

Thesis publicly defended by **Jérôme PIRART** on Monday 3 December 2018 at 14 :00 hrs.

Amphitheatre Sadron, CNRS Orléans

**Platinum and silver based nanoalloys: phases transitions, kinetics effects and reactivity.**

Metal nanoalloys are widely study due to the diversity of their physical and chemical properties depending on their structure and induced by the size reduction and the surface effect. However, these atomic arrangements are influenced by the growth kinetic and the environment. Among the Ag-based nanoalloys, the originality of the AgPt system comes from the competition between the alloy and the segregation effects. Following the nanoscale atomic arrangement during the structural evolution (phase transition, temperature, reactive gases) is the main challenge, especially in the case of nanoalloys which exhibit a large structural landscape (ordered, disordered, or segregated structures). The solution is to control, at the same time, the environment and the investigations techniques that are the transmission electron microscopy (HRTEM, HAADF) and the grazing incidence at small and wide angle X ray scattering (GISAXS, GIWAXS).

The studied nanoparticles (between 1 and 5 nm in diameter) show a transition from a disordered state to an ordered state ( $L1_1$  type). The superficial Ag segregation influence the stability of this phase at the nanoscale, which decreases with the increase in the size except when there are defects within the nanoalloy allowing the stress relaxation. This phenomenon is counter-intuitive since the size reduction generally leads to a narrowing stability for ordered phases.

AgPt nanoparticles are followed under atomic O and CO exposure. Thus, total or partial oxidation and reduction mechanisms, inducing segregation effects, have been shown. The first structurally irreversible step during the 1<sup>st</sup> oxidation is followed by a reversibility between the two states (oxidized, reduced).

Even if AgPt is allied and ordered at a lower temperature than the CoPt system, the study of tri-metallic (CoPtAg) nanoparticles show that the CoPt alloy is always favored except if there is Pt excess within the nanoparticle. This result is in good agreement with the formation enthalpy of both systems.