cluster (i.e., made of only one type of metal), and $E_{\text{(Au)atom}}$ is the energy of atomic gold. The structures of the monometallic clusters were first optimized and, next, reoptimized after exchanging one of their atoms with atomic gold. A similar procedure was followed when considering the exchange of one Au atom by one triade atom in gold clusters. The Bader decomposition method$^{68}$ was also applied to estimate the charge acquired by atomic gold in the mixed clusters. Relative Gibbs free energies (referred to as $\Delta G_{\text{mixed}}$) were calculated as well using the thermochemistry output of the ORCA$^{61}$ code. The inner energy term accounted for the zero-point energy, the thermal vibrational contribution (i.e., as coming from the population of excited vibrational states at a given temperature), thermal rotational, and translational terms. Entropy contributions due to spin multiplicity were automatically included. The configurational entropy contribution (referred to as $\Delta S_{\text{conf}}$) was also calculated using the standard Boltzmann’s entropy expression. Finally, it is worth recalling that the pseudo-potentials used in periodic and cluster calculations are different as they reproduce properties of solids and atomic spectra, respectively. In order to explore the impact of having used different pseudo-potentials, we have calculated the cohesive energy of a six-atom nickel cluster, finding that our periodic and cluster model approaches provide very similar values (2.60 and 2.53 eV, respectively).

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**Notes**

The authors declare no competing financial interest.

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