In-situ TEM Heating Study of Cu and Ag Nanoparticle Interactions

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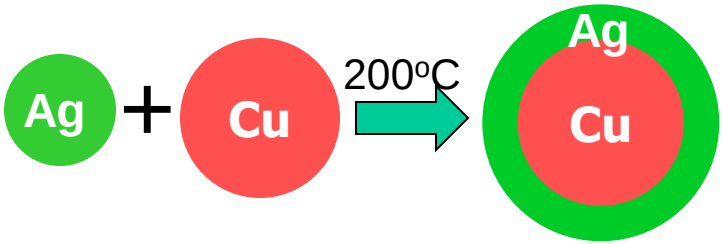
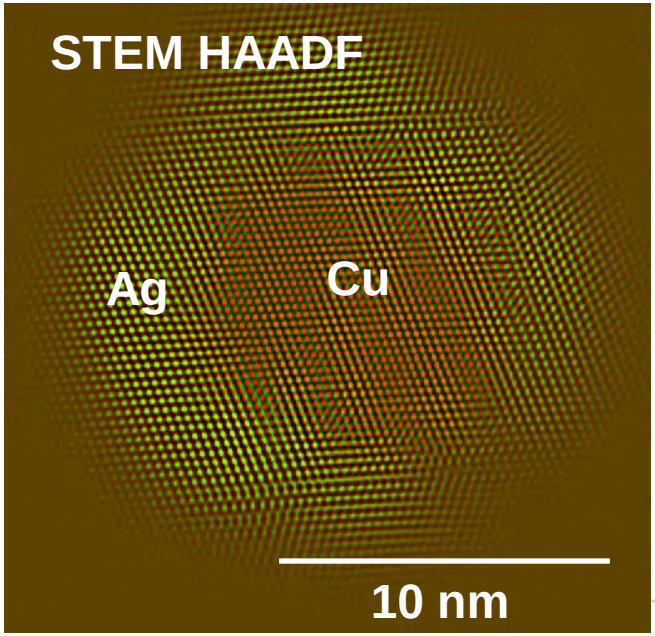
Albuquerque, NM





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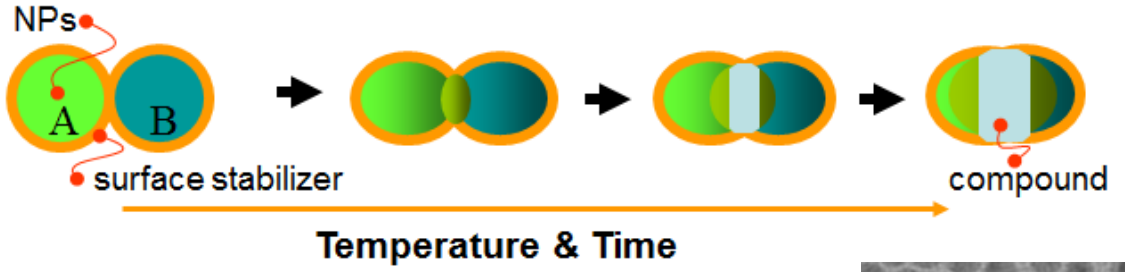
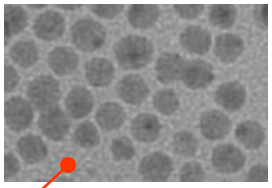
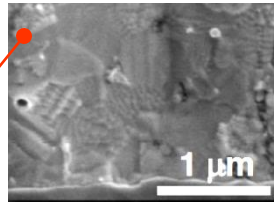
Motivations

- **Science – how do metallic nano-particles (NPs) interact at elevated temperatures? what are the equilibrium nano-alloy structures?**



- **Applications – metallic NP solders**
  - **Low processing temperatures**
  - **High service temperatures**
  - **Ag/Cu system: bonding at ~200°C and applications at above 350°C**





