Ordering and Oxygen Adsorption in Au–Pt/Pt(111) Surface Alloys

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ABSTRACT: Bimetallic surface alloys are considered a promising type of catalyst for improved activity and selectivity. Using first-principles density functional calculations and the cluster expansion (CE) method, we have studied the surface structure and ordering of a mixed Au–Pt surface layer on Pt(111). Even though the Au–Pt system is well-known to phase-separate in the bulk, we predict a series of \( T = 0 \) K energetically stable, laterally ordered striped structures in the Au–Pt(111) surface. The formation of such ordered structures is the result of a competition between the strain relaxations (favoring short-period stripe ordering) and the unfavorable Au–Pt bonds at stripe interfaces (favoring long-period phase separation). We have also investigated the oxygen adsorption on these ordered structures and a disordered Au–Pt(111) surface alloy. The disordered surface is modeled by a two-dimensional special quasirandom structure (SQS) that mimics the pair and triplet correlation functions of a disordered binary distribution. The oxygen binding energy is highly correlated with the number and type of the nearest neighbor metal surface atoms to the adsorbed oxygen.

I. INTRODUCTION

Bimetallic alloy surfaces are promising candidates for designing heterogeneous catalysts because of the possibility to control the surface electronic and geometric structures that determine reactivity.1–11 Alloying of Pt catalysts, for instance, has been found to improve selectivity, activity, and to reduce Pt loadings.12 In particular, Pt surface alloys where the solute concentration near the surface differs from the bulk have proven quite successful. For example, a Cu/Pt surface alloy shows better activity than Pt for the water–gas shift reaction as the surface alloy better activates \( \text{H}_2\text{O} \) and at the same time binds CO more weakly.13 Similarly, a Pt monolayer on Pd(111) has improved activity for the oxygen reduction reaction as compared to a pure Pt catalyst.14 The improved catalytic performance of these surface alloys mainly originates from two factors that differentiate the bimetallic surfaces from the pure metal surfaces: the strain effect from the size-mismatch of the component metal atoms, and the ligand effect from the heterometallic interactions between the surface and substrate metal atoms.15 The combination of these two effects changes the electronic structure and catalytic properties of the surfaces. While heterolayers of one surface element on the substrate of another element is a widely studied morphology for surface alloys, the effect of lateral heterogeneity of the component elements within the bimetallic surface is also important, but has received less attention. An understanding of the stability and chemical properties of these laterally heterogeneous surfaces is essential to utilize these structures in the pursuit of the intelligent design of catalysts.

Some recent experimental studies have led to the discovery of a range of interesting two-dimensional (2D) domain structures. Among these results include the surprising observations of some ordered surface structures composed of metals that are immiscible in the bulk. Examples include the “droplet” and “stripe” structures in Cu–Pb films on Cu(111)16 and the compositionally modulated stripe and droplet structures of Co–Ag on Ru(0001).17 These ordered domain structures are energetically stable and can be characterized by their unique round or striped shape depending on the interactions between surface elements. The origin of these self-assembled lateral structures has been explained both by continuum elastic theory18 and by atomic models.19,20 The energy cost associated with the domain boundaries between two immiscible surface elements can be compensated by some other interaction that favors such boundaries, such as the elastic strain due to the size-mismatch of the component elements.21

The local arrangement of atoms can have an important influence on the reactivity of catalysts, but designing specific structures for catalytic purposes is complicated by the fact that a given surface structure might not be stable under reaction conditions. In the presence of adsorbates, the surface composition may change due to the adsorbate effect on solute segregation tendencies.22,23 The atomic ordering of surface atoms can also be altered by the presence of adsorbates due to interactions among surface atoms to accommodate the preferred surface composition.24 Stable ordered or disordered surface lateral structures could be promising for catalytic applications as they offer a variety of adsorption sites for catalytic processes.
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The morphology of precipitates\(^6\) is a property of the precipitation system and can be determined by analyzing the morphology of the precipitates under different conditions. The precipitation process involves nucleation and growth of precipitates from the solution. The morphology of precipitates is influenced by factors such as the concentration of the dissolved species, the temperature, and the stirring rate.

II. METHODS

A. Density Functional Theory Calculations. Total energy calculations are performed using density functional theory (DFT) as implemented within the Vienna ab initio Simulation Package (VASP) using the projector augmented wave (PAW) method.\(^6\) The generalized gradient approximation of Perdew and Wang is used to approximate the electronic exchange and correlation.\(^6\) The plane-wave basis set for the electronic wave functions is defined by a cutoff energy of 520 eV for surfaces with oxygen adsorbates.

