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# Segregation at the PdAg(111) surface: Electronic structure calculations

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An efficient procedure to calculate surface segregation profiles of substitutionally disordered binary alloys is presented. We show that a simple thermodynamic model with realistic atomic configurations at the surface region combined with the total energies obtained from exact muffin–tin orbitals calculations leads to accurate surface segregation profiles. We find that the calculated surface segregation energies in random alloys show significant dependence on the local environment of the atoms involved in the segregation process. Correspondingly, the alloy surface energy is significantly affected by the subsurface atomic layers. As an example the PdAg(111) surface is considered.

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## I. INTRODUCTION

Surface related phenomena play an important role in various fields of human interest. The reaction paths and rates of the surface processes depend crucially on the properties of the considered surface. One natural way to produce a surface having optimal properties for a specific task is to exploit segregation at alloy surfaces. To benefit most of this quasi-two-dimensional world requires the understanding of the foundations of surface chemistry and surface physics at the atomic level. Unfortunately, the experimental data about the multilayer surface segregation are scarce. Concentrations within the top surface layer have been obtained, e.g., by Auger electron spectroscopy (AES),[1] scanning tunneling microscopy (STM)[2] and electronic work function measurements.[3] However, it is very difficult to get reliable data of the segregation in the subsurface layers. Thus, accurate theoretical determination of the segregation profiles of alloy surfaces is of high importance.

Former theoretical segregation profiles have also been inadequate. Most of the first principles computational investigations have been focused on dilute alloys at the impurity level [see, e.g., (Ref. 4) and references therein]. Here we present a new procedure based on *ab initio* alloy theory to investigate surface segregation profile in random substitutional alloys. To elucidate our approach we study the (111) surface of face centered cubic (fcc) $Pd_{0.5}Ag_{0.5}$ random alloy. Pd and its alloys are important materials in chemical industry as catalysts and in hydrogen technology as storage and sensor materials.[5–7] In addition, the PdAg alloy is also interesting from a theoretical point of view as an example of alloys having continuous solid solubility in the fcc crystallographic structure.

The present surface segregation model is described in Sec. II, where, for completeness, we also give the most important numerical details of our calculations. The theoretical results for the segregation profile, segregation energies, and surface energy are presented and discussed in Sec. III.

## II. METHOD

### A. Theory

Our procedure is based on electronic structure calculations for realistic atomic configurations at the surface region by using the full charge density (FCD)[8] exact muffin–tin orbitals (EMTO)[9–11] method combined with a simple thermodynamic model.[12,13] Within the EMTO formalism we calculate the one-electron kinetic energies exactly for the optimized overlapping muffin–tin potential, so it provides an excellent ground for accurate FCD based calculations. Combined with the Coherent Potential Approximation (CPA)[14] the EMTO method is superior compared to the former approaches within the alloy theory.[13,15,16]

The semi-infinite bulk surface system is modeled by a slab consisting of $N_t$ atomic layers parallel to the surface. The layers are divided into two groups: surface region (marked by s) of thickness $N_s$ layers and bulk region ($b$) consisting of $N_b$ layers. To retain the periodicity of the model system an infinite array of the slabs separated by $N_e$ vacuum layers is considered. The number of atoms within the unit cell belonging to the layer $i$ is $n_i$, whereas $n_b$ and $n$ denote the average number of atoms per layer in the bulk region and in the whole slab, respectively.

Let us consider a binary alloy of components $A$ and $B$ with concentrations $c_i^A = c_i$ and $c_i^B = 1 - c_i$ in the layer $i$. The conservation of the total number of atoms within the unit cell leads to the condition

$$N_b n_b c_b + 2\sum_{i=1}^{N_s} n_i c_i = N_t n c, \tag{1}$$

where $c_b$ is the average concentration of the atoms $A$ in the bulk and $c$ is the average concentration of $A$ atoms within the whole slab. The factor 2 appears because the slab has two identical surfaces.

