NANOPOWDER DIFFRACTION

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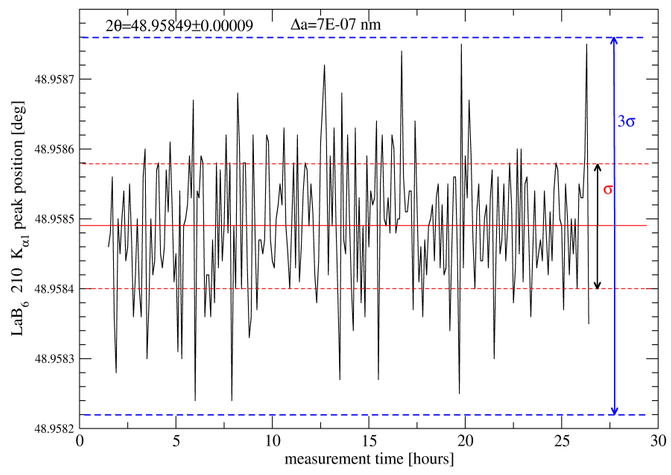
The technique

In situ diffraction method addressing structure of nanocrystals.

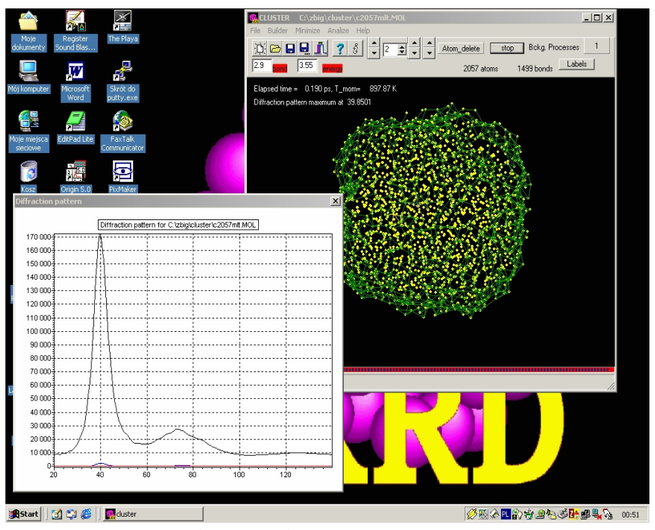
Novelty

> Nanopowders - large fraction of surface atoms interacting with gas environment. Diffraction response from the surface has amorphous character but changes on chemisorption phenomena.

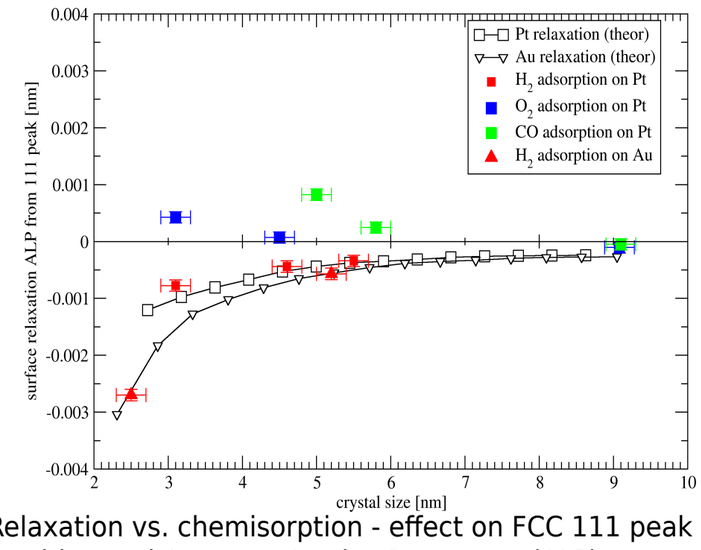
> Employing precise peak position monitoring (repeatability up to 10^{-4} deg) + peakj intensity, width and gas phase mass spec. control (chemistry).



> Interpretation via atomistic simulations merged with Debye summation pattern calculation.

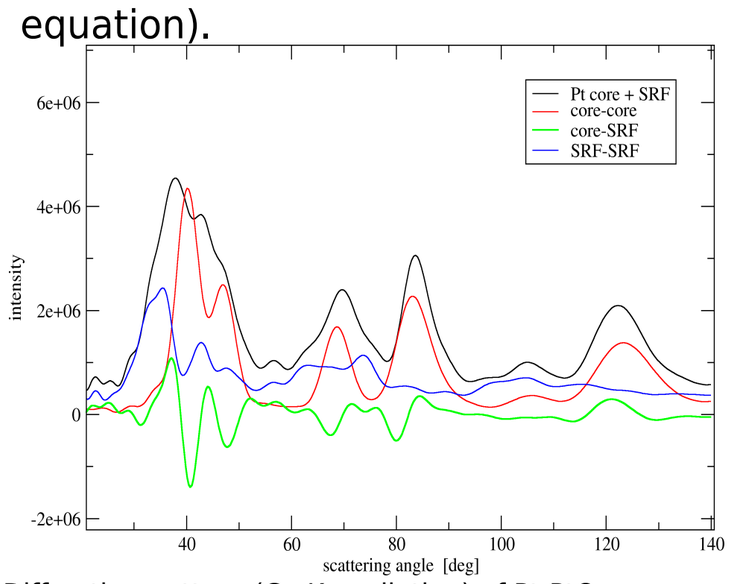


Program Cluster layout



Relaxation vs. chemisorption - effect on FCC 111 peak position and Apparent Lattice Parameter (ALP).

> Non-applicability of Rietveld refinement - phase analysis versus interatomic distance analysis (Debye equation).

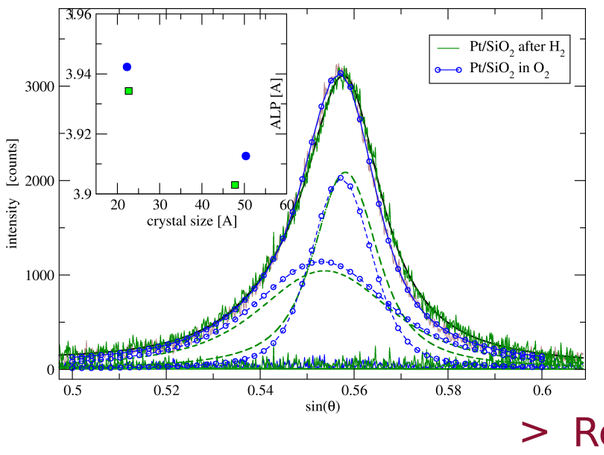


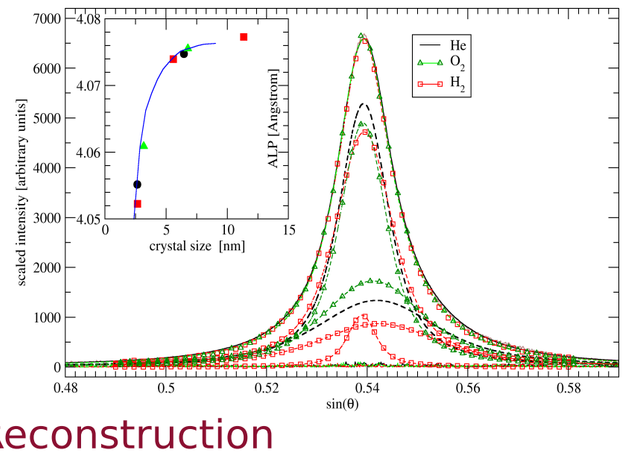
Diffraction pattern (Cu K_α radiation) of Pt-PtO_2 core-shell(SRF) nanocrystal (black line) with contribution from core-core distances (red line), SRF-SRF distances (blue line) and core-SRF distances (green line).

Some results

> Relaxation

Surface controlled inward relaxation (Laplace pressure)- dangling bonds causing lattice contraction.

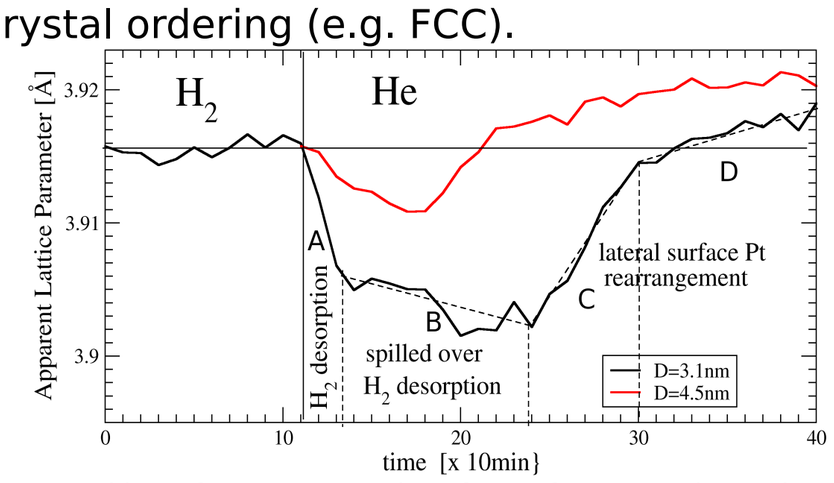




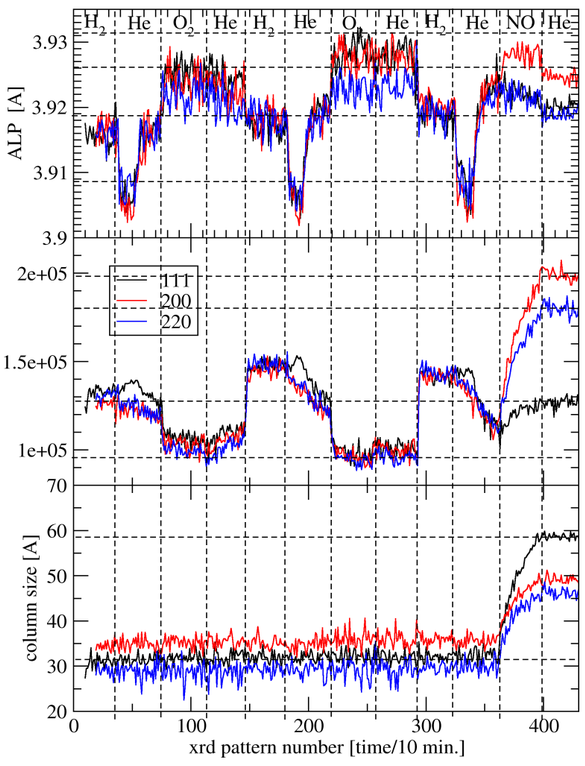
Voigt-functions fit to 220 reflection of Pt/SiO2 (left) and Au/C (right) proving applicability of simulation approach (J. Appl. Cryst. (2017), 50, 585-593).

> Reconstruction

Surface environment energy minimization causing surface departure from crystal ordering (e.g. FCC).

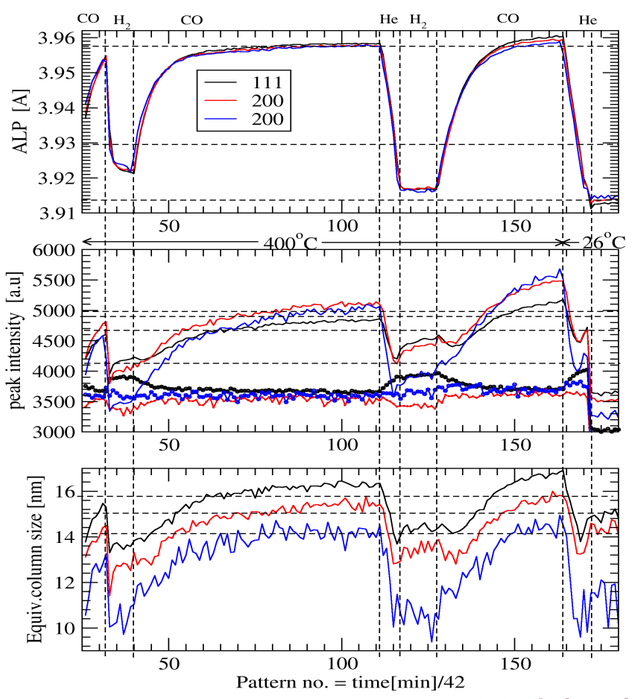


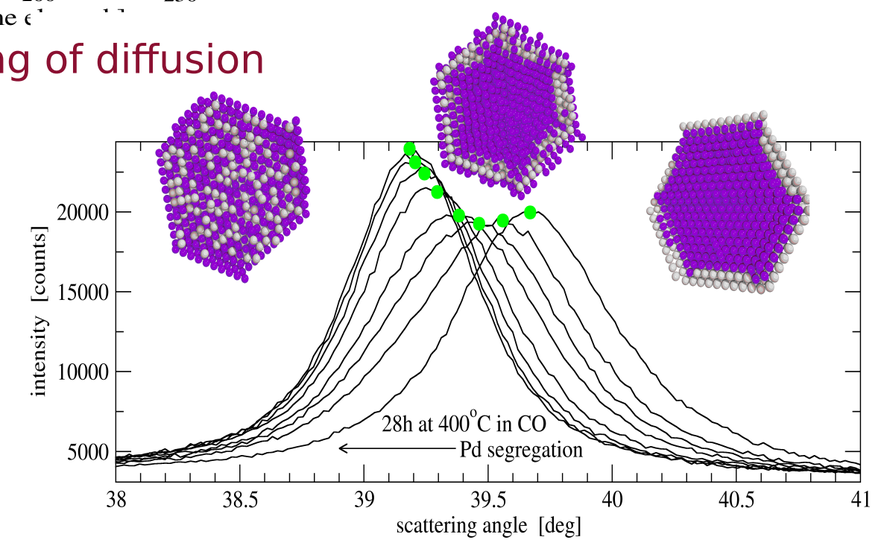
Repeatable surface reconstruction of Pt surface on H_2 desorption (slowed down to hours by reverse spill-over) (J.Appl.Cryst.,(2014), 47, 2069-2077).



Left - Pt low temp. coalescence driven by surface reconstruction dependence on coverage. The cyclic phenomenon makes a molecular engine propelling coalescence. At 150°C (h) NO desorbs leaving characteristic ALP evolution mark (RSC Adv.(2014), 4 (28), 14758 – 14765).

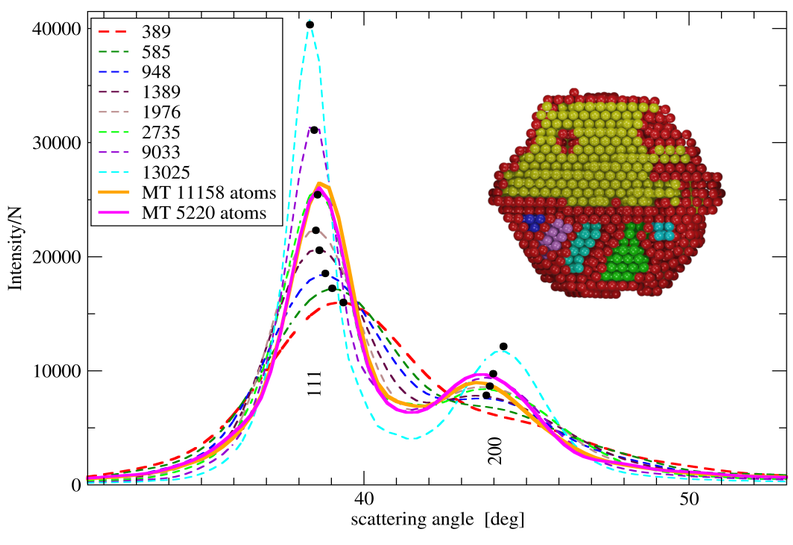
> Monitoring of diffusion





Surface segregation of Ag in PdAg alloy reversed when exposed to CO. Kinetics of the process prompts for different diffusion mechanism (PCCP (2015), 17, 28250 - 28255). Fixing Pd at the surface by CO chemisorption hinders surface dynamics and vacancy creation.

> Multitwinning in FCC



Most of chemically synthesized FCC nanometals consists of multidomain, multiply twinned across 111 planes, clusters. We have developed method to determine average number and size of the domains (Nanoscale (2023) 15, 8633). Such clusters can be modeled by random deletion of atoms (more than 13%) and relaxation. Then, domains of FCC arrangement appear separated by atoms of HCP coordination. The net effect is a decrease of 200 to 111 height ratio and non-Bragg peak shift with the peaks mutual approach and building up 'bridge' intensity between (arxiv.org/pdf/2409.01254). The pattern resembles one of decahedral structure.