To calculate the total energies of different Au–Pt surface alloys for cluster expansion input, a slab model with 5 atomic layers and a vacuum region of 10 Å in thickness is used, which gives a surface energy converged to about 1 meV per surface atom. The top layer of the slab contains both Au and Pt in various configurations, and the remaining layers consist entirely of Pt. The bottom two layers are fixed at the bulk equilibrium positions of Pt with a lattice constant of 3.985 Å, while all other layers are fully relaxed. The Brillouin-zone integrations are performed using Monkhorst-Pack \(k\)-point meshes, scaled according to the size of the cells to correspond as closely as possible to a \(21 \times 21 \times 1\) grid for a \(1 \times 1\) surface unit cell. The \(k\)-point meshes for each supercell are scaled to keep the \(k\)-points per reciprocal surface atom roughly constant.

\(1/2\text{O}_2 + * \rightarrow \text{O}^*\)

The \(\text{O}^*\) binding energy is a descriptor for, among other things, \(\text{O}_2\) dissociative adsorption relevant to catalytic oxidations.\(^6\)

In this Article, we report the ordering and oxygen adsorption of Au–Pt surface alloys on Pt(111) using the above procedures. While bulk Au–Pt alloys are well-known to exhibit a miscibility gap, we find that Au–Pt surface alloys exhibit a series of stable, low-temperature lateral ordered striped structures, as predicted from our 0 K first-principles calculations. The existence of such structures can be explained by the competition between the energy penalty of Au–Pt bonds at the boundaries between the stripes and the favorable strain relaxation from forming stripes. We calculate molecular oxygen dissociative binding energies for different adsorption sites of the ordered stripe structures as well as a disordered Au–Pt surface alloy. We model the disordered surface alloy by constructing a two-dimensional special quasi-random structure (SQS) for the (111) surface. The SQS is constructed so as to mimic the short-range pair and multibody correlation function of the random alloy, within a computational efficient small unit cell.\(^6\) For both the ordered and the disordered surface alloys, we find a strong correlation between the oxygen binding energy and the local Au/Pt environment of the surface adsorbate.

wide range of material problems,\(^27\)–\(^32\) such as phase diagrams and order–disorder transition temperatures,\(^33\)–\(^36\) ground-state structures and ordering,\(^36\)–\(^42\) short-range order in disordered systems,\(^43\)–\(^48\) the morphology of precipitates,\(^49\)–\(^52\) intercalation voltages in battery materials,\(^53\)–\(^55\) and also, more recently, ordering in surface alloys.\(^56\)–\(^60\) Using the CE Hamiltonian, the ground-state surface structures can be efficiently determined by enumerating all surface configurations up to a specified cell size, and searching for the low energy structures from this large pool of candidate surface configurations. The final step to correlate the surface structure and the surface chemistry is to calculate the relevant surface properties, such as the binding energy of adsorbates. In this case, we use DFT models to calculate oxygen binding energies as a function of local surface environments:
We calculate the segregation energy of Au from the bulk to the Pt(111) surface by the difference between the total energy of a slab with a surface Pt atom replaced by a bulk Au atom and the total energy of a slab with a pure Pt surface and a Au atom in the bulk. Negative segregation energy indicates an energetic preference for the Au atom to segregate to the surface of Pt. A slab model of 7 layers of atoms is used in the segregation energy calculations. The bottom three layers are fixed, and the remaining four layers are relaxed. The “bulk” Au atom is situated in the fourth layer of the slab. The segregation energy is calculated using a 2 × 2 supercell for both a clean surface and a surface with adsorbed oxygen. To calculate the segregation energy with oxygen adsorbate, we assume that the Au atom segregates to one of the nearest neighbor positions of the oxygen atom.

The dissociative oxygen binding energy on ordered or disordered Au−Pt/Pt(111) surface alloys is calculated as:

$$E_{\text{bind}}(O) = E_{\text{O/slab}} - \frac{1}{2} E_{\text{O(g)}} - E_{\text{lab}}$$

where \(E_{\text{O/slab}}\) is the total energy of the slab with an oxygen atom adsorbed on a surface site, \(E_{\text{O(g)}}\) is the total energy of \(O_2\) in the gas phase, and \(E_{\text{lab}}\) is the total energy of the slab in vacuum. The five-layer slab contains the same ordered or disordered Au−Pt surface layer configuration in both terms in eq 1, \(E_{\text{O/slab}}\) and \(E_{\text{lab}}\). In the binding energy calculations, we only consider oxygen adsorption on fcc sites, which are experimentally observed to be the stable adsorption sites on Pt(111) \(^{69,70}\).