The surface segregation profile is obtained by minimizing the Helmholtz free energy $F$ of the unit cell

$$F = U - TS, \tag{2}$$

where $U$, $T$, and $S$ are the internal energy, temperature, and entropy. The internal energy is obtained from self-consistent EMTO-CPA calculations. For the entropy we use the configurational mean field expression:

$$\begin{aligned} S = & - k_B N_b n_b [c_b \ln c_b + (1 - c_b)\ln(1 - c_b)] \\ & - 2k_B \sum_{i=1}^{N_s} n_i [c_i \ln c_i + (1 - c_i)\ln(1 - c_i)], \end{aligned} \tag{3}$$

where $k_B$ is the Boltzmann constant. For a fixed average slab concentration $c$ the optimal surface segregation profile $(c_1^o, \ldots, c_{N_s}^o)$ is obtained from a set of equations

$$\left. \frac{\delta F(c_1, c_2, \ldots, c_{N_s}; c_b)}{\delta c_i} \right|_{c_i = c_i^o} = 0, \tag{4}$$

with $i = 1, 2, \ldots, N_s$. In these equations $c_1, c_2, \ldots, c_{N_s}$ are treated as independent variables, while $c_b$ is determined from the condition (1).

### B. Numerical details

In the EMTO-CPA calculations the one-electron equations were solved within the scalar-relativistic and soft-core approximations. The Green function was calculated for 16 complex energy points distributed exponentially on a semicircular contour. In the EMTO basis set we included *s*,*p*, and *d* orbitals. The exchange-correlation potential was introduced within the local density approximation according to Perdew and Wang.[17] The slab calculations for the PdAg alloy were carried out using the theoretical equilibrium lattice parameter 7.513 a.u. This value is very close to 7.517 a.u. obtained in experiments.[18]

The atomic positions were fixed to the ideal fcc lattice sites. The atomic defects, relaxations and vibrations were not included in the present model. Former investigations based on the embedded-atom method[19] show that the average effects of the local lattice relaxation and vibrational entropy on the segregation energy in PdAg alloys are about 23% and 4%, respectively. According to experiments[20] and calculations[5] there is no reconstruction on the (111) surface of PdAg. Using the EMTO method we estimated the effect of the surface relaxation on the segregation profiles to be less than 1%.

For the unit cell we use the following notations: each atomic layer is shown within the brackets (), surface layer is 1, next layer is 2, etc. If atomic layers are identical they appear within the brackets [], and if atomic layers have the same concentration they appear within the brackets {}. When the composition of layers is fixed the Ag concentration is indicated by a subscript. The self-consistent calculations were carried out for 8- and 14-layers slabs using the unit cells (1s)(2s){(3b)(4b)} and (1s)(2s)(3s)(4s){(5b)[(6b)(7b)]}; where due to the symmetry of our slab only half of the atomic layers are specified. For the eight-layers cell $c_1$ and $c_2$ were chosen as the independent variables, and the concentration of the third and fourth layers were calculated according to Eq. (1). For the 14-layers cell we optimized the concentrations of the third and fourth atomic layers as well. All these unit cells included $N_e = 4$ vacuum layers.

The convergence of the total energy with respect to the number of $\boldsymbol{k}$-points and the thickness of the slab was tested in detail. We found that 141 $\boldsymbol{k}$-points in the irreducible wedge of the Brillouin zone and eight atomic layers within the slab are sufficient to obtain the required accuracy in the total energy.

## III. RESULTS

### A. Atomic interactions

To investigate the range of the atomic interactions we performed two test calculations for an additional 14-layers slab (1s)(2s){(3b)(4b)}{(5b)[(6b)(7b)]}$_{0.5}$, with the constraint $c_3 = c_4$ and $c_5 = c_6 = c_7 = 0.5$. In the first case we lifted the restriction that atoms belonging to the four central atomic layers of the unit cell to be identical, but still keeping the concentrations of the atomic layers fixed to 0.5, i.e., unit cell (1s)(2s){(3b)(4b)}{(5b)(6b)(7b)}$_{0.5}$. A 0.1 meV change in the total energy per atom was obtained. However, the slope of the total energy with respect to the concentration of the surface was not changed. This indicates that the surface induced oscillations of the electronic structure are small in the fifth and deeper atomic layers. Moreover, the fluctuations of the surface concentration have a negligible effect on these oscillations. The above conclusions are in accordance with the results obtained for pure elements.[21]

In the second test we increased the number of identical atomic layers in the central part of the slab from four to eight and introduced the concentration of the atomic layers to be equal from third atomic layer and onwards, i.e., considered the unit cell (1s)(2s){(3b)[(4b)(5b)(6b)(7b)]}. This changed the total energy per atom by more than 0.1 meV. What is more important, the slope of the total energy with respect to the surface concentration was significantly changed. This shows that the surface effects penetrate up to the third and fourth atomic layers inside the material.

