

# First principles study of Ag, Au, and Cu surface segregation in FePt-L1<sub>0</sub>

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Doping FePt nanoparticles could be a possible approach to achieve high L1<sub>0</sub> order and magnetic anisotropy. To address stability, first-principles studies of surface segregation of dilute Ag/Au/Cu solutes at and near the (001)/(100)/(111) surfaces of FePt-L1<sub>0</sub> are performed. It is found that a strong surface segregation tendency at first outer layer is present in all the cases. For Cu, segregation is less than half of Ag and Au. Ag and Cu segregate to Fe sites at surfaces and preferentially substitute for Fe in the bulk, whereas Au substitutes for Fe at surfaces and for Fe and Pt in the bulk. © 2010 American Institute of Physics. [doi:10.1063/1.3522652]

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.<sup>1-6</sup> The critical issue for information-storage application is the presence of magnetic anisotropy offering sufficiently large thermal stability. In FePt, a high magnetic anisotropy is guaranteed by an ordered L1<sub>0</sub> phase. However, experimental observations<sup>4-6</sup> have shown a difficulty in obtaining a high degree of L1<sub>0</sub> order in FePt nanoparticles annealed at  $T \leq 600$  °C with diameter less than  $\sim 4$  nm. The phenomenon has been explained with size, kinetic, and surface segregation effects.<sup>7-13</sup>

One of the possible approaches to achieve high L1<sub>0</sub> order and a correspondingly high magnetic anisotropy is by doping FePt nanoparticles with a third element.<sup>1,3</sup> Atomic species such as Ag,<sup>14-20</sup> Au,<sup>17,19-25</sup> and Cu<sup>25-27</sup> have been previously tested. To follow this approach, it is imperative to determine whether dopants concentrate inside the particle cores or segregate at the surfaces. In the latter case, the additional surface vacancies generated by the atoms rearranging on the surface during segregation upon annealing might increase Fe and Pt mobilities and help the particles to reach their L1<sub>0</sub> equilibrium.<sup>16,21,27</sup> Moreover, modeling and explaining surface segregation phenomena are important to understand catalysis, oxidation, and corrosion in nanostructured 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 L1<sub>0</sub> 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 cubes, tetrahedrons, octahedrons, cubeoctahedrons, truncated cubes, and the truncated octahedrons experimentally observed.<sup>28-30</sup>

We consider (001), (100), and (111) slabs with perfect L1<sub>0</sub> 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  $\sim 12$  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  $A$  ( $A = \text{Fe}, \text{Pt}$ ) is substituted with the segregating species  $X$  ( $X = \text{Ag}, \text{Au}, \text{and Cu}$ ) in the  $l$ th atomic layer. Accordingly, the segregation energy  $\varepsilon_{A(l)}^X$  is defined with respect to a “bulk” value (i.e., the fifth layer)

$$\varepsilon_{A(l)}^X \equiv E_{A(l)}^X - E_{\text{Fe}(\text{bulk})}^X = E_{A(l)}^X - E_{\text{Fe}(5)}^X, \quad (1)$$

where  $E_{A(l)}^X$  is the substitutional formation energy

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

$$E_{\text{Pt}(l)}^X = E_{\text{slab}}^{\text{uc}}[\text{Fe}_N \text{Pt}_{N-1} X^{\text{Pt}(l)}] - \mu_{\text{Fe}}N - \mu_{\text{Pt}}(N-1) - \mu_X, \quad (2)$$

$E_{\text{slab}}^{\text{uc}}$  is the energy of a slab (per unit cell) with one atom  $X$  at  $l$ th atomic layer substituting iron [ $X^{\text{Fe}(l)}$ ] or platinum [ $X^{\text{Pt}(l)}$ ],  $\mu_\alpha$  ( $\alpha = \text{Fe}, \text{Pt}, X$ ) 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  $E_{\text{Fe}(\text{bulk})}^X$  in Eq. (1) is arbitrary. A different choice, such as  $E_{\text{Pt}(\text{bulk})}^X$ , would not modify the differences between segregation energies. The combination of Eqs. (1) and (2) leads to

