In the past decade, FePt nanoparticles have been extensively investigated in view of possible future applications as an ultrahigh-density information-storage medium and high-performance permanent magnets.1–6 The critical issue for an ultrahigh-density information-storage medium and high-sensitivity investigated in view of possible future applications as a medium, kinetic, and surface segregation effects.7–13 Doping FePt nanoparticles with a third element.1,3 Atomic ordering and a correspondingly high magnetic anisotropy is by shown a difficulty in obtaining a high degree of L1₀ order in their L1₀ equilibrium.16,21,27 Moreover, modeling and ex-
increase Fe and Pt mobilities and help the particles to reach cores or segregate at the surfaces. In the latter case, the ad-
predominantly tested. To follow this approach, it is imperative to defined with respect to Ref.9
and Cu solutes on and near the (001)/[100]/[111] systems to have eight layers, while for the systems with high surface to volume ratio.

In this letter, we study the segregation of dilute Ag, Au, and Cu solutes on and near the (001), (100), and (111) surfaces of FePt crystals with perfect L1₀ order (directions are defined with respect to Ref. 9). The results can also be used to draw conclusions regarding surface segregation in FePt nanocrystals with (001) and [111] facets such as cubics, tetrarhedrons, octahedrons, cuboctahedrons, truncated cubes, and the truncated octahedrons experimentally observed.28–30

We consider (001), (100), and (111) slabs with perfect L1₀ order. For the (100) and (111) cases we choose the systems to have eight layers, while for the (001) slabs we consider nine layers (see Fig. 1 of Ref. 9). The vacuum thickness between the periodic replica of the slabs is fixed at ~12 Å. One substitutional impurity of Ag, Au, and Cu per slab unit cell is injected into different layer positions, and each unit cell is chosen to have eight atoms per layer to minimize the interaction between impurity replicas. The matrix atom A (A=Fe, Pt) is substituted with the segregating species X (X =Ag, Au, and Cu) in the lth atomic layer. Accordingly, the segregation energy \( E_A^{(l)} \) is defined with respect to a “bulk” value (i.e., the fifth layer)

\[
E_A^{(l)} = E_A^{(l)} - E_{\text{Fe(bulk)}} = E_A^{(l)} - E_{\text{Fe(5)}},
\]

where \( E_A^{(l)} \) is the substitutional formation energy

\[
E_A^{(l)} = E_{\text{slab}}[\text{Fe}_{N-1}\text{Pt}_N\text{X}^{(l)}] - \mu_{\text{Fe}}(N-1) - \mu_{\text{Pt}}N - \mu_X,
\]

\[
E_A^{(l)} = E_{\text{slab}}[\text{Fe}_N\text{Pt}_{N-1}\text{X}^{(l)}] - \mu_{\text{Fe}}N - \mu_{\text{Pt}}(N-1) - \mu_X. 
\]

\( E_{\text{slab}} \) is the energy of a slab (per unit cell) with one atom X at lth atomic layer substituting iron [\( \text{X}^{(0)} \)] or platinum [\( \text{X}^{(n)} \)], \( \mu_\alpha (\alpha=\text{Fe, Pt}, X) \) is the chemical potential of atom \( \alpha \) in its pure fcc structure, and \( 2N \) is the total number of atoms in the slab unit cell. The use of the reference \( E_{\text{Fe(bulk)}} \) in Eq. (1) is arbitrary. A different choice, such as \( E_{\text{Pt(bulk)}}^{(l)} \), would not modify the differences between segregation energies. The combination of Eqs. (1) and (2) leads to

\[
E_{\text{Fe(c)}} = E_{\text{slab}}[\text{Fe}_{N-1}\text{Pt}_N\text{X}^{(l)}] - E_{\text{slab}}[\text{Fe}_{N-1}\text{Pt}_N\text{X}^{(5)}],
\]

\[
E_{\text{Pt(c)}} = E_{\text{slab}}[\text{Fe}_N\text{Pt}_{N-1}\text{X}^{(l)}] - E_{\text{slab}}[\text{Fe}_N\text{Pt}_{N-1}\text{X}^{(5)}] + \mu_{\text{Pt}}
\]

\[
- \mu_{\text{Fe}}.
\]

The slab configurations and calculations are performed within the high-throughput computational framework AFLOW/ACONVASP.31,32 All the quantum mechanical energies are obtained from first principles within the generalized gradient approximation using projector augmented wave pseudopotentials, as implemented in the VASP package.34 Calculations are spin polarized, at zero temperature, and without zero-point motion. The effect of lattice vibrations is omitted. Structures are fully relaxed (shape and volume of the cell and cell-internal positions of the atoms), and the amount of vacuum between the slabs is preserved. Perfect fcc-based configurations are used as starting point for further relaxations. Numerical convergence to within about 1 meV/
atom is ensured by enforcing a high energy cut-off (400 eV). For the bulk equations of state we use dense 16×16×16 Monkhorst–Pack k-point mesh whereas for slabs, the in-plane k-point meshes contain 7×7, 7×7, and 7×3 points for (001), (100), and (111), respectively, and one Γ-point is used in the axial direction. The chemical potential reference in Eq. (3) is \( \mu_{Pt} - \mu_{Fe} = 2.1 \text{ eV} \) based on the first principles calculations of Pt and Fe in pure fcc configurations.

Figure 1 shows the calculated surface segregation energies. The following facts are relevant. In all the considered cases, the lowest energies occur always for the most outer layer. In the first layer the energies are considerably lower for Fe substitution than those for Pt. The fact agrees with the results can be extended for nanocrystals with different shapes. For Au and Ag substitutional solutes, obtained from Eq. (3) with \( \varepsilon = \varepsilon(\mu_{Pt} - \mu_{Fe}) \) and in pure Fe or Pt (dash lines and open symbols, obtained in Refs. 40 and 41 with the KKR-ASA LDA method).

In our calculations, we assume that Fe and Pt atoms form a perfect L1₀ structure. This is an approximation, as Pt and Fe have segregation tendencies in the first and second layers of L1₀,7-13 and L1₀ order is also known to decrease with increasing temperatures. Furthermore, our calculations make use of large super cells, therefore the corresponding results are valid in the case of dilute solute composition, when solute-solute interaction is negligible and without clustering of solutes. In addition, we have also considered nanoparticles suspended in vacuum instead of being encapsulated in the typically used polymeric medium. Surface segregation may also change at small particle sizes (less than \(~2\) nm in diameter) as the surface energy changes42 and surface-tension effects might become relevant.43,44 These approximations could affect the equilibrium stability45,46 if the magnitude of the segregation energies were not as strong as the ones we found (e.g., the smallest \( |\varepsilon_{Fe}(i)|/k_B \approx 4677 \text{ K} \)).

Our finding corroborate previous experimental reports of Au and Ag segregation in FePt.18,19,47 Among Au, Ag,
and Cu in FePt, the weakest segregation energy was obtained for Cu, and accordingly, only Cu-alloying was achieved experimentally. As the segregation energy of Cu is still found to be large, the experimentally observed alloying of Cu might be explained by entropic promotion at high temperature and consequent freezing out of a metastable phase. Moreover, our results agree with the ab initio conclusion of Ref. 48, in which the magnetic atoms (Fe in our case) prefer to lie embedded in the non- or low-magnetic substrates (Pt, Cu, Au, and Ag in our case). The lowest surface segregation tendency of Cu could be attributed to the substantially smaller atomic volume of Cu (7.1 cm$^3$/mol) in comparison to Ag and Au (10.3 and 10.2 cm$^3$/mol).

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