A simple descriptor and predictor for the stable structures of two-dimensional surface alloys

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Predicting the ground state of alloy systems is challenging due to the large number of possible configurations. We identify an easily computed descriptor for the stability of binary surface alloys, the effective coordination number $E$. We show that $E(M)$ correlates well with the enthalpy of mixing, from density functional theory (DFT) calculations on $M_x$Au$_{1-x}$/Ru [$M$ = Mn or Fe]. At each $x$, the most favored structure has the highest [lowest] value of $E(M)$ if the system is non-magnetic [ferromagnetic]. Importantly, little accuracy is lost upon replacing $E(M)$ by $E^*(M)$, which can be quickly computed without performing a DFT calculation, possibly offering a simple alternative to the frequently used cluster expansion method.

INTRODUCTION

The goal of rational materials design is the in silico engineering of novel materials which possess optimal properties for specific applications [1]. However, this still remains a daunting task; a significant obstacle is that we do not, at present, have any simple way of predicting the structure that corresponds to the global minimum in the configurational space of a material with a given chemical composition. One therefore has to examine a large number of candidate structures before one can be reasonably confident that one has found the structure corresponding to the ground state. This procedure is time-consuming, both because of the very large number of configurations that have to be screened, and because each individual calculation (typically performed using ab initio density functional theory) can itself be computationally demanding.

In order to save computational time, one therefore looks for 'descriptors' [2]. A good descriptor is a quantity that is easily computed, yet correlates well with the property of interest (e.g., the structural stability). Moreover, to be truly useful, a descriptor should ideally also function as a predictor, i.e., one should be able to foretell the properties of a new system with high accuracy, without having to perform the ab initio calculation at all. Though certain descriptors also incorporate a degree of physical insight (e.g., the d-band center [3] or the generalized coordination number [4], both of which have been shown to correlate well with catalytic activity), in more complex cases, it is difficult to attribute physical interpretations to the form of the descriptor. For instance, it is possible to systematically build up multi-dimensional descriptors for various properties of materials using machine learning algorithms. This has been shown, e.g., by Ghiringhelli et al. for the crystal structures of binary octet compounds [5].

One area of condensed matter physics which would benefit greatly from efforts to develop such descriptors is the study of alloys. This could offer an alternative to the cluster expansion method (CEM), which has hitherto been perhaps the most promising approach toward tackling the challenging problem of computing stable alloy phases [6,7]. In the CEM, a set of dominant interactions is determined by fitting to a database of first-principles results; this expansion is then used to extrapolate to much larger unit cells. The advantage of the CEM is that it can save considerable time (compared to a full-fledged DFT calculation), the disadvantage is that there is no general rule about how many or which terms in the expansion should be retained, and large databases may be necessary. There have also been several attempts by previous authors to rationalize the phase diagrams of bulk alloys in terms of a few simple parameters [9–13], with mixed success. Here we consider the somewhat more tractable problem of two-dimensional binary surface alloys. We show that a single easily computed descriptor, the 'effective coordination number' $E$, correlates well with the energetics of various alloy configurations. Interestingly, we show that the most favored value of $E$ flips, depending on whether the system is non-magnetic or ferromagnetic. Moreover, we show that though $E$ requires knowledge of the relaxed structure (which, in principle, would be known only at the end of a DFT calculation), it can be replaced, with little loss of predictive power, by another quantity $E^*$ which makes use of unrelaxed geometries.

As proof-of-concept, we present results on four systems: (i) non-magnetic and (ii) ferromagnetic states of two binary systems: (a) Fe-Au and (b) Mn-Au, always on a Ru(0001) substrate.

Surface alloys are systems with two or more elements forming a two-dimensional alloy on a substrate [14]. These alloys display atomic level mixing in the surface layer; magnetic surface alloys are particularly appealing, both because it has been shown theoretically that exchange interactions can contribute significantly to miscibility [15,16], and because of the possibility of using them in a variety of applications related to magnetic memory storage and spintronics. The reduced symmetry in such a system could conceivably lead to a variety of interesting properties, such as enhanced magnetic moments and/or an increase in the magnetic anisotropy energy. It is especially intriguing to note that it is possible to form surface alloys out of elements that are immiscible in the bulk [14,17]. Of
the binary systems considered in this study, we remark that Fe and Au are essentially immiscible in the bulk, though they have been shown to form a stable surface alloy with long range order when co-deposited on Ru(0001); however, Mn and Au do form stable bulk alloy phases \[15, 16\].