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

$$\varepsilon_{\text{Pt}(l)}^X = E_{\text{slab}}^{\text{uc}}[\text{Fe}_N \text{Pt}_{N-1} X^{\text{Pt}(l)}] - E_{\text{slab}}^{\text{uc}}[\text{Fe}_{N-1}\text{Pt}_N X^{\text{Fe}(5)}] + \mu_{\text{Pt}} - \mu_{\text{Fe}}. \quad (3)$$

The slab configurations and calculations are performed within the high-throughput computational framework AFLOW/ACONVASP.<sup>31,32</sup> All the quantum mechanical energies are obtained from first principles within the generalized gradient approximation<sup>33</sup> using projector augmented wave pseudopotentials, as implemented in the VASP package.<sup>34</sup> 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/

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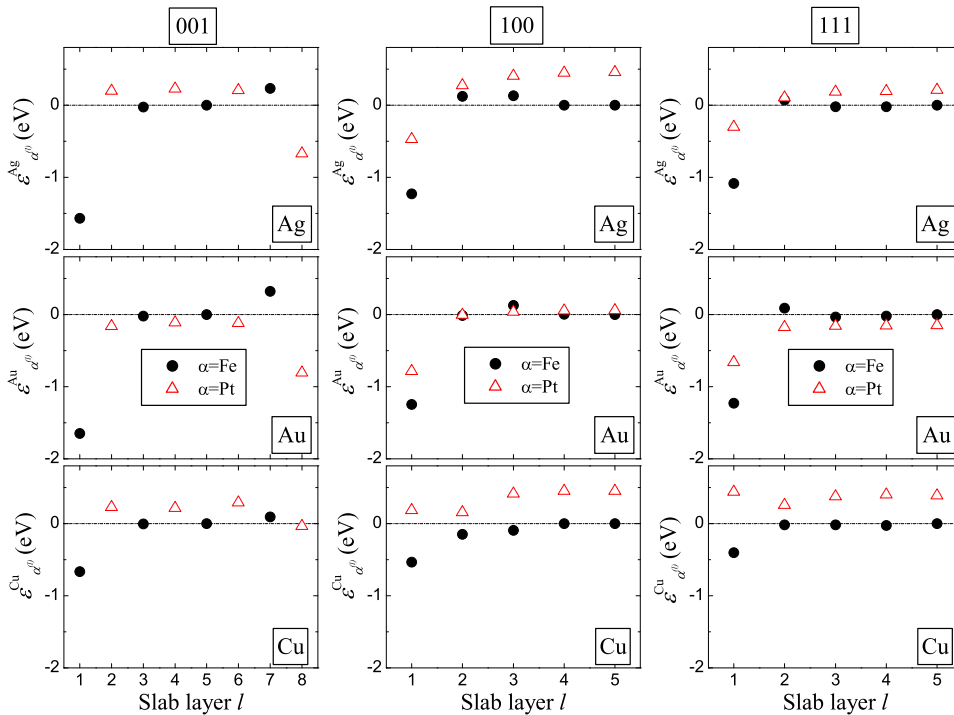


FIG. 1. (Color online) Surface segregation energies [see Eq. (3)] of Ag, Au, and Cu (first, second, and third rows, respectively) in ordered FePt-L<sub>10</sub> as function slab layer. (001), (100), and (111) surfaces correspond to first, second, and third columns, respectively. All graphs use the same energy scale and designations. Fourth and fifth slab layers are the central positions, whereas first and eighth layers correspond to the slab surface. In the case of (100) and (111), only one-half of slabs is shown because of their symmetry.