### B. Searching for Low-Energy Ordered Surface Structures from the Cluster Expansion Method

For a surface layer with \(N\) surface sites each containing either Au or Pt, there is an astronomical number, \(2^{2N}\), of different surface configurations possible for the Au−Pt surface alloy. Even for a modest \(N\), this number is clearly beyond the capability of direct exploration via DFT calculations. To solve this problem, we use the cluster expansion (CE) formalism to find the stable ordered surface structures. In this generalized Ising-like model, a surface site occupied by Pt is assigned a spin occupation variable \(S_i = +1\), and a Au site is assigned \(S_i = -1\). The total energy of any configuration \(\sigma\) for the surface can be written as:

$$E(\sigma) = J_0 + \sum_i J_i S_i(\sigma) + \sum_{j<i} J_{ij} S_i(\sigma) S_j(\sigma) + ...$$

where the coefficients \(J_i\) are effective cluster interactions (ECIs) associated with clusters of lattice sites (pairs, triplets, and quadruplets, etc.). A structure-dependent correlation function \(\Pi_F(\sigma)\) can be defined for each cluster \(F\):

$$\Pi_F(\sigma) = \frac{1}{D_F} \sum_f S_f(\sigma) S_2(\sigma) ... S_m(\sigma)$$

where the spin products of all \(m\) sites of the cluster \(F\) are summed over \(N\) times \(D_F\) equivalent figures for the configuration \(\sigma\), where \(N\) is the number of lattice sites and \(D_F\) is the number of symmetry-equivalent cluster \(F\). By choosing appropriate clusters, the expansion in eq 2 can be truncated to include a finite set of clusters and still gives converged result. An optimal set of ECIs is obtained by minimizing the cross-validation (CV) score of the CE fitting across the DFT energies of a set of input surface configurations. The CV score serves as a measurement of the predictive power of the cluster expansion and is calculated as follows:

$$CV = \sqrt{\frac{1}{N} \sum_{i=1}^{N} [E_i - \hat{E}_i]^2}$$

where \(E_i\) is the DFT energy of an input structure, \(\hat{E}_i\) is the predicted energy of the structure \(i\) by the CE Hamiltonian from a least-squares fit to the \(n - 1\) energies of the remaining structures in CE fitting. The value of the CV score can be considered a measure of the predictive error of the cluster expansion energies to reproduce DFT energetics. We cluster expand the formation energies of various surface structures with 2D clusters using the ATAT package.\(^{71}\) The formation energy of a Au−Pt surface structure is defined as follows:

$$E_F(\text{Au}_{1-x}\text{Pt}_x) = [E(\text{Au}_{1-x}\text{Pt}_x) - (1 - x)E(\text{Au}) - xE(\text{Pt})]/N$$

where \(E(\text{Au}_{1-x}\text{Pt}_x)\) is the total energy for a Au−Pt/Pt(111) surface structure with a Pt surface coverage of \(x\), and \(E(\text{Au})\) and \(E(\text{Pt})\) are the energies for pure Au/Pt(111) and Pt/Pt(111) surfaces. The formation energies are normalized to energy per surface atom.

The construction of CE is usually accomplished through an iterative procedure by finding the best set of clusters and ECIs that is able to give the correct ground-state structures and good energy prediction of any atomic configurations of the system.\(^{72}\) The CE fitting procedure starts with a trial set of clusters and ECIs from a few input structures. Using this trial CE Hamiltonian, the formation energies for a larger set of structures are predicted, and from this larger set, the lowest-energy ground-state structures are determined. If new ground-state structures different from any input structures are predicted from the CE Hamiltonian, DFT energies of these structures are calculated and included in the next iteration of CE fitting. This procedure continues until: (1) the predicted ground-state structures are in agreement with those from DFT calculations, and (2) the CV score is within an acceptable error for energy prediction. For the Au−Pt/Pt(111), because of the small negative formation energy (see below) and the very small energy differences between low energy structures, it is difficult to get a perfectly converged CE meeting both the above requirements. We stopped adding new structures to the CE fitting when a very small cross-validation score (<1 meV per surface atom) and an obvious pattern of low-energy structures emerged, as discussed below.