- **Few in-situ TEM experiments on dissimilar metal NPs**

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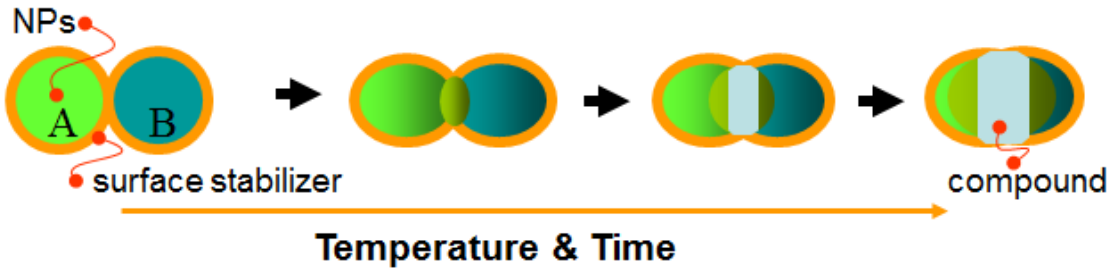
R&D Goals & Approach

- **In-situ TEM observation & Atomic-scale MD modeling**



- In-situ, aberration-corrected STEM will used to obtain ***atomic-scale*** images (at T, t).

- ***Direct comparison*** between the experiment and theory (MD) will be used to understand the reaction model.

- FEI Titan G2 80-200kV – a probe corrector + *ChemiSTEM Technology*
- Protochips Aduro in-situ heating holder – 1000°C/sec heating rate
- Gatan 626 single tilt heating holder

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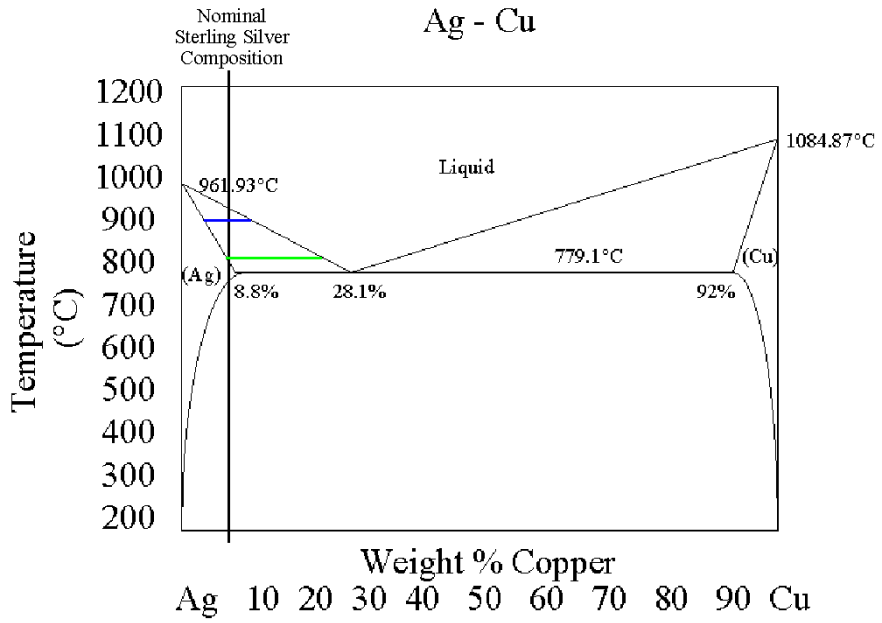
Ag/Cu Phase Diagram



- Eutectic system
- Not miscible
- This is bulk, is nanoscale different?