atom is ensured by enforcing a high energy cut-off (400 eV). For the bulk equations of state we use dense  $16 \times 16 \times 16$  Monkhorst-Pack  $\mathbf{k}$ -point mesh whereas for slabs, the in-plane  $\mathbf{k}$ -point meshes contain  $7 \times 7$ ,  $7 \times 7$ , and  $7 \times 3$  points for (001), (100), and (111), respectively, and one  $\Gamma$ -point is used in the axial direction. The chemical potential reference in Eq. (3) is  $\mu_{\text{Pt}} - \mu_{\text{Fe}} = 2.1$  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 Pt segregation tendency previously observed and calculated in FePt.<sup>9-13,35-39</sup> The data show that  $\varepsilon_{\alpha(1)}^X(001) < \varepsilon_{\alpha(1)}^X(100) < \varepsilon_{\alpha(1)}^X(111)$ , leading to the conclusions that the Fe<sup>(1)</sup>(001) sites are the most energetically favorable positions for Cu, Au, and Ag substitutional solutes. For Cu, the first layer segregation energies are less than half of the values for Ag and Au:  $\varepsilon_{\text{Fe}(1)}^{\text{Cu}} \leq \varepsilon_{\text{Fe}(1)}^{\text{Ag, Au}}/2$ . Away from the surface, Cu and Ag substitutions of Fe sites are more energetically favorable than substitutions of Pt sites, while for Au there both cases are approximately equal. The results can be extended for nanocrystals: the segregation tendency in systems with only (111) facets (tetrahedrons and octahedrons) would be smaller than that of nanocrystals with different shapes.

We perform a comparison between the most-outer-layer surface segregation energies of Ag, Au, and Cu in L<sub>10</sub>-FePt and those in pure Fe or Pt as previously calculated with the Korringa-Kohn-Rostoker atomic sphere and local density approximation (KKR-ASA-LDA) method.<sup>40,41</sup> For this task, we restrict Eq. (3) to  $\mu_{\text{Pt}} = \mu_{\text{Fe}}$  and define  $\varepsilon \equiv \varepsilon(\mu_{\text{Pt}} = \mu_{\text{Fe}})$ . Based on these assumptions, the (001) results are expected to represent an average between the corresponding (001) and (100) values. Figure 2 shows that the segregation tendencies of Ag, Au, and Cu are similar in binary L<sub>10</sub>-FePt and in pure Fe and Pt.

In our calculations, we assume that Fe and Pt atoms form a perfect L<sub>10</sub> structure. This is an approximation, as Pt and Fe have segregation tendencies in the first and second layers of L<sub>10</sub>,<sup>7-13</sup> and L<sub>10</sub> 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  $\sim 2$  nm in diameter) as the surface energy changes<sup>42</sup> and surface-tension effects might become relevant.<sup>43,44</sup> These approximations could affect the equilibrium stability<sup>45,46</sup> if the magnitude of the segregation energies were not as strong as the ones we found (e.g., the smallest  $|\varepsilon_{\text{Fe}(1)}^{\text{Cu}}|/k_B \approx 4677$  K).

Our finding corroborate previous experimental reports of Au and Ag segregation in FePt.<sup>18,19,47</sup> Among Au, Ag,

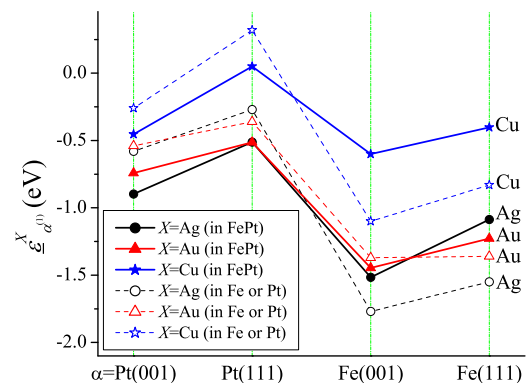


FIG. 2. (Color online) Surface segregation energies of Ag, Au, and Cu for the first outer layer ( $l=1$ ) in ordered FePt-L<sub>10</sub> [solid lines and filled symbols, obtained from Eq. (3) with  $\varepsilon \equiv \varepsilon(\mu_{\text{Pt}} = \mu_{\text{Fe}})$ ] and in pure Fe or Pt (dash lines and open symbols, obtained in Refs. 40 and 41 with the KKR-ASA LDA method).

and Cu in FePt, the weakest segregation energy was obtained for Cu, and accordingly, only Cu-alloying was achieved experimentally.<sup>47</sup> 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<sup>3</sup>/mol) in comparison to Ag and Au (10.3 and 10.2 cm<sup>3</sup>/mol).<sup>49</sup>

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