To validate both the use of DFT and the CE for the Au−Pt system, we also calculate the bulk phase stability of Au−Pt by DFT calculations along with a bulk, three-dimensional (3D) CE. The procedure for the bulk CE is similar to the surface CE, but 3D clusters are used here to expand the formation energies of bulk Au−Pt structures. We also perform grand-canonical Monte Carlo (MC) simulations using the CE Hamiltonian to obtain the composition−temperature phase diagram for the bulk Au−Pt system within the ATAT package.\(^{72}\) Details of the MC simulation method and the phase boundary tracing algorithm can be found in the paper by van de Walle et al.\(^{73}\)

### C. First-Principles Calculations of Disordered Surface Alloys

We have calculated the oxygen dissociative binding energy of different fcc adsorption sites on ordered structures obtained from the CE structure search. In addition to this conventional supercell method, we also wish to explore the bonding energies on disordered
Au–Pt surfaces. To that end, we generate a 16-atom 2D special quasirandom structure (SQS)74 for the fcc(111) surface at 50% composition. A direct simulation of a random surface from DFT calculations would require very large supercells, making this approach computationally prohibitive. SQS offers an efficient tool to overcome this difficulty and to simulate the random surfaces with moderate computational cost. The SQS mimics the surface disorder by arranging the atoms in a way that reproduces, as closely as possible, the short-range pair and multibody correlation functions of a perfectly random structure. The SQS allows one to study the properties of a disordered structure from DFT at a relative small computational cost. SQS structures have been generated for binary ordering on fcc,75–77 bcc,78,79 and hcp80 lattices as well as ternary ordering on these lattices.81 However, to our knowledge, 2D surface SQS have not yet been reported.

We construct the 2D binary SQS by enumerating all possible atom configurations up to a 16-atom fcc(111) surface lattice and picking the configuration whose pair and triplet correlation functions are closest to the short-range correlation functions of the random alloy.72 The correlation functions of the perfect random alloy at 50% composition are zero for all pairs and triplets. However, because of the limited cell size for the SQS, the pairs and triplet correlations of the SQS will only match those of the random alloy up to a certain size. This “short-range” assumption is reasonable due to the presumption that the dominant interactions between alloy elements in eq 2 will be short-ranged. In other words, long-ranged figures (where the SQS correlations do not match the random alloy) have very small interactions and hence very low weight in the expansion of eq 2. In judging the quality of the SQS to match the random alloy, we consider pair correlation functions up to the seventh nearest neighbor. We also consider three triplet correlation functions with pairs that do not exceed the third nearest neighbor. This 2D SQS should be generally useful to many problems involving disordered bimetallic surfaces, and we give the coordinates of this structure in the Appendix.

In contrast to a mean-field approach describing the random alloy as some “average” structure, the SQS contains the same distribution of different local atomic environments that exist in the random alloy. For example, an oxygen atom adsorbed to the fcc(111) surface will have three metal atoms as nearest neighbor (NN). These adsorption sites have a distribution of metal NN sites of type AAA, AAB, ABB, and BBB. The SQS gives us the ability to explore these different local environments. To explore the oxygen adsorption on the Au–Pt surface alloy as a function of local surface environment, the binding energies of oxygen on all fcc sites of the 16-atom 2D SQS are calculated.

III. RESULTS AND DISCUSSION

A. Au–Pt Bulk Phase Stability. We first validate the use of DFT+CE method by studying the phase stability of the bulk Au–Pt system using the first-principles CE method. The calculated DFT+CE results for formation energies and phase diagram are shown in Figure 2. The CE for bulk Au–Pt includes 11 pairs, 7 triples, and 1 quadruplet, giving a CV score of 6 meV/site. In the ground-state plot (Figure 2a), the red dots are DFT energies of the input structures, and the green dots are formation energies predicted from the CE Hamiltonian. From Figure 2a, we see that the only ground-state structures are pure Au and Pt, and all of the other structures have positive formation energies (i.e., higher than the tie-line connecting the end points). The fact that no ordered Au–Pt structure has a negative formation energy indicates the bulk Au–Pt is a phase-separating system, which is in agreement with the experimental phase diagram.82 In the bulk phase diagram calculated from MC simulations of the CE Hamiltonian (Figure 2b), the system has a miscibility gap extending up to approximate 1200 °C. Our calculated phase diagram not only reproduces the asymmetry of the experimental phase diagram, but also gives a quantitatively accurate temperature for the top of the miscibility gap as compared to experimental observations (1260 °C).82 This quantitative agreement is somewhat surprising, because overestimation of calculated phase-transition temperatures is common in phase diagrams predicted from methods based on DFT calculations, especially when the vibrational entropy is not considered.83–86 Because of the relatively small size-mismatch between Au and Pt (≈4% in lattice parameter mismatch), we hypothesize that the vibrational entropy does not greatly influence the transition temperature.

