Core-shell morphologies of FePt and CoPt nanoparticles: An \textit{ab initio} comparison

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Core-shell morphologies of FePt and CoPt nanoparticles: An \textit{ab initio} comparison

Markus Ernst Gruner
Faculty of Physics and Center for Nanointegration, CENIDE, University of Duisburg-Essen, 47048 Duisburg, Germany
E-mail: Markus.Gruner@uni-due.de

Abstract. Large-scale first principles calculations for near-stoichiometric FePt and CoPt clusters with up to 923 atoms are presented including unconstrained structural relaxations. The energetic order and magnetic properties of 561 atom FePt and CoPt nanoparticles are evaluated with emphasis on segregated morphologies with Pt covered surfaces. The results imply that for CoPt particles segregation of Pt to the surface and the formation of a Pt depleted subsurface layer is dominant also for nanometer-sized single crystalline particles and may help to stabilize particles with partial L1\textsubscript{0} order, while for FePt multiple twinning is the most important mechanism at small particle sizes. The mixed (100) surfaces of the fully L1\textsubscript{0} ordered FePt and CoPt isomers exhibit a characteristic reconstruction.

1. Introduction
The amazing exponential evolution of supercomputing power during the past one and a half decades has now reached a point where geometric optimizations of metallic materials with system sizes of several hundred to even more than one thousand atoms have become feasible using state-of-the-art computer hardware [1–6] from first principles, i.e., without the need for empirical parameters. Only well known quantities, as positions and core charges of the atoms are required. This development opens new possibilities for the design or improvement of novel materials, e.g., allowing a detailed investigation of the interplay of electronic and structural properties of metallic nanoparticles with diameters around 3 nm and beyond. While the treatment of large systems is still limited to zero temperature or short time scales, large scale \textit{ab initio} calculations provide benchmark results for (semi-)empirical methods which are easily capable of handling large systems and time scales. They also ideally complement experimental approaches, as several important properties of nanoparticles, as composition and morphology, which often cannot be controlled effectively in experiment, can be made subject to a systematic variation, here.

A well suited target for large-scale \textit{ab initio} investigations are FePt and CoPt nanomaterials, which obtained significant attention due to their possible use as storage ultra-high-density-storage materials in their ordered L1\textsubscript{0} phase. This structure is characterized by a layerwise stacking of Fe (Co) and Pt planes in (001) direction leading to an unusually large magnetocrystalline anisotropy [7; 8]. Previous experimental and theoretical studies suggest, however, that L1\textsubscript{0} particles with diameters of a few nanometers are difficult to fabricate, which may be due to surface-induced disorder and segregation [9–12] or the competition of multiply twinned morphologies [5; 13–15]. Recent investigations reported on segregated icosahedral FePt
Figure 1. Ordered and core-shell motives of FePt and CoPt nanoparticles after structural relaxation (dark brown: Pt, bright blue: Fe/Co): (a) fully L1\(_0\) ordered Fe\(_{440}\)Pt\(_{483}\) showing characteristic reconstruction of the (100) surfaces, (b) segregated L1\(_0\) isomer (296 Pt atoms, 265 Fe/Co atoms) with Pt-covered surface and Pt-depleted subsurface shell, (c) Fe\(_{265}\)Pt\(_{296}\) with L1\(_2\) ordered core and fully Pt-covered surface shell, (d) Fe\(_{265}\)Pt\(_{296}\) and (e) Co\(_{265}\)Pt\(_{296}\) isomers with Pt only in the sub-subsurface shell and outside (full Pt covering), (f) and (g) 561 atom icosahedral motifs corresponding to (a) and (e), respectively. The isomers (b)-(f) are shown as complete clusters (left side) and in cross section through the particle center (right side).

particles with a magnetic core and a Pt-enriched catalytic shell from gas phase experiments [16; 17]. The focus of this contribution is to provide from first principles a systematic comparison of near-stoichiometric FePt and CoPt nanoparticles with Pt-enriched surface shells and diameters of 2.5-3 nm with respect to their energetic order and magnetic properties.
Table 1. Comparison of energies and spin magnetic moments (total $M_{\text{tot}}$ and averaged site resolved $m_{\text{Fe,Co,Pt}}$) of relaxed morphologies of Fe$_{265}$Pt$_{296}$ and Co$_{265}$Pt$_{296}$ according to Fig. 1. Energies $\Delta E = E - E_{L10}$ are relative with respect to the perfect L1$_0$ cuboctahedron (a) of the respective compositions.

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<th>(a)</th>
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<th>(f)</th>
<th>(g)</th>
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<tbody>
<tr>
<td>$\Delta E$ (meV/atom)</td>
<td>6</td>
<td>34</td>
<td>33</td>
<td>-2</td>
<td>-23</td>
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<td>$M_{\text{tot}}$ ($\mu_B$/cluster)</td>
<td>925</td>
<td>878</td>
<td>842</td>
<td>839</td>
<td>912</td>
<td>811</td>
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<td>$m_{\text{Fe}}$ ($\mu_B$/atom)</td>
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<td>2.90</td>
<td>2.85</td>
<td>2.82</td>
<td>2.98</td>
<td>2.73</td>
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<tr>
<td>$m_{\text{Pt}}$ ($\mu_B$/atom)</td>
<td>0.39</td>
<td>0.32</td>
<td>0.26</td>
<td>0.27</td>
<td>0.36</td>
<td>0.27</td>
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<th></th>
<th>(a)</th>
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<tbody>
<tr>
<td>$\Delta E$ (meV/atom)</td>
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<td>-35</td>
<td>-22</td>
<td>-116</td>
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<tr>
<td>$M_{\text{tot}}$ ($\mu_B$/cluster)</td>
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<td>564</td>
<td>637</td>
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<td>$m_{\text{Co}}$ ($\mu_B$/atom)</td>
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<td>1.85</td>
<td>1.96</td>
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<tr>
<td>$m_{\text{Pt}}$ ($\mu_B$/atom)</td>
<td>0.42</td>
<td>0.31</td>
<td>0.26</td>
<td>0.40</td>
<td>0.25</td>
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2. Results and discussion

The calculations have been carried out within the the framework of spin-polarized density functional theory using the plane wave code VASP [18; 19], for details, see [5; 6]. Previous cluster and surface energy calculations strongly indicate that Pt-covered surfaces are preferred over Fe-covered surfaces [20; 21]. Consequently, this work concentrates on motifs with Pt segregation to the surface, having, accordingly, slightly Pt-enriched compositions. Snapshots of the considered isomers can be found in Fig. 1. For the fully L1$_0$ ordered isomer, structural relaxation leads to a characteristic reconstruction of the (100) surfaces. Here, the atoms of adjacent Pt-(001)-layers tend to form dimer-like pairs, alternatingly between the upper and lower layer, which also imposes a corresponding movement of the Fe atoms. Such displacements are not present in the particle core. The energies and magnetic moments corresponding to morphologies (b)-(f) are listed in Tab. 1. All energies are given with respect to the fully L1$_0$ ordered FePt and CoPt isomers. At a given composition, the perfect realisation of an ordering motif is usually only possible for one morphology, which is in this case motif (a). For the others, the excess atoms of one species were distributed randomly over the anti-sites. The spin moments given in Tab. 1 are particle averages; typically, the moments of the 3$d$ element increase with decreasing coordination, whereas the induced Pt-moments benefit from the spin-polarization of surrounding atoms. A more detailed discussion of the site-resolved spin moment distribution of selected FePt isomers can be found in Ref. 6.

Morphology (b) represents a particle with L1$_0$ order in the particle core, but also a Pt-covered surface and Pt-depleted subsurface shells to accommodate segregation tendencies reported from previous ab initio and model calculations [5; 11]. For FePt, its energy is nearly degenerate with the fully L1$_0$ ordered cuboctahedron (a), which should be expected to show the largest possible magnetocrystalline anisotropy energy of all considered morphologies. This clearly confirms that surface segregation competes with L1$_0$ ordering and must be considered a significant obstacle for obtaining small clusters with large magnetocrystalline anisotropy as predicted from previous model calculations [9; 11]. On the other hand, a fully segregated morphology with L1$_2$ ordering inside (c) is considerably higher in energy, although the Pt-segregation allows a nearly perfect Fe$_3$Pt stoichiometry in the particle core. Despite of the cubic symmetry of the L1$_2$ phase, the cluster was initialized with a slight tetragonal distortion, which was maintained during the optimisation. This is in accordance with the observation of a fct phase at low temperatures for bulk Fe$_3$Pt, which also attracted interest due to its magnetic shape memory behaviour [22]. Similarly uncompetitive is the onion-shell morphology (d). The tetragonal-like deformation of the cluster shape is caused by a partial transformation to a bcc structure originating from the
Fe-rich sections of the cluster. Accordingly, for the CoPt counterpart (e) similar distortions are not encountered. The multiply twinned icosahedron (g) which is connected to the initial configurations (d) and (e) by a Mackay-transformation [23], however, belongs to the lowest energy structures at this size for FePt as well as for CoPt.

In both cases, a morphology with Pt-surface, Pt-depleted subsurface-shell and L1₀ core (b) is more favorable than the onion-shell arrangement (d)/(e) and provides for CoPt a considerable decrease in energy in comparison to perfect L1₀ ordering (a). Also, with respect to the other core-shell motifs, a smaller degradation of magnetic properties is encountered. This implies that for CoPt a core-shell environment with onion-ring type outer layers may help to stabilize single crystalline structures with L1₀ core with respect to multiply twinned structures for larger particles.

Acknowledgments
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