Detection of vacancies in FCC solid and their effect on twinning

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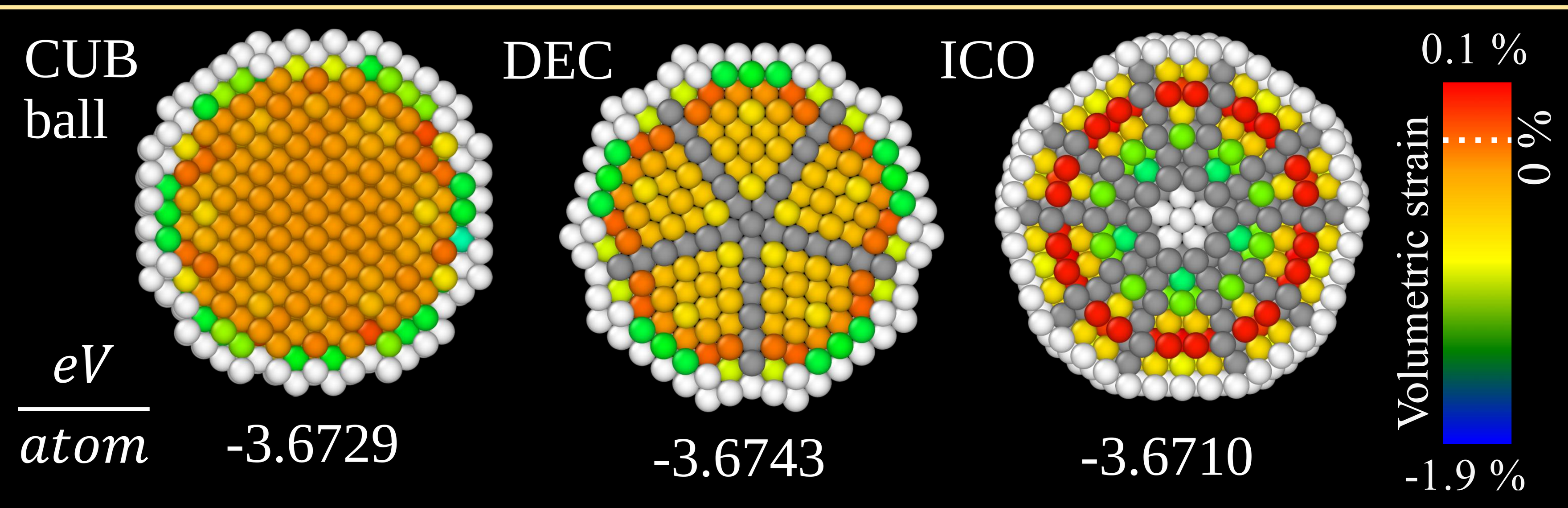
WHAT IS THE MOST STABLE FORM ?