B. Surface Segregation of Au to Pt(111). To study the surface ordering of Au–Pt, we first need to understand the segregation tendency of Au atoms to the Pt surfaces to help choose the appropriate surface model for the surface cluster expansion. We have calculated the segregation energy of Au to the clean Pt(111) surface. Using a 2 × 2 supercell (1/4 ML Au), the segregation energy for each Au atom to segregate from the bulk to the Pt(111) surface is −0.47 eV. The segregation value is consistent with other DFT calculations.26,87 The moderate negative segregation energy implies that Au atoms have an energetic preference to segregate to the surface sites of the Pt(111) in vacuum, rather than to stay in the bulk. It has also been observed experimentally that Au atoms...
coexist with Pt on Pt(111). The segregation energy is similar when using a 1 × 1 (1 ML Au, −0.48 eV per Au) and 3 × 3 (1/9 ML Au, −0.50 eV per Au) supercell. The subsurface segregation of Au is not energetically favorable to the surface segregation. The segregation energy of a Au atom (1/4 ML Au) to the subsurface Pt layer is 0.37 eV higher than to the surface Pt layer. Using a mean-field model Langmuir–McLean equation,24 we estimate from the layer-dependent segregation energy that the concentration of Au as a function of surface layer would then show a monotonic behavior at finite temperature, with the highest concentration at the surface, but a slightly enriched concentration at the subsurface as well. There is a general trend of segregation that in phase-separating systems, the segregation profile as a function of surface layer should be monotonic, but for an ordering system, the segregation profile should be oscillatory. The monotonic profile of concentration is in agreement with the fact that Au–Pt is phase-separating in the bulk and implies that Au–Pt bonds are always of “phase-separating type”.

There are two factors contributing to the surface segregation of Au to Pt(111). First, the surface energy of Au(111) is lower than that of Pt(111). According to our DFT calculations, the surface energy of Pt(111) is 0.64 eV/atom, while Au(111) is only 0.33 eV/atom. When ignoring the interactions between the Au and Pt atoms in the surface, an alloy surface with a mixture of Au and Pt atoms would have lower surface energy than pure Pt surface. Second, the number of Au–Pt bonds is reduced for Au atoms at the surface than in bulk. The bulk immiscibility of Au–Pt implies the bonds between Au and Pt atoms are energetically unfavorable. In the bulk, a Au atom would have 12 nearest-neighbor Pt atoms. However, a surface Au atom would only have nine Pt nearest-neighbors. The reduced number of the unfavorable Au–Pt bonds in surface Au atoms lowers the total energy of the system. The reduction in nearest neighbor bonds is even more pronounced for the (100) and (110) surfaces, which have eight and seven bonds, respectively. We have also calculated the segregation energy of Au to Pt(100) and Pt(110) facets to be −0.63 and −0.65 eV per Au, respectively. These negative segregation energies indicate that Au atoms have an even greater tendency to segregate to the clean Pt(100) and Pt(110) surfaces.

The surface segregation trend of Au on Pt(111) is significantly affected by the presence of oxygen adsorbates. We use a 2 × 2 supercell (i.e., 25% Au composition in the surface with 25% oxygen coverage) to calculate the segregation energy of Au to Pt(111) with atomic oxygen adsorbates. Contrary to a moderate negative segregation energy for the clean surface, the segregation energy is 0.02 eV per Au in the presence of oxygen. The tiny positive segregation energy indicates the Au atom has essentially no energy preference to stay in the bulk or segregate to the oxygen covered Pt surfaces. In this case, the segregation has the same two factors as above, but now there is a third competing factor, which is the interaction of the adsorbed oxygen with Au versus Pt. Because the oxygen binds more strongly to Pt, this disfavors the segregation of Au to the surface and essentially cancels the segregation tendency in vacuum.

On the basis of the segregation energy results, we choose a single Au–Pt monolayer on a Pt(111) surface to study the surface ordering of a clean Au–Pt surface in surface CE. The model treats Au segregated to the surface and allows Au and Pt at the surface layer to adopt any possible 2D configurations. The oxygen binding energies are also calculated on ordered and disordered Au–Pt alloy surfaces.

C. Au–Pt Surface Phase Stability

1. Surface Ordering in Au–Pt: The Existence of “Striped” Structures

Even though the bulk Au–Pt alloys energetically prefer to phase separate, we find the Au–Pt/Pt(111) surface alloys exhibit stable ordered structures from the surface CE. We enumerate all binary configurations of the surface alloy up to 4 surface sites (e.g., 1 × 1, 1 × 2, 2 × 3, 1 × 4, and 2 × 2 surface supercells) and compute the energies of these surface cells from DFT. We use these DFT energies as the initial input to the CE. We then use the CE Hamiltonian to find low energy structures, calculate these new structures with DFT, and include them in a new CE. We repeat this process and iteratively improve the CE fitting. The resulting CV score for the surface CE is ∼2 meV per surface site. Figure 3 shows the DFT energies of about 90 structures that are used as input to train the surface CE Hamiltonian. There are many low energy structures that have negative formation energies with respect to the pure Au/Pt(111) and pure Pt/Pt(111) surfaces. We can draw lines connecting the low-energy structures to form a convex hull, indicating the existence of stable ordered surface structures in the surface. Interestingly, when examining these low-energy structures in detail, we find that these structures are all Au and Pt “striped” structures of different periods, as shown in Figure 4a. These striped structures are plotted as red dots in Figure 3 with the size of the dots demonstrating the period of the stripes. For long supercells with alternating Au–Pt stripes, the average period of these stripes is used (e.g., for the striped structure Au3/Pt2/Au3/Pt3, the average period is 5.5). Similar striped structures have also been observed in surfaces of other bulk-immiscible metals.20