Our calculations have been performed using either spin-polarized or non-spin-polarized density functional theory (DFT) as implemented in the Quantum ESPRESSO package \[21\], which uses a plane-wave basis set. The plane-wave cutoffs for the expansion of the electronic wave functions and the related charge densities were set as 40 and 400 Ry, respectively. Ultrasoft pseudopotentials \[21\] were used to describe the ion-electron interactions, while the exchange-correlation functional was treated within a generalized gradient approximation of the Perdew-Burke-Ernzerhof form \[22\].

In this paper, we restrict ourselves to considering pseudomorphic surface alloys, by which we mean that the atomic density in the surface layer is equal to that in the substrate layers. This approximation is expected to be valid for both systems considered by us, since the bulk nearest neighbor (NN) distance of the Ru substrate lies in between that of Au and that of either Fe or Mn. However, we can either choose to permit in-plane as well as out-of-plane relaxations of the atoms in the surface layer (we will refer to this as PR, for pseudomorphic relaxed), or force the surface atoms to remain at the hexagonal close packed (hcp) sites on the Ru(0001) surface (PU, for pseudomorphic unrelaxed). Note that the PR positions can only be obtained by performing an \textit{ab initio} DFT calculation where the geometries are relaxed making use of Hellmann-Feynman forces, whereas no DFT calculation is necessary to obtain a PU structure. In the PR calculations, the threshold for convergence of forces was kept at 0.025 eV/Å.

For every surface alloy composition $M_x\text{Au}_{1-x}/Ru(0001)$ an infinite number of atomic configurations is possible, with varying numbers of atoms in the surface unit cell. As already mentioned above, this is what makes the problem of finding the most stable structure by a search through all possible configurations intractable. We therefore first generate all possible structures containing one to five atoms per surface unit cell, and several containing six atoms; in this way, we obtain 41 distinct symmetry-invariant periodic structures \[16\]. For each structure, we both ‘permit’ magnetism (by performing a spin polarized DFT calculation) and ‘suppress’ magnetism (by performing a non-spin-polarized calculation). We divide these 41 structures, according to their structural similarities, into nine groups (A)–(H) \[see supplementary material\]. We used these to group the ion-electron interactions, while the exchange-correlation functional was treated within a generalized gradient approximation of the Perdew-Burke-Ernzerhof form \[22\].

For all the structures considered here, we find that the FM and NM states, the enthalpy of mixing $\Delta H$ for the surface alloy, relative to the phase segregated components $M/Ru$ and $Au/Ru$, is given by:

$$\Delta H = E(M_x\text{Au}_{1-x}/Ru) - xE(M/Ru) - (1-x)E(Au/Ru),$$ \[1\]

where $E(X)$ is the total energy of system $X$, and the first two terms on the right-hand-side are both evaluated in the corresponding magnetic state, while the third term is always non-magnetic. For a given surface alloy to be stable, a necessary but not sufficient condition is that $\Delta H < 0$.

In Figs. 1(a) – (d), we have plotted the enthalpy of mixing $\Delta H_{NM}$ and $\Delta H_{FM}$, for all the structures in the NM and the FM states, respectively \[we note that the results in Figs. 1(b) & (d) are very similar to those previously published in Ref. 15\]. These graphs have several noteworthy features: (i) though $\Delta H_{FM} < 0$ always, in some cases $\Delta H_{NM} > 0$, i.e., in some cases the stability is provided solely by exchange interactions, (ii) $|\Delta H_{FM}| \gg |\Delta H_{NM}|$, i.e., even in the other cases, a large part of the stability arises from magnetism \[15, 16\], and (iii) of particular interest for the issues we wish to focus on in this paper, in general, the lowest energy configurations (see the colors of the circled dots) differ in the NM and FM cases (except for a few configurations at large $x$).

To determine which of these lowest energy configurations of $M_x\text{Au}_{1-x}/Ru(0001)$ are stable with respect to phase segregation, we have computed the NM and FM convex hulls \[shown by the dashed and solid lines, respec-
surface. Instead, we define the effective coordination number of nine for any atom on a hcp(0001) plane. The coordination number of nine for any atom on a hcp(0001) plane would not suffice, yielding a nominal coordination number of less than nine. Since in the bulk structure of the atom the sum is taken over all the neighboring atoms, the sum is taken over all the neighboring atoms, of type \( T_j \), at a distance \( r_{ij} \) from the \( i \)th atom in the surface layer. The denominator is evaluated in the bulk structure of the atom \( i \), the sum is taken over all the neighboring atoms, of type \( T_j \), at a distance \( r_{ij} \) from the \( i \)th atom in the surface layer.

\[
\mathcal{E}(i) = \frac{\sum_j \rho_{T_j}(r_{ij})}{\sum_j \rho_{T_j}(r_{ij})}
\]

where in the numerator, the sum is taken over all the neighboring atoms, of type \( T_j \), at a distance \( r_{ij} \) from the \( i \)th atom in the surface layer. The denominator is evaluated in the bulk structure of the atom \( i \), the sum is taken over all the neighboring atoms, of type \( T_j \), at a distance \( r_{ij} \) from the \( i \)th atom in the surface layer.