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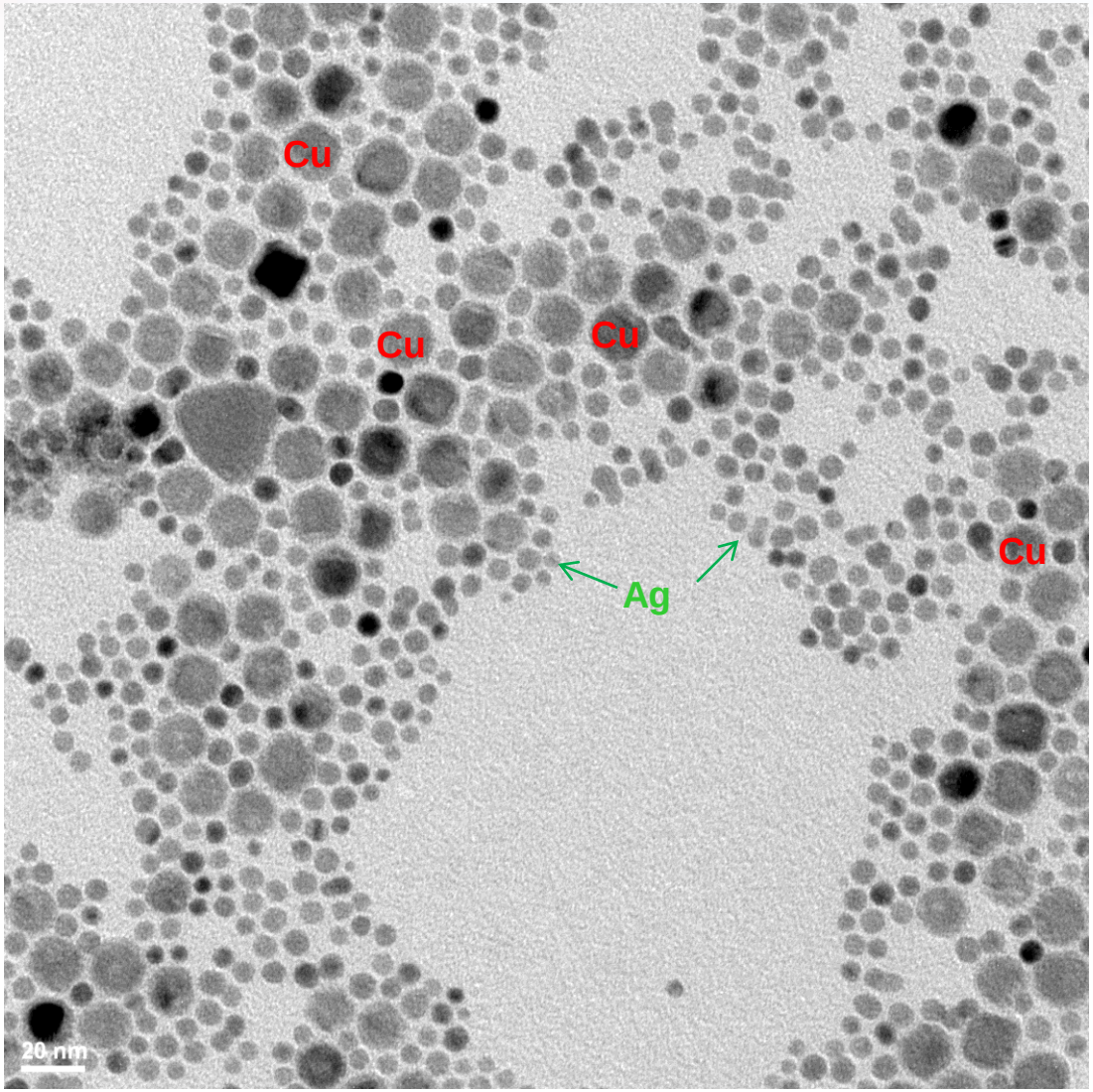
Ag/Cu assembly before in-situ heating



- Cu NPs – 12-15nm
- Ag NPs – 6 nm
- Mixed in toluene and drop deposited on carbon film
- Ag NPs are present in between Cu NPs

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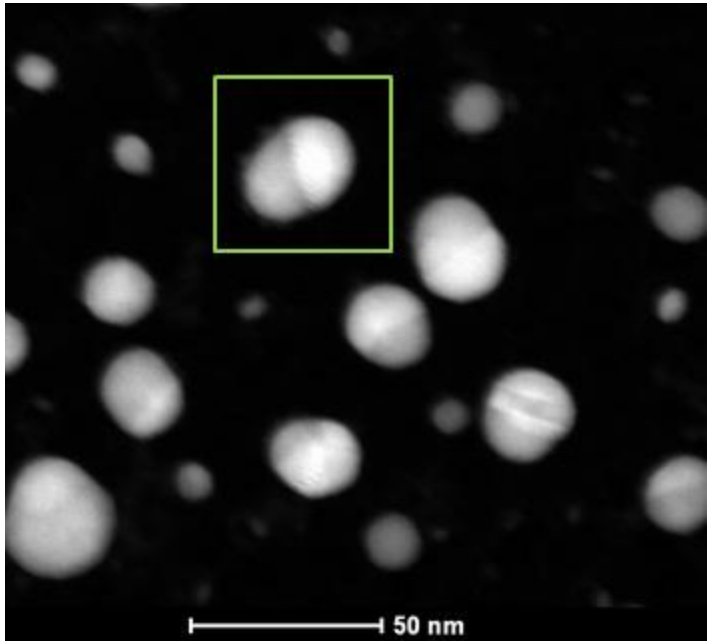
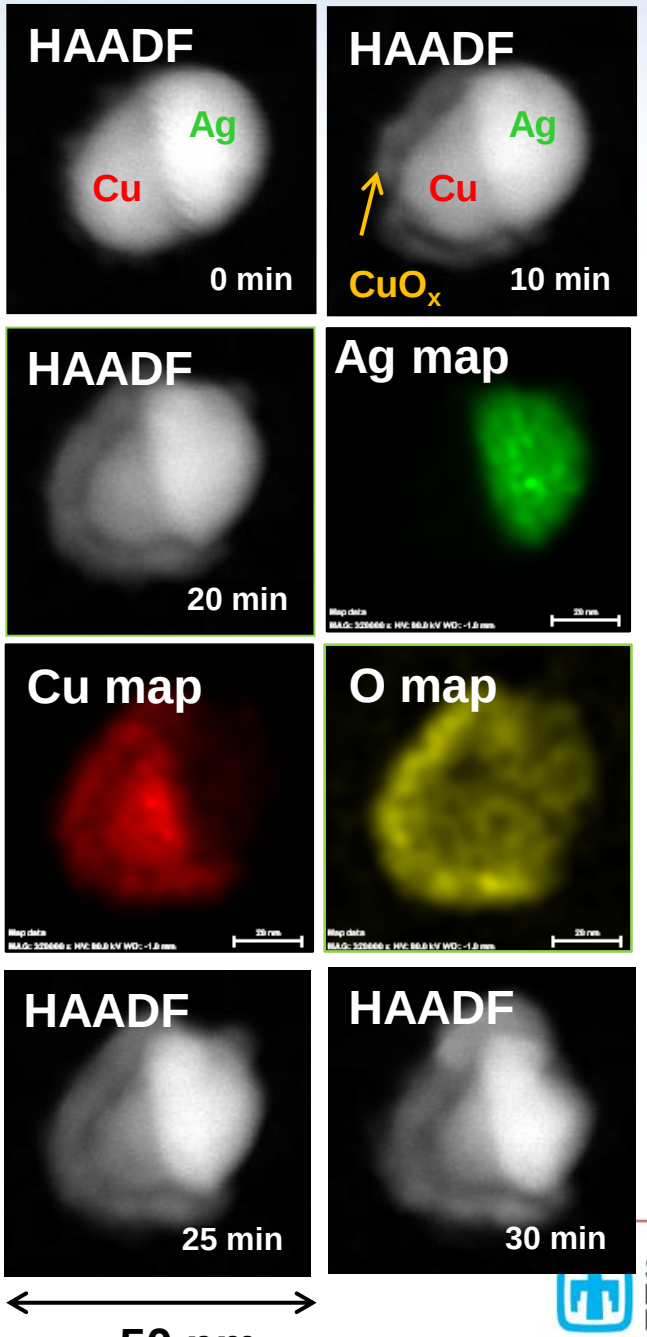
In-situ TEM Challenges

- **Electron beam irradiation effects**:
  - Electron beam exposure makes metallic NPs less active.
  - Electron beam exposure also leads to oxidation of Cu NPs





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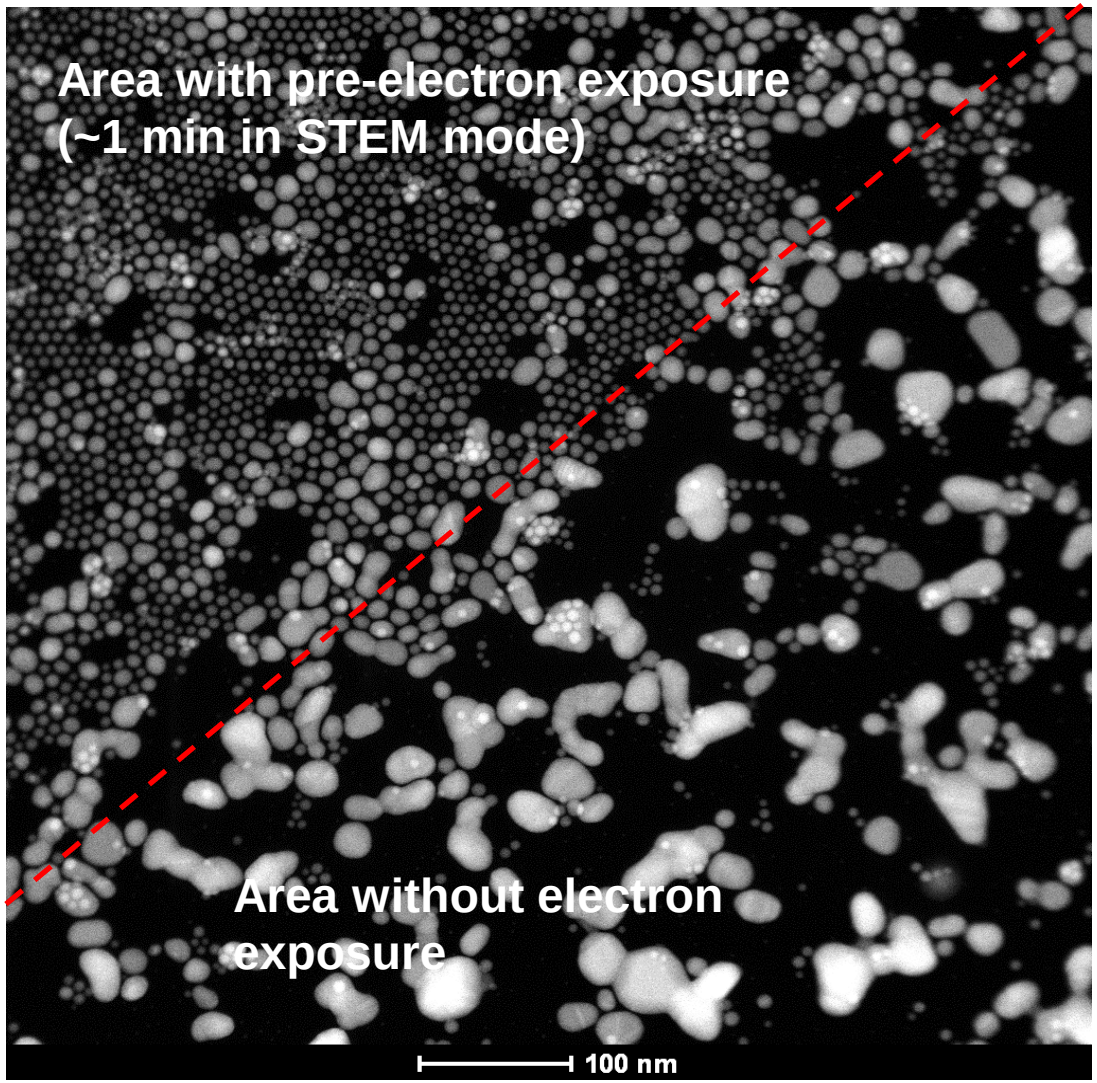
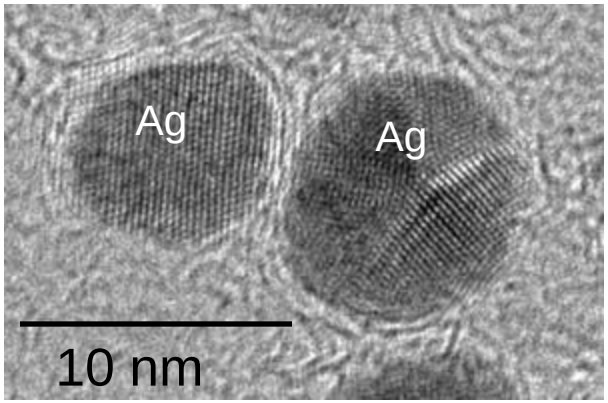
Avoiding the electron irradiation effect is critical in in-situ experiment!

Ag NPs in-situ heating 160°C, 5 min



Formation of a graphitic shell on Ag NPs under electron beam irradiation



A similar effect was reported by Sutter *et al* for Au NPs at higher temperatures (Nano Letter 5, 2092, (2005))

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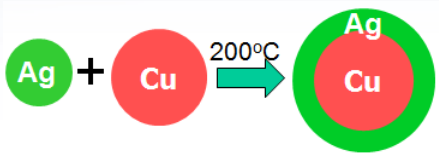
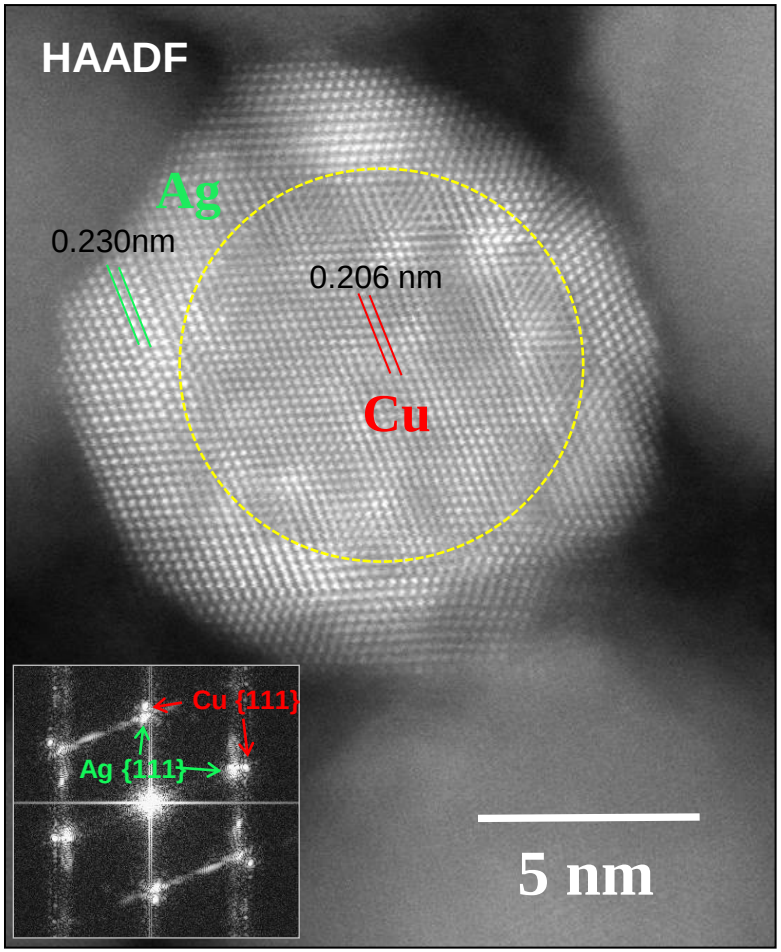