![Figure 3](image-url)

**Figure 3.** GGA calculated formation energies of Au–Pt surface alloys on Pt(111). The gray lines connecting the lowest energy structures show a convex hull, indicating ordered structures exist for the surface. Red dots are striped structures (Figure 4a) with the size of the circles showing the average period of the stripes. The black line shows the formation energies of the random surfaces, and the green square is the formation energy of the 2D SQS (Figure 7).

![Figure 4](image-url)

**Figure 4.** The striped (a) and herringbone (b) structures on Au–Pt (111) surface. The striped structure is more stable than the herringbone structure because the atoms at boundaries have less energetically unfavorable Au–Pt bonds. The yellow balls are Au atoms, and the gray balls are Ag atoms.
Table 1. Formation Energy $E_F$ of Au–Pt/Pt(111) Striped Structure ($3 \times 3$) (Similar to Figure 4a) at 50% Composition with Different Exchange-Correlation Functions

<table>
<thead>
<tr>
<th>XC</th>
<th>$E_F$ (meV/surface atom)</th>
</tr>
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<tbody>
<tr>
<td>PW91$^{168}$</td>
<td>-12.7</td>
</tr>
<tr>
<td>PBE$^{95}$</td>
<td>-9.1</td>
</tr>
<tr>
<td>LDA</td>
<td>-5.2</td>
</tr>
</tbody>
</table>

We note that the ground-state striped structures have formation energies that are negative, but very small in magnitude, only a few meV per surface atom. To verify that the relatively small negative formation energy is not an artifact of a particular exchange-correlation functional, we calculate the formation energy of the Au$_3$/Pt$_3$ striped structure (similar to Figure 4a) using three different functionals (Table 1). There are small differences in the energies between the different exchange-correlation functions, but all formation energies are negative, indicating the stability of these ordered striped phases with respect to decomposition into pure Au and pure Pt surface layers.

Our results suggest an energy preference for striped structures relative to other ordered surface structures in Figure 3. For example, the formation energy for the Au$_3$/Pt$_3$ striped structure along [1T2] (Figure 4a) is $-3.0$ meV per surface atom (striped structures of fcc(111) are always along the symmetrically equivalent [1T2] directions), but for a similar herringbone structure along [110] (Figure 4b), the formation energy increases to $+2.8$ meV per surface atom. Although these two surface structures both have an equal number of Au and Pt atoms, the ordering of the Au and Pt atoms in the surface determines the stability of the surface alloy. The subtle structural difference between these two structures is the number of Au–Pt bonds that the boundary atom has. For the striped structure, each atom at the stripe boundary has 2 Au–Pt bonds, but the boundary atom in the herringbone structure has an average 2.67 Au–Pt bonds. Because Au–Pt is immiscible in the bulk, the Au–Pt bonds are energetically unfavorable in the bulk. Assuming the Au–Pt bonds are still unfavorable in the surface and the striped structure has fewer such bonds at the Au–Pt boundaries, the striped structure is energetically stable while the herringbone structure is not. We will show that the existence of the striped ordered phases can be rationalized even with unfavorable Au–Pt bonds.

The prediction of the 0 K stable striped structures in Au–Pt surface alloys from our DFT+CE method indicates an ordering tendency for the Au–Pt/Pt(111) surface. Characteristics of ordered Au–Pt surface structure have been observed by LEED,$^{90}$ TEM,$^{90}$ and STM studies,$^{88}$ suggesting Au–Pt is likely to form small ensembles with a preference of like atoms to be neighbors in the surface. Stephens et al.$^{31}$ calculated the shape distributions of Pt ensembles in Au–Pt/Pt(111) at finite temperatures from Monte Carlo simulations. They also concluded that the interactions between like atoms are favored over Au–Pt interactions for the Au–Pt/Pt(111). These experimental and theoretical results are in agreement with our CE result. Because of the iterative procedure in our CE study that is able to include very long supercells to simulate the striped structures, we predict the existence of stable ordered Au–Pt striped structures that have not been identified before.