Note the clustering of points that belong to the same group of configurations, for both the magnetic and non-magnetic cases. Not only is \( \mathcal{E}(M) \) simple to compute, it also lends itself easily to physical interpretation, and provides an ideal tool for examining two of the principal interactions that compete in determining the stability of surface alloys, viz., the band energy \( E_b \) and magnetic energy \( E_m \).

\[
E_b = \int_{\Delta E_F} \epsilon n(\epsilon) \, d\epsilon
\]

\[
E_m = \sum_{\alpha} \sum_{\beta} E_{\alpha \beta}
\]

It is known that the stability of a surface alloy is determined mainly by two factors: the band energy and (if magnetic) the exchange energy terms [23]. The exchange energy terms are given by

\[
\mathcal{E}(M) = \sum_{j} \rho_{T_j}(r_{ij})
\]

where \( \rho_{T_j}(r_{ij}) \) is the atomic charge density at a distance \( r_{ij} \) from the nucleus of an isolated atom of type \( T_j \). When computing the denominator in Eq. [2], we have considered the \( \alpha \)-Mn structure for Mn, the bcc structure for Fe, and the fcc structure for Au. In those two-dimensional surface alloy structures that contain more than one kind of symmetry-invariant atom of species \( \alpha \), we compute \( \mathcal{E}(i) \) by taking an appropriately weighted average over the different kinds of \( i \) atoms. \( \mathcal{E}(i) \) reflects the ambient electron density at the site of the atom \( i \), in the spirit of the embedded atom model or effective medium theory [25, 27].

In Figs. 2(a) – (d), we plot the values of \( \mathcal{E}(M) \) for the PR structures of all the 41 configurations considered by us; note the clustering of points that belong to the same group of structures. Importantly, we see that for the two NM systems, the lowest energy structure is almost always the structure with the largest value of \( \mathcal{E}(M) \) [see the positioning of the red circles at each value of \( x \)]. However, the situation is exactly the opposite when we go to the FM cases: the lowest energy structure is almost always the one with the smallest value of \( \mathcal{E}(M) \) [see the black circles]. Moreover, we find that at each value of \( x \), in general, as \( \mathcal{E}(M) \) increases, \( \Delta H_{NM} \) decreases, and \( \Delta H_{FM} \) increases. On the whole, \( \mathcal{E}(M) \) acts as an excellent descriptor, indicating not just the best possible structure of the surface alloy, but also the relative ordering of the entropy of formation of different configurations, for both the magnetic and non-magnetic cases.

Not only is \( \mathcal{E}(M) \) simple to compute, it also lends itself easily to physical interpretation, and provides an ideal tool for examining two of the principal interactions that compete in determining the stability of surface alloys, viz., the band energy \( E_b \) and magnetic energy \( E_m \). When \( \mathcal{E}(M) \) is large, hybridization between \( M \) atoms is enhanced, and the bandwidth is increased. As a result, \( E_b \) becomes large, where \( \epsilon \) runs over the electronic energies, \( n(\epsilon) \) is the electronic density of states, and \( E_F \) is the Fermi energy (set equal to 0). Note that with this definition, \( E_b < 0 \). Note also that a large \( \mathcal{E}(M) \) would imply a broad and low \( n(\epsilon) \), and thus a low value of \( n_{NM}(E_F) \), the non-magnetic density of states at the Fermi energy. According to the Stoner model [28], this would disfavor ferromagnetism. In contrast, when \( \mathcal{E}(M) \) is

![FIG. 2: (Color online) Value of the descriptor \( \mathcal{E} \) for all 41 configurations considered, as a function of \( x \), the concentration of Mn or Fe atoms, for (a) – (c) \( Mn_{1-x}Au_x/Ru(0001) \) and (d) – (f) \( Fe_{x}Au_{1-x}/Ru(0001) \). See supplementary material for the structures in groups (A)-(H). NM, FM and PU refer to the non-magnetic, ferromagnetic and pseudomorphic unrelaxed cases, respectively. Configurations have been grouped according to their symmetry, with each group indicated by a different color. The points corresponding to the lowest energy NM and FM configurations have been circled in red and black, respectively. Note that in Fig. (e) the red and black circles coincide for \( x \geq 0.75 \), whereas in Fig. (f), they coincide only for \( x = 0.67 \).](Image)
is low, the bandwidth is decreased, and exactly the reverse arguments apply. Thus, in such a situation, $E_b$ would be small and $E_m = -Im^2$ would tend to be large, where $I$ is the Stoner parameter, and $m$ is the magnetic moment. Thus, our findings should hold for systems where the stability of surface alloys is dominated by either band energy or exchange energy terms. It remains to be verified whether this continues to hold true, e.g., when magnetic moments on the $M$ atoms are small, or elastic effects are strong.