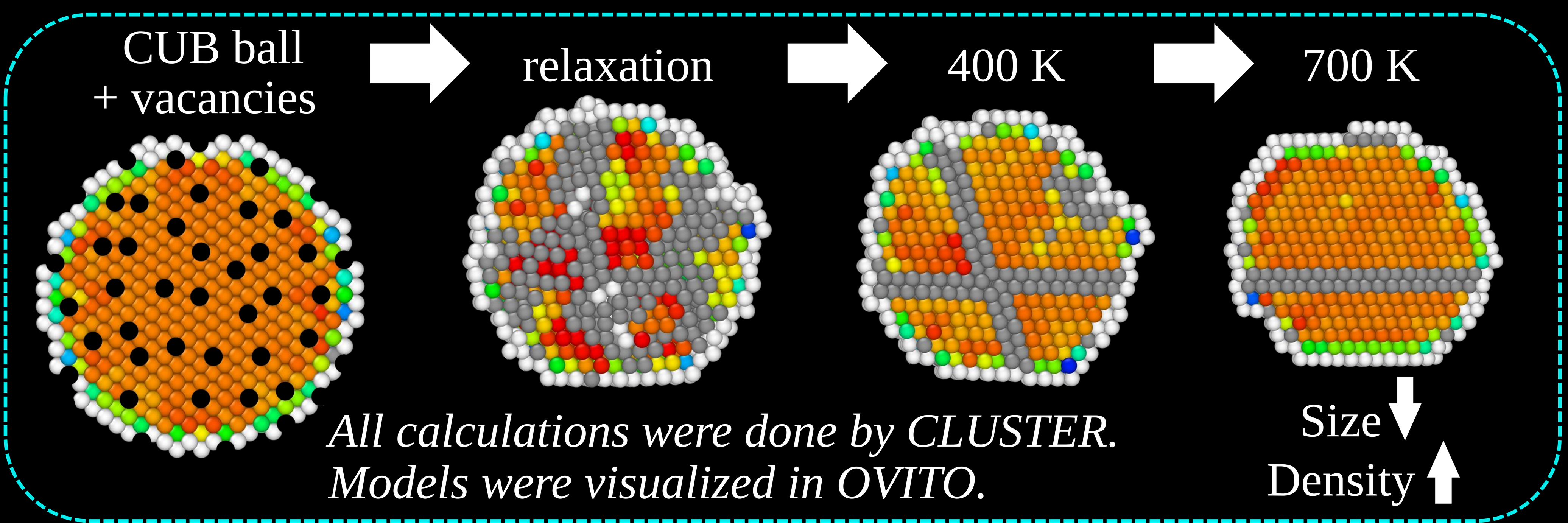


FCC nanoparticles (NPs) possess a variety different morphologies: cuboctahedron (CUB), decahedral (DEC), or icosahedral (ICO). Different structures possesses different catalytic, electronic and optical properties.

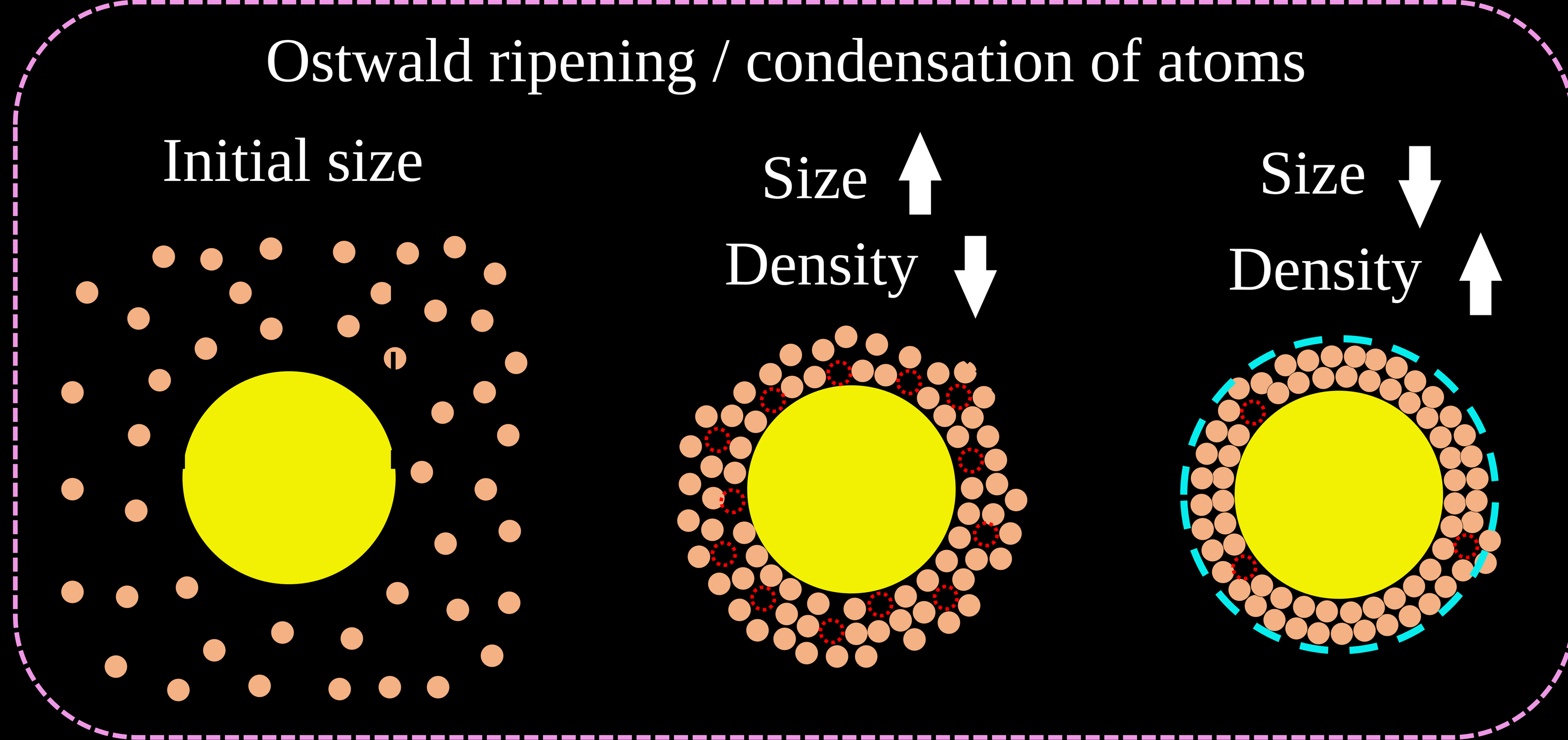
The appearance of one or another morphology is considered as depended on the minimum free energy per atom. Meanwhile, the exact mechanism that triggers the twinning is unknown.

HOW DO VACANCIES AFFECT TWINNING ?

Initial **ISOLATED** computational model (top => bottom)

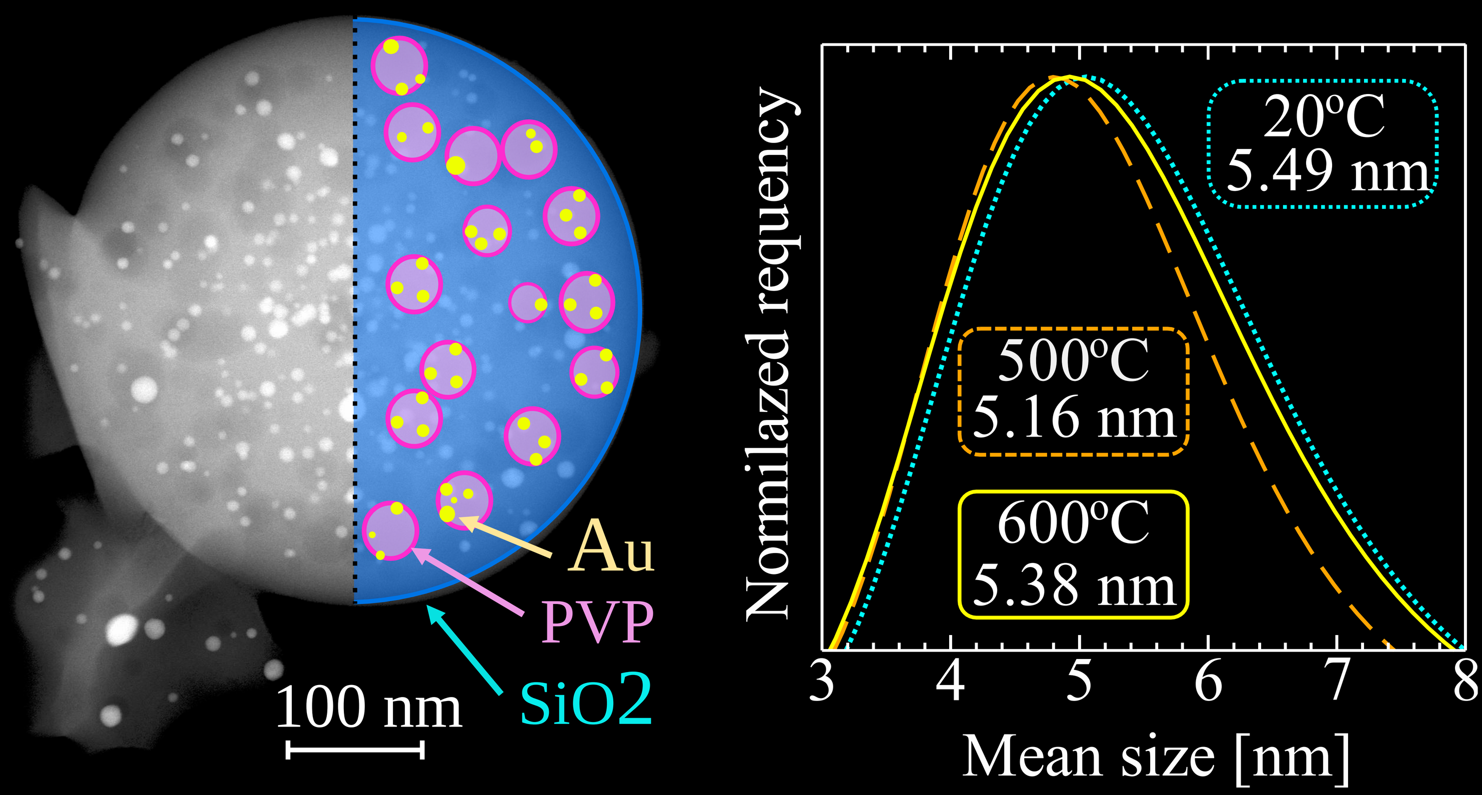


NON ISOLATED model (bottom => top)

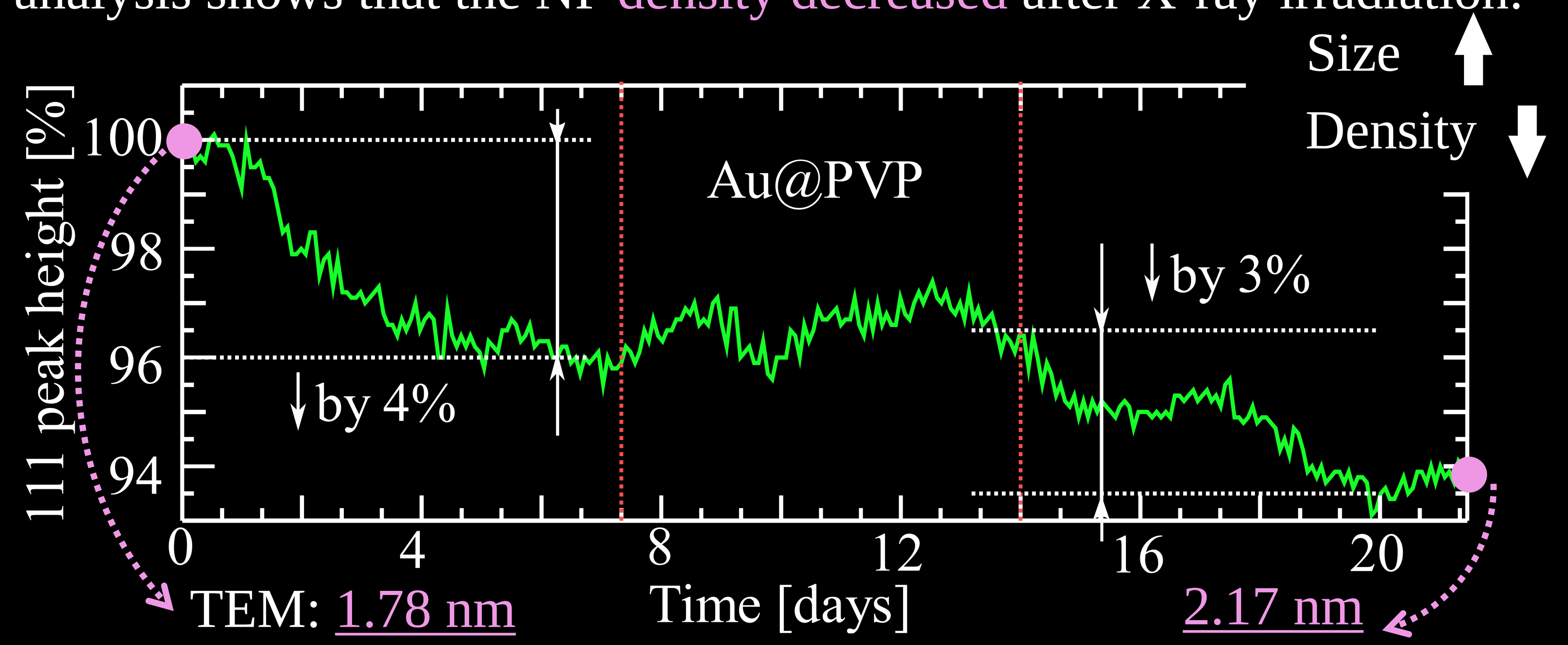


HAVE WE SEEN ANY OF THESE MODELS ?

The encapsulation of Au NPs in SiO_2 can slow down the growth of particles. This feature makes the change in internal morphology more noticeable. As a result, the ex-situ heating of Au NPs in a He flow leads to a decrease in the mean size. Meanwhile SAXS analysis shows an increase in density.

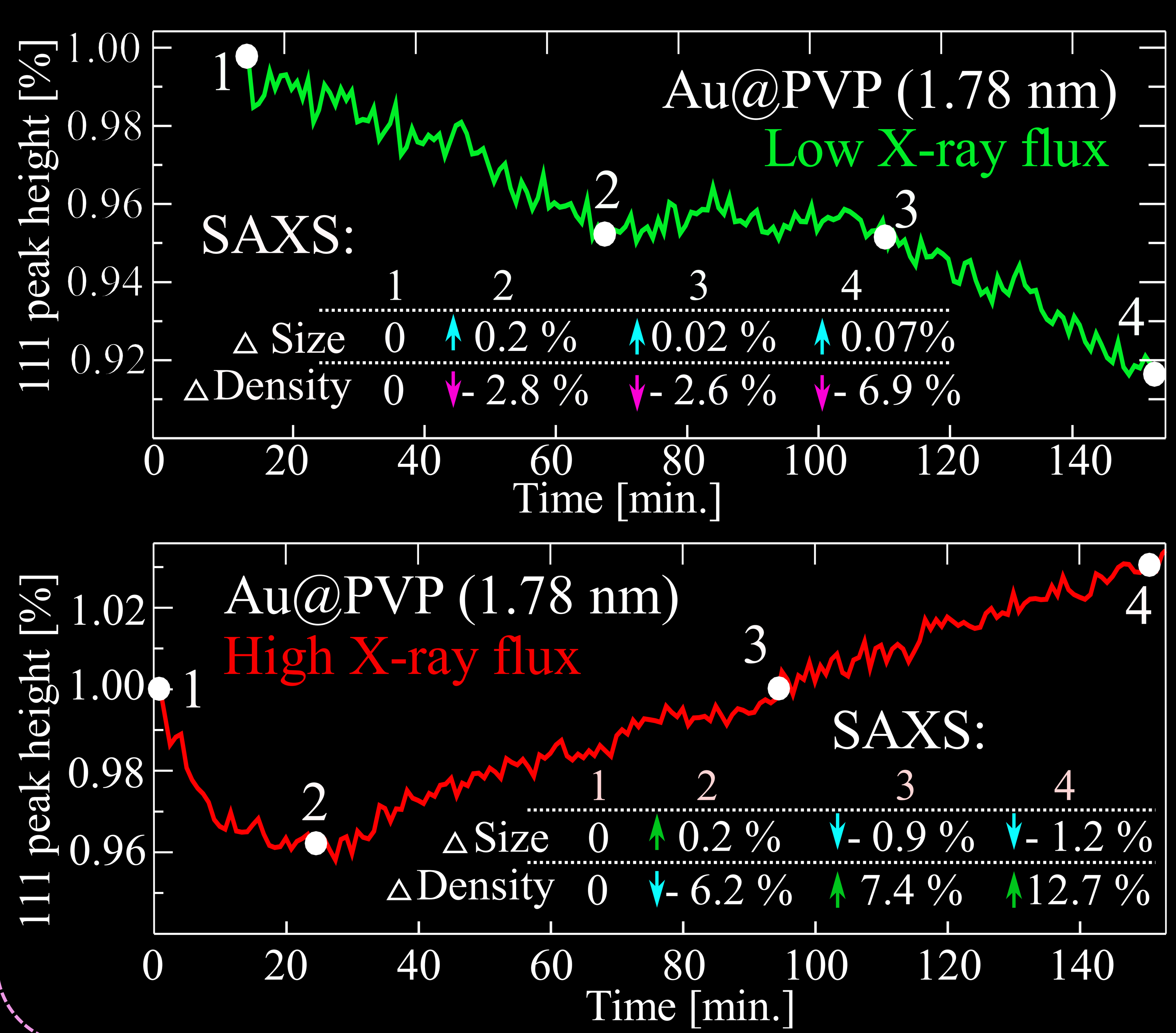


We found that FCC metals evolve under constant exposure to Cu laboratory X-rays. It has been tested for Cu, Ir, Pt, Ni, and Au. Small 1.78 nm Au@PVP NPs grew to 2.17 nm after 3 weeks of continuous regular XRD scanning. At the same time, the height of the 111 diffraction peak was continuously decreasing. SAXS analysis shows that the NP density decreased after X-ray irradiation.



IN-SITU SAXS & WAXS ANALYSIS

Change of 111 peak height caused by synchrotron X-ray



CONCLUSIONS:

Vacancies driven twinning is the completely new concept and requires detailed verification. The key aspect of which is the detection of vacancies in NPs. Direct observation of vacancies is impossible, so we can only measure related parameters: density and size of particles.

It can be done with relatively simple tools as TEM and XRD. However it's time consuming and key parameters can't be measured parallelly.

The combination of WAXS and SAXS allows to:

- to measure both key parameters with excellent time resolution;
- to get more information about the diffusion of vacancies. When exposed to a high X-ray flux, the vacancies are likely to disappear. X-ray radiation with a low flux leads to a slow accumulation of vacancies.

ACKNOWLEDGEMENTS

- We thank DESY for supplying beamtime for this project under proposal number: I-20210744 EC;
- Dr. Sylvio Haas (DESY, beamline P62, Hamburg) for help in organizing the measurements and data collection / reduction;
- Ph.D. Marion Flatken (Helmholtz-Zentrum Berlin) for help with data collection