2. Determining the Period of Stripe Ordering: Strain versus Ligand Effects. The formation energies of the striped structures also show some interesting behavior as a function of the period of the stripes. For example, we calculated formation energies of five striped structures of different periods at 50% Pt composition and show them as the purple dots of different sizes in Figure 3. The size of the dot is related to the period of the striped structure. For the four smaller periods (Au$_3$/Pt$_1$, Au$_4$/Pt$_2$, Au$_5$/Pt$_3$, and Au$_6$/Pt$_4$ stripes), the formation energy of the striped structure decreases as the period increases. However, the longest period (Au$_8$/Pt$_8$ stripes) has higher energy than the second largest dot. Similar trends are also found in striped structures at other compositions (e.g., 43% and 57% Pt). [For other compositions (e.g., 25% and 66% Pt), we only calculate the formation energies of striped structures with smaller period.] The existence of a minimum in the formation energy versus stripe period can be explained in terms of two competing forces that result in a surface striped structure with an optimum period.$^{21}$ The formation of a long-period striped structure serves to reduce the unfavorable bonds between unlike atoms at stripe boundaries (ligand effect), while a short period stripe helps relax the strain energy due to the size-mismatch between the surface and subsurface atoms (strain effect).

To further explore this connection between the stable striped period and the competing forces of strain and ligand effects, we use DFT to calculate the formation energies of striped structures at 50% composition with different periods for three different surface alloy systems: Au–Pt/Pt(111), Pt–Pd/Pt(111), and Au–Pd/Pd(111) (Figure 5). These three alloys span a range of size-mismatch and bulk ordering or phase-separating behavior, and hence span a range of ligand and strain contributions. Both Au–Pt and Pt–Pd phase separate in the bulk, but Au–Pd is ordered in the bulk.$^{82}$ Au–Pt has a size-mismatch of $\sim 4\%$, while Pt–Pd is $\sim 2\%$ and Au–Pd is $\sim 5\%$. For Au–Pt and Pt–Pd surface alloys, the formation energies of the striped structures of the two surfaces show a similar dependence on the stripe periods. For stripes of shorter periods, the ligand effect of unfavorable bonds dominates the formation energy, which decreases quickly with increasing stripe period. The size-mismatch between surface and subsurface atoms causes an accumulation of strain energy with increasing period of the stripes and leads to a gradual increase in formation energy for structures of larger period. Because of the smaller difference in the size between Pt and Pd, the long-period strain effect has a smaller contribution for the Pt–Pd/Pt(111). The energetic trend of striped structures is different for Au–Pd surface alloys, which increases with the stripe period monotonically. Distinct
from the other two alloys, the Au—Pd bonds are energetically favorable as Au—Pd is ordered in the bulk. Although striped structure is not the ground-state structure of Au—Pd/Pd(111) surface, the energetics of the Au—Pd stripes can also be explained from the strain and ligand effects. The formation of stripes in the surface reduces the number of favorable Au—Pd bonds. Thus, the ligand effect in this alloy prefers short-period stripes. Because strain effect still favors shorter stripes, there is no competition between the two effects for Au—Pd, and the lowest energy striped structure is the structure with the shortest period.

We quantitatively decompose the formation energy of Au—Pt striped structures into the strain relaxation and surface ligand effect in Figure 6. The energy decrease from strain relaxation is calculated from DFT by computing the energy difference between the slab where surface atoms are fully relaxed and the slab with atoms fixed at their bulk equilibrium positions. The energy change associated with the ligand effect is calculated as the formation energy minus the strain relaxation energy. For the structure with the shortest period of 2 atoms, the energy associated with the surface ligand effect, or the energetically unfavorable Au—Pt bonds, is \( \sim 60 \text{ meV} \) per surface atom. Although the strain relaxation for the structure is the largest \( \sim 40 \text{ meV} \) per surface atom), many of the surface ligand effect, and as a result, the formation energy for the striped structure is still positive. The energy change from surface ligand effect decreases as the period increases and is roughly proportional to \( 1/\text{period} \). As compared to the Au\(_2\)/Pt\(_3\) striped structure, the energy decrease for the Au\(_4\)/Pt\(_4\) striped structure from the ligand effect is 31 meV per surface atom, but the energy increase from strain accumulation is only 5 meV per surface atom. For longer periods, the increase of the strain accumulation overtakes the reduction in surface ligand effect, making the formation energy increase gradually with period.