### B. Surface segregation profile

The surface segregation profile at 0 K was determined up to the fourth surface layer using the 14-layers slab (1s)(2s)(3s)(4s){(5b)[(6b)(7b)]}. We found that the concentration profile corresponds to alternate Ag and Pd layers, with 100% Ag in the top layer. However, deeper in the bulk this profile is mainly due to bulk rather than to surface effects. This is because for bulk the ordered structure with alternate Pd and Ag (111) layers has lower energy than the substitutional disordered phase. Using the energy differences we estimated that the third and fourth layers reach the average disordered bulk structure at ~150 K. Therefore, our investigation at higher temperatures was restricted to the seg-

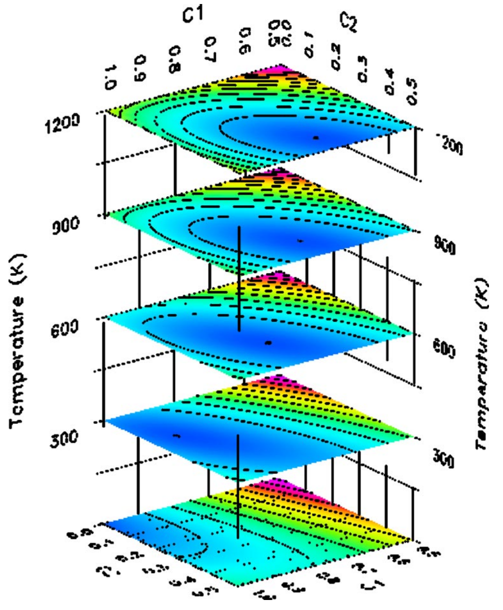

FIG. 1. (Color online) The Helmholtz free energy per unit cell of the PdAg slab as a function of the Ag concentration of the surface atomic layer ($c_1$) and the subsurface atomic layer ($c_2$). The separation between the constant-energy contours is 0.03 eV. To allow direct comparison between the plots at different temperatures the energy scale of each subplot is changed in such a way that the minimum of the free energy (shown as a black dot) corresponds to 0 eV in each subplot. For the minimum points see Table I.

TABLE I. Surface segregation profile for fcc (111) surface of PdAg random alloys: (1) is the Ag concentration in the surface layer, and (2) in the next layer. In our calculations "bulk" refers to the average Ag concentration within the whole slab [i.e., to $c$ from Eq. (1)], and the average concentration of layers 1 and 2 was balanced by using the bulk region as a reservoir. $T$ is the temperature and the last column shows whether the work is experimental (expt.) or theoretical (theor.).

| At. % Ag | | | | | |
|---|---|---|---|---|---|
| Bulk | (1) | (2) | $T$ (K) | Ref. | Method |
| 50 | 100 | 0 | 0 | [a] | Theor. |
| 50 | 92 | 19 | 300 | [a] | |
| 50 | 81 | 35 | 600 | [a] | |
| 50 | 75 | 41 | 900 | [a] | |
| 50 | 72 | 44 | 1200 | [a] | |
| 50 | 70–99 | | 673-873 | 1[b] | expt. |
| 50 | 54–63 | | | 1[c] | |
| 33 | 95 | | 820 | 2 | |
| <33 | 93 | | 720 | 2 | |
| <33 | 91 | | 770 | 2 | |
| <33 | 91 | | 820 | 2 | |
| <33 | 90 | | 920 | 2 | |
| 33 | 92 | | 250 | 20 | |
| 50 | 78 | | 870 | 23 | theor. |
| 50 | 75 | | 1000 | 24 | |
| 50 | 84 | | 800 | 25 | |

[a] Present work.

[b] AES data obtained without matrix correction.

[c] AES data with matrix correction included.

regation profile within two atomic layers at the surface using the (1s)(2s){(3b)(4b)} slab.

