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Title: **Morphology evolution in mono- and bimetallic FCC nanoparticles**

Abstract

The main objective of the thesis is to explore elementary mechanisms of structural and morphological evolutions in mono and bimetallic Face-Centered Cubic (FCC) nanoparticles. Comparison of X-ray diffraction (XRD) measurements with atomistic simulations strongly sugests that most of synthetized FCC nanoparticles has internal multidomain structure with domains connected in 3D via stacking fault or twin (111) planes. To get insight into this structure three tasks were set: a) development of a tool for bulk morphology analysis, b) understanding of stacking defects formation mechanisms, and c) analysis of temperature-induced evolution of structure and morphology in mono and bimetallic samples. To complete each task, extensive computational simulations involving energy minimization and molecular dynamics calculations were used. After that, the obtained theoretical predictions were verified by experimental observations.

Noble metal nanoparticles (NPs) are promising materials in a wide range of fields: catalysis, medicine, fuel cells, sensors, and so on. Researchers often consider nanoparticle properties as a function of their size and size distribution; meantime NPs interior is neglected. Although several theoretical and experimental studies indicate that the appearance of structural defects can affect resulting properties. So far, the bulk morphology analysis was mainly studied by high-resolution microscopy techniques, which has drawbacks making it not applicable as a routine tool and unavailable for many scientists.

The first part of the thesis is devoted to the development of a bulk morphology analysis method based on X-ray diffraction (XRD). It's known that cuboctahedron (CUB), decahedron (DEC), and icosahedron (ICO) XRD patterns are different. The differences resemble 1D effect of small stacking and twinning probabilities described by Warren in 1960s. However for 2D stacking (DEC) or 3D (ICO), the appearance of a local 5-fold rotation symmetry axis, non-compatible with FCC lattice, causes additional strain. Using computational simulations, one can disassemble a decahedron into segments (domains) and meticulously explore the 3D twinning effect on XRD patterns. This approach allowed development of the multidomain XRD (MDXRD) method to perform improved mean size and bulk morphology analysis of noble metal NPs. MDXRD approach was verified on various mono – and bimetallic samples and showed a good agreement with a reference techniques.

The thesis's second part focused on mechanisms of the formation of a stacking defects. The existing concepts describe them mainly on the level of elementary processes and cannot describe the

formation of DEC or ICO. During the development of MDXRD, it was found that vacancies inside NPs may cause twinning. Once the vacancy concentration in the perfect FCC lattice exceeds a critical concentration, the cluster structure becomes unstable, causing the formation of stacking defects. This approach, when one adds vacancies to the existing cluster, allows computational simulations of the appearance of various multiply twinned particles. Even more, the vacancy driven twinning approach allows obtaining locally a hexagonal close packed (HCP) gold!

The last part of the work explores the structural and morphological evolution of immiscible bimetallic Au-Pt samples during heating. Au-Pt phase diagram predicts the formation of alloy, core-shell, and Janus particles, wherein one structure may transform to another. Despite great interest to the material (in particular Au-Pt), elementary processes of these structural transitions are not well explored. The effect of morphology was only theoretically considered. The development of MDXRD and vacancy driven twinning allowed unrevealing new trends and elementary steps in phase separation and segregation processes.