**D. Oxygen Adsorption on Disordered Au—Pt Surface Alloy.** Ordered striped structures are the stable 0 K ground states of Au—Pt/Pt(111), but the small negative formation energies of these ordered structures suggest that they might undergo order—disorder transformations at low temperatures. In Figure 3, we show the formation energies of random surfaces (i.e., random arrangements of Au and Pt in the surface layer) at different compositions calculated using the CE Hamiltonian. The random surfaces of Au—Pt have small positive formation energies. At 50% Pt, the difference in formation energies between the random surface and the stable Au\(_4\)/Pt\(_4\) striped structure is only 23 meV per surface atom (corresponding to \( kT \) near 300 K). To study oxygen adsorption on the Au—Pt surface as a function of temperature, we must consider both the ordered striped structures as well as a disordered surface alloy.

We have generated a 16-atom SQS for a binary fcc(111) surface at 50% composition (Figure 7). An ideal binary random surface at 50% composition has all pair and multibody correlation functions to be zero. The generated SQS has similar values in correlation functions with the pair correlation functions for the first three nearest neighbor sites to be exactly the same value as a random surface (Table 2). The DFT formation energy of the SQS is 11 meV per surface atom, which is \( \sim 3 \text{ meV} \) higher than the formation energy of a random surface from the surface CE (Figure 3).

We calculate the oxygen binding energy for each of the 16 fcc sites of the SQS (Figure 8) using eq 1. These 16 binding energies show a

![Figure 6. Decomposition of the formation of energy into the surface ligand effect and strain relaxations. The combination of the surface ligand effect and the strain effect results in an optimum stripe period of the lowest energy.](image-url)

![Figure 7. 16-atom SQS for binary fcc(111) surface at 50% composition. Circled numbers are fcc adsorption sites for binding energy calculations.](image-url)

![Figure 8. Oxygen binding energy of different fcc sites on 2d SQS structure for AuPt/Pt(111). Triangular dots show the number of first nearest neighbor Au atoms to oxygen. Dashed lines show the binding energy of oxygen on fcc sites of Pt(111) and a monolayer of Au/Pt(111). A strong correlation between binding energy and the type of first nearest neighbor atoms is observed.](image-url)

<table>
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**Table 2. Correlations 1/F of 2D SQS for fcc(111) Surface at 50% Composition (Figure 7)**
The oxygen binding energies exhibit some interesting properties due to the special geometry of the striped structure. For the fcc sites with all nearest neighbors to be Pt atoms (site 5 and 6) on the striped structure, there is a considerable deviation of the oxygen binding energy from the pure Pt surface. The oxygen binding energy at site 6 is 0.47 eV per oxygen smaller than a pure Pt surface and about 0.34 eV per oxygen smaller than site 14 in Figure 7, on a disordered surface. This change in the oxygen binding energy is probably related to the compressive strain in the Pt stripes of the Au–Pt surface. Because the compressive strain between the alloy surface and its substrate usually induces a downward shift of the d-band of the overlayer transition metal, the binding energies are usually smaller on these surfaces because of the weaker interactions between the adsorbates and metal surface. Another interesting property is that the binding energies are different for different sides of the same stripes (site 1 and site 4) because of the different local environment of these sites. There are two Au nearest neighbor atoms for site 1 but only one Au nearest neighbor atom for site 4.

IV. CONCLUSIONS

We studied the surface structure and ordering of Au–Pt/Pt(111) using a first-principles cluster expansion method. A series of thermodynamically stable, laterally ordered striped structures of Au–Pt were found in the surface of this bulk phase-separating system. We have calculated the formation energy change with the stripe period and the effect from surface ligand effect and strain relaxation. It is shown that the formation of such ordered structures is the result of a competition between the strain relaxations from stripes and the unfavorable Au–Pt bonds at stripe boundaries. We have also investigated the oxygen adsorption on these ordered structures and disordered Au/Pt/Pt(111). The disordered surface is modeled by a 2D special quasirandom structure that has similar pair and triple correlation functions of a disordered binary distribution. The oxygen binding energy is found to be highly correlated with the type of nearest neighbor surface atoms of oxygen in both cases. The surface alloy thus induces a heterogeneous distribution of surface reactive sites, much like the heterogeneity that arises from geometric defects in a metal surface, which is intrinsic to multifaceted metal particles, or that arises from interactions between adsorbates at finite coverage. The work reported here is a step forward in learning to control this heterogeneity through alloying that may ultimately be useful for catalyst design.

APPENDIX: DESCRIPTION OF 16-ATOM SQS STRUCTURE FOR FCC(111)

The following table gives the lattice vector and atomic coordinates of the SQS structures used for fcc(111) at x = 1/2. Lattice vector and the atomic coordinates are given in Cartesian coordinates in the unit of fcc unit cell vector a. The correlation functions of the SQS are listed in Table 2.

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<th>lattice vectors</th>
<th>atomic occupations and positions</th>
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<tr>
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