The Helmholtz free energy $F(c_1,c_2)$ from Fig. 1 was calculated at five different temperatures from 0 to 1200 K. The surface segregation profile [see Eq. (4)] at each temperature corresponds to the minimum point $[c_1^{\mathrm{o}}(T),c_2^{\mathrm{o}}(T)]$ of the free energy. The equilibrium concentrations $c_1^{\mathrm{o}}$ and $c_2^{\mathrm{o}}$ are given in Table I, where we also list the available experimental and former theoretical data.

At low temperature the surface layer of PdAg alloy is calculated to be Ag rich and the subsurface layer Pd rich. This is due to the higher surface energy of Pd compared to that of Ag. With increasing temperature the substitutional disordering is twice as rapid in the second layer as in the first layer (see also Fig. 1). Around 600 K this tendency towards disorder with increasing temperature begins to have equal rates in the first and second atomic layers.

In the following we compare our segregation results from Table I to the available experimental data. From detailed literature search we have found three independent measurements on the surface segregation of PdAg random alloys.[1,2,20] First we consider data reported in AES measurements.[1] In the AES experiments the surface composition is estimated from the Auger current. Due to the approximate relation between current and concentration, there is a significant uncertainty associated with these measurements. Following Reniers's suggestion[1] the true surface composition should be between the two sets of AES values from Table I. Accordingly, we estimate the average AES surface Ag concentration to be around 72%. The model employed in the interpretation of the AES data[1] assumes bulk like composition from the second surface layer. Lifting this constraint results in ~5% increase in the surface concentration. Taking into account these uncertainties in the experimental data we conclude that the average AES concentration is in very good agreement with our value of 75% near 900 K.

Wouda *et al.*[2] investigated surface segregation at the (111) surface of $\mathrm{Pd_{67}Ag_{33}}$ alloy by the STM technique. The Ag surface concentration was observed to decrease from 93% to 90% as the temperature is increased from 720 to 920 K. Based on semiempirical studies, Wang *et al.*[22] have shown that at moderate temperatures the top layer concentration is not very sensitive to the bulk concentration. This result indicates that it is meaningful to compare surface segregation data obtained for alloys encompassing 50% and 30% Ag. Therefore, we use the STM data to judge the accuracy of our results for the temperature induced changes in the surface Ag concentration. Using our surface concentrations from Table I, at temperatures between 600 and 1200 K for the average concentration slope $(\partial c_1/\partial T)$ we obtain −1.5% per 100 K. This value is in perfect agreement with the one calculated from the STM segregation profile between 720 and 920 K.[2] Finally, the 92% Ag surface concentration by Noordermeer *et al.*,[20] obtained at 250 K using thermal desorption spectroscopy, is also in very good agreement with our value at 300 K.

TABLE II. Segregation energies of Ag from the bulk to the first ($E_{\mathrm{segr}}^{1,\mathrm{b}}$) and to the second ($E_{\mathrm{segr}}^{2,\mathrm{b}}$) layers and from the second to the first layer ($E_{\mathrm{segr}}^{1,2}$).

| $c_1$ | $c_2$ | $E_{\mathrm{segr}}^{1,\mathrm{b}}$ (eV) | $E_{\mathrm{segr}}^{2,\mathrm{b}}$ (eV) | $E_{\mathrm{segr}}^{1,2}$ (eV) |
|---|---|---|---|---|
| 1.0 | 0.0 | −0.08 | 0.03 | −0.11 |
| 0.9 | 0.1 | −0.12 | 0.01 | −0.13 |
| 0.8 | 0.2 | −0.16 | −0.02 | −0.14 |
| 0.7 | 0.3 | −0.20 | −0.04 | −0.16 |

The results of Vurens *et al.*[23] were obtained by using the Monte-Carlo method with experimental parameters, while Foiles[24] used the embedded atom method. Their results, listed in Table I, suggest a surface segregation close to what we have obtained. Rousset *et al.*[25] used the equivalent-medium approximation with a modified tight-binding scheme. They predict a somewhat higher Ag surface concentration compared to our results.