An important question remains: can one predict the lowest energy configuration without doing the DFT calculations? Note that while calculating $\delta(M)$ to obtain the points in Figs. 2(a) – (d), we made use of fully relaxed atomic PR coordinates, which one can obtain only after performing DFT calculations. We now check what would happen if we instead used the PU coordinates. The effective coordination number thus obtained is defined as $\delta^*$ and is plotted in Figs. 2(e) and (f). We see that for the most part, the correct lowest energy structure is predicted even using $\delta^*(M)$.

As a test of the performance of $\delta^*(M)$ as a predictor, in Fig. 3 we have plotted four graphs; as the abscissa we have $\delta^*(M)$, and as the ordinate we have $\Delta H$ as calculated from DFT. If $\delta^*(M)$ is a good predictor, it should correctly identify the configuration with the lowest $\Delta H$. We see that for the sample case that we have plotted ($x = 0.4$), $\delta^*(M)$ correctly predicts the lowest energy structure in all four cases, and further, there is a reasonably good correlation between the values of ordinate and abscissa, with only small deviations from monotonicity. There are two ways in which $\delta^*$ can ‘underperform’: the lowest energy structure may not correspond to an extremal value of $\delta^*(M)$, though it may lie close in energy; alternatively, more than one structure could conceivably correspond to the extremal value of $\delta^*(M)$, because of the high symmetry of the PU structures. However, one can still save considerable computational time by first generating PU configurations, calculating $\delta^*(M)$, thus identifying a pool of ‘best’ candidate structures (the ones that are predicted to be the lowest few in energy), and then performing ab initio calculations on only this reduced pool of structures.

One can also try to understand why, in some cases, $\delta^*(M)$ predicts the ground state structure incorrectly. For example in Fig. 2(e) and (f), at $x = 0.5$, we find that the NM configuration with the highest $\delta^*(M)$ has a rather high and anisotropic stress, and the system instead chooses to form in a structure which, while having a reasonably high $\delta^*(M)$, has an isotropic surface stress.

In summary, we suggest that a quantity that is easy to compute, the effective coordination number $\delta^*$, serves as a good descriptor for the stability of binary surface alloys on a substrate. For magnetic surface alloys, the lowest energy configuration is almost always the one with the lowest value of $\delta^*(M)$; in contrast, in the non-magnetic case, the most favored configuration tends to have the highest value of $\delta^*(M)$. We note that though in the systems studied in this paper, $M$ is always the ‘magnetic’ element, for a general binary alloy comprised of non-magnetic atoms, $M$ will correspond to the atom with the smaller atomic radius.

Further, even if one instead calculates $\delta^*(M)$ using ‘pseudomorphic unrelaxed’ coordinates (sidestepping the need for an ab initio calculation) one can predict, with a high success rate, the configuration which will have the lowest energy. The success rate can be further improved by extending the pool of candidate structures to include the few configurations which have the highest (for NM) or lowest (for FM) values of $\delta^*(M)$ and then performing first-principles calculations only on this considerably reduced number of structures. Here, we have demonstrated that the above statements hold for four model systems (two magnetic and two non-magnetic). The ease of computation of $\delta^*$ allows one to greatly expand the space of alloy configurations searched, at minimal additional cost, thus making it ideal for incorporation within high-throughput programs of computational materials discovery targeted at specific applications.

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Supplementary Information to the paper “A simple descriptor and predictor for the stable structures of two-dimensional surface alloys”

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Here, we have listed the optimized structures of all the configurations considered by us for the ferromagnetic (FM) case [see Figs. S1–S8]. The relaxation of the overlayer atoms are slightly different in the non-magnetic (NM) configurations (not shown here). Note that all the structures are grouped according to their structural similarities. The dark (blue online) and gray (golden online) spheres represent the Mn and Au atoms, respectively; the smaller black dots represent the positions of the Ru atoms on the first substrate layer.

FIG. S1: Group A

FIG. S2: Group B
FIG. S3: Group C

FIG. S4: Group D

FIG. S5: Group E
FIG. S6: Group F

(a) $x = 0.33$

(b) $x = 0.4$

FIG. S7: Group G

(a) $x = 0.5$

FIG. S8: Group H

(a) $x = 0.6$

(b) $x = 0.67$

(c) $x = 0.67$

(d) $x = 0.75$

(e) $x = 0.75$

(f) $x = 0.8$

(g) $x = 0.83$