Modeling of Multicomponent Nanoalloys

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Title of the thesis subject:

Multicomponent nanoalloys: phase diagram and dynamics at the nanoscale.

Description of the thesis subject:

Metallic nanoparticles [1] are widely used in catalysis and have potential applications in opto-electronic devices, ultra-high density magnetic storage, cancer detection and treatment, etc... The study of their physico-chemical properties requires a precise knowledge of their structure and morphology. Combining different elements (i.e. alloying) in the same nanoparticle greatly enhances these properties, as is well known in metallurgy. Typically, alloying can improve mechanical, magnetic and/or plasmonic properties, but also, in a large scale, catalytic activity and selectivity, which are important features for applications in green chemistry. In order to achieve specifically tailored properties, it is of prime importance to control shape and chemical arrangement of the alloyed nanoparticles.

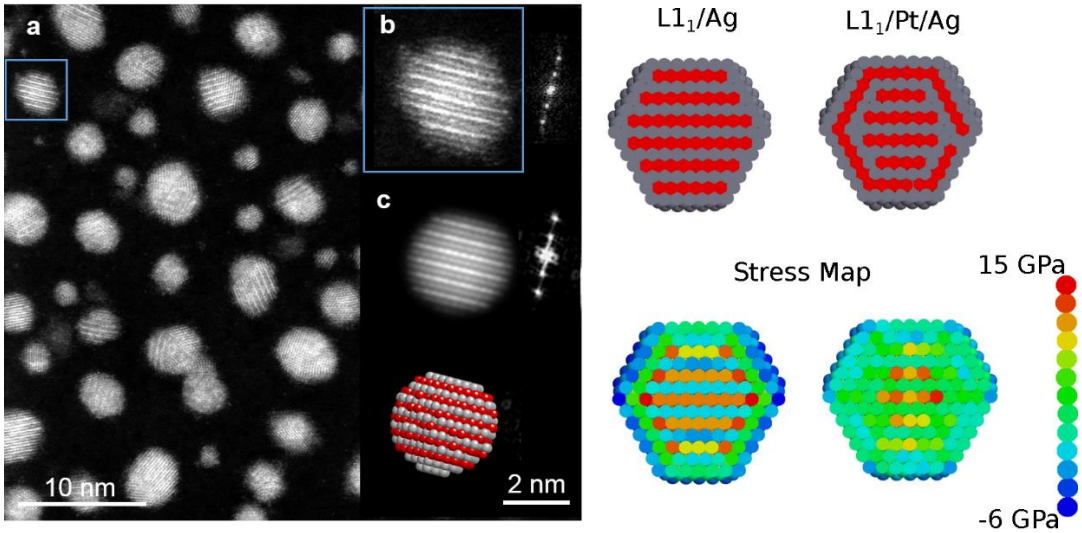

Figure caption: High resolution transmission electron images of Pt-Ag nanoparticles and modeling of their chemical arrangement and atomic local stress [5].Silver atoms in grey and Platinum in red.

We know that the geometric structure of small clusters can differ from the one of bulk material. In case of transition and noble metals, the nanoparticles can adopt fivefold symmetries like icosahedra or decahedra. In these structures, surface energy is optimized at the expense of some stress in the

nanoparticle core. By increasing nanoparticle size, the core stress increases and finally destabilizes the structures with fivefold symmetries. This means that there is a structural transition towards the bulk crystals structure and to the corresponding optimal crystal shapes, which are truncated octahedra for FCC metals [2]. By putting different elements with different atomic radius, the internal stress can be modulated in order to change the size at which the structural transition occurs [3] or create morphological instabilities in core-shell nanoparticles [4]. Stress/strain is therefore a driving force which contributes to determine the optimal chemical arrangement. In the case of Pt-Ag nanoparticles [5] (see the figure above) we expect to observe nanoparticles presenting the $L1_1$ ordered phase as in the bulk alloy (this is clearly observed experimentally) but in addition we expect also silver surface segregation because silver has a much lower surface energy than platinum. This creates a very thin Ag shell (an Ag-skin) around the $L1_1$ ordered phase which induces important stress in the core because Ag atoms are larger than Pt atoms. The stress increases with the cluster size and leads to the breaking of the ordered phase for sizes above 3 nm.

Adding a third element as Co or Ni in the binary Pt-Ag nanoalloys is expected to lead to very interesting behaviours in terms of surface segregation and chemical ordering. (Co,Ni)-Pt systems display ordered phases with an alternation of pure or mixed atomic planes in the (100) direction [6], whereas Pt-Ag displays the alternation of pure atomic planes in the (111) direction. Moreover (Co, Ni)-Ag displays a large miscibility gap in the bulk phase diagram leading to a strong Ag surface segregation and core-shell or Janus structures in nanoparticles[4]. From the dynamical point of view, Ag surface segregation could be an accelerator to the chemical phase ordering.

In this PhD thesis we **propose to study by numerical simulations the equilibrium and dynamical properties of nanoparticles of (Co, Ni)-Pt-Ag ternary alloys.** These nanoparticles are expected to present high performances in different applications. From the catalytic point of view, the ternary alloys allow to explore new selectivity properties and at the same time to reduce the cost by using a smaller amount of Pt. From the magnetic point of view, the high magnetic anisotropy of the (Co, Ni)-Pt ordered phase is expected to stabilize the magnetic moment of the nanoparticle for ultrahigh magnetic data storage of next generation devices.

The applicant will develop **new codes for ternary systems at finite temperature based on Monte Carlo simulations for equilibrium phases and molecular dynamics for diffusion and time evolution.**

References:

[1] R. Ferrando, *Structure and properties of nanoalloys*, Elsevier (2016); D. Alloyeau, C. Mottet, C. Ricolleau (Eds.), *Nanoalloys: Synthesis, Structure and Properties*, Springer-Verlag London (2012); *Nanoalloys: From Theory to Application*, **Faraday Disccussions 138** (2008).
[2] F. Baletto, R. Ferrando, A. Fortunelli, F. Montalenti, C. Mottet*, Crossover among structural motifs in transition and noble-metal clusters***, J. Chem. Phys. 116**, 3856 (2002).
[3] B. Zhu, H. Guesmi, J. Creuze, B. Legrand and C. Mottet, *Crossover among structural motifs in Pd-Au nanoalloys*, **Phys. Chem. Chem. Phys. 17**, 28129-28136 (2015).
[4] D. Bochicchio, R. Ferrando, *Morphological instability of core-shell metallic nanoparticles*, **Phys. Rev. B 87**, 165435 (2013).
[5] J. Pirart, A. Front, D. Rapetti, C. Andreazza-Vignolle, P. Andreazza, C. Mottet, R. Ferrando, *Reversed size-dependent stabilization of ordered nanophases***, Nature Communications 10**, 1982 (2019).
[6] A. Front, C. Mottet, *Ordering frustration in large-scale Co-Pt nanoalloys*, **J. Phys. Chem. C 125**, 16358 (2021)