In relation to the free energy surface from Fig. 1 we note the small asymmetry of the slope of $F(c_1,c_2)$ with respect to the $c_1=-c_2+1$ line. This suggests that diffusion in PdAg surfaces at various depths, relative to the surface, could be investigated by annealing. Denoting the diffusion rate of Ag between the atomic layers $i$ and $j$ by $R_D^{i,j}(T)$ the initial evolution of the concentration of Ag in the first and second layers of originally homogeneous disordered PdAg with increasing temperature is expected to be in between the limits $c_2\approx$constant ($R_D^{1,2}\approx R_D^{2,3}$) and $c_1\approx -c_2+1$ ($R_D^{1,2}\gg R_D^{2,3}$).

### C. Surface segregation energy

The surface segregation energy defined is the energy cost of interchanging an atom $A$ in the bulk with an atom $B$ at the surface. It can be calculated as the difference in the energies per unit cell of the system with atom $A$ at the surface and in the bulk, i.e.,

$$E_{\mathrm{segr}}^{1,b} = \frac{U_1 - U_b}{2n\Delta c_1}, \tag{5}$$

where $n$ is the number of atoms in one atomic layer within the unit cell. $U_1$ and $U_b$ are the energies per unit cell for the cases where the atom $A$ is at the surface and in the bulk, respectively. $\Delta c_1$ is the change in the concentration of the atomic type $A$ in the surface layer. Number 2 appears in the denominator because the unit cell contains two identical surfaces. In our case $n=1$ and in the limit $\Delta c_1\to 0$ we can write

$$E_{\mathrm{segr}}^{1,b} = \lim_{\Delta c_1\to 0}\frac{U_1 - U_b}{2\Delta c_1} = \frac{1}{2}\frac{dU}{dc_1}. \tag{6}$$

As above we can define the segregation energy for the second layer as $E_{\mathrm{segr}}^{2,b}=1/2\, dU/dc_2$ as well as the segregation energy from the second to the first layer $E_{\mathrm{segr}}^{1,2}=1/2\left(dU/dc_1-dU/dc_2\right)$.

The present results for the segregation energies are given in Table II, where the concentrations $c_1$ and $c_2$ are chosen in such a way that the concentration of the bulk part of our slab is the same ($c_b=0.5$) for all considered cases, thus enabling comparison between different cases in a consistent way.

As Table II shows the segregation energies depend drastically on the atomic environment. Therefore, the conventional way of relying only on the data of the pure elemental metals or on the impurity level data in predicting the surface concentration of PdAg alloys leads to inevitable errors. Interestingly, the calculated segregation energy $E_{\mathrm{segr}}^{1,b}$ of Ag with increasing homogeneity of the slab approaches the segregation energies obtained by Ruban *et al.*[4] for a Ag impurity segregating from the bulk to the surface of pure Pd (−0.26 eV) and for a Pd impurity segregating from the surface of pure Ag to the bulk (−0.28 eV). The present result for Ag in the homogeneous 50% PdAg is −0.28 eV, which compares very well with the above data by Ruban *et al.*. The similarity of the segregation energy in the cases of the homogeneous 50% alloy and the impurities in elemental metals can be related to the homogeneity of the solvent. In each case the segregating atom in the initial and final states is surrounded by alloys having the same local environments.

The temperature dependent surface concentration of alloys is frequently evaluated using the Langmuir-MacLean formula. Solving the formula

$$\frac{c_1}{1-c_1} = \frac{c_b}{1-c_b}\exp\left(\frac{-E_{\mathrm{seg}}^{1,b}(c_1,c_b)}{k_B T}\right) \tag{7}$$

with the segregation energy Eq. (6) is equivalent with minimizing the Helmholtz free energy (2). However, the usual way of taking the segregation energy $E_{\mathrm{seg}}^{1,b}$ to be independent of the local environment can lead to substantially wrong results. For instance, using the segregation energy of the homogeneous 50% PdAg alloy (−0.28 eV) in Eq. (7) leads to the Ag surface concentration of 97% at 900 K. This value is much higher compared to the calculated 75% from Table I.

### D. Surface energy

At temperature $T$ the surface free energy of an infinitely large slab is defined as

$$\gamma(T) = \frac{F_{\mathrm{slab}}(T) - F_b(T)}{2A}, \tag{8}$$

where $F_{\mathrm{slab}}(T)$ and $F_b(T)$ are the Helmholtz free energies corresponding to the unit cells (equal number of atoms) in the slab and the bulk calculations, and $A$ is the surface area. The present surface energies of the PdAg alloy are listed in Table III for five temperatures between 0 and 1200 K. For comparison, in table we also give the surface energies of the pure end members. All the surface energies were calculated at the theoretical lattice parameters 7.513, 7.374, and 7.672 a.u. obtained for PdAg, Pd, and Ag, respectively. Because of the angular momentum cutoff at $l=2$ the present surface energies for Pd and Ag are lower compared to those reported in, e.g., Ref. 26. However, the obtained trends of the surface energy are not expected to be affected by this.

At low temperatures due to the strong Ag segregation the surface energy of alloy is close to the surface energy of pure Ag. The suppressed surface segregation at higher tempera-

TABLE III. Surface energy of PdAg random alloy as a function of temperature ($T$). Number in parentheses give the estimated surface energies obtained from the surface energies of pure Pd ad Ag (shown at the bottom of the table) in combination with the surface concentrations from Table I. For comparison we also give the surface energy of the completely homogeneous PdAg alloy.

| | | $\gamma$ | |
|---|---|---|---|
| | $T$ (K) | (eV/surface atom) | (J/m$^2$) |
| PdAg | 0 | 0.509 (0.501) | 1.19 (1.12) |
| | 300 | 0.537 (0.517) | 1.26 (1.17) |
| | 600 | 0.547 (0.539) | 1.28 (1.23) |
| | 900 | 0.553 (0.551) | 1.29 (1.27) |
| | 1200 | 0.557 (0.557) | 1.30 (1.29) |
| Pd | | 0.701 | 1.70 |
| Ag | | 0.501 | 1.12 |
| PdAg[a] | | 0.588 | 1.37 |

[a] Homogeneous alloy.

tures leads to a more homogeneous alloy. Therefore, with increasing temperature the surface energy of PdAg alloy should approach the surface energy of the completely homogeneous PdAg alloy. Our results from Table III support this trend.

According to Eq. (8) $\gamma(T)$ depends on the temperature directly through the entropy term TS and, implicitly, via the temperature dependent surface composition. In PdAg about 25% of the increase in the surface energy with increasing temperature is due to the entropy term, while the rest of the increase is is due to surface segregation and the higher surface energy of Pd compared to that of Ag. We find that $\gamma(T)$ shows a strongly nonlinear temperature dependence. With increasing temperature $\partial\gamma/\partial T$ decreases from $2.3\times10^{-4}$ mJ/m$^2$K, calculated near 0 K, to $3.3\times10^{-5}$ mJ/m$^2$K, corresponding to $\sim$1000 K.

In Table III we also list the surface energy (numbers in parentheses) estimated from a linear rule of mixture as $\gamma_{\text{est}} = c_1\gamma_{\text{Ag}} + (1-c_1)\gamma_{\text{Pd}}$, where $c_1$ is the equilibrium surface concentration of Ag (Table I), and $\gamma_{\text{Ag}}$ and $\gamma_{\text{Pd}}$ denote the surface energies of Ag and Pd (Table III). Note how well this surface energy follows the calculated trend of $\gamma(T)$: the 2% difference between $\gamma$ and $\gamma_{\text{est}}$, calculated at 0 K, gradually vanishes with increasing temperature. However, when such a simple approximation is made one should also take into account the volume effect in the surface energy. Decreasing the lattice parameter of pure Ag from the equilibrium value of 7.672 a.u. to the lattice parameter of PdAg alloy leads to 7% decrease in the surface energy, i.e., to 0.464 eV/surface atom. This surface energy is already with 9% lower compared to the surface energy of PdAg alloy at 0 K (Table III). Consequently, the surface energy of PdAg is not exclusively determined by the surface atomic layer, but the subsurface layers have also significant contributions to the alloy surface energy.

## IV. CONCLUSIONS

Using a simple thermodynamic model in combination with the EMTO-CPA *ab initio* method we have investigated the composition of the surface and subsurface atomic layers of the (111) surface of the substitutionally disordered 50% PdAg alloy. The calculated surface segregation profile and its temperature dependence are in good agreement with the available experimental data. The details of the energetics of the considered surface show that at high concentrations even the properties of this relatively simple inhomogeneous binary system differ drastically from those predicted by impurity level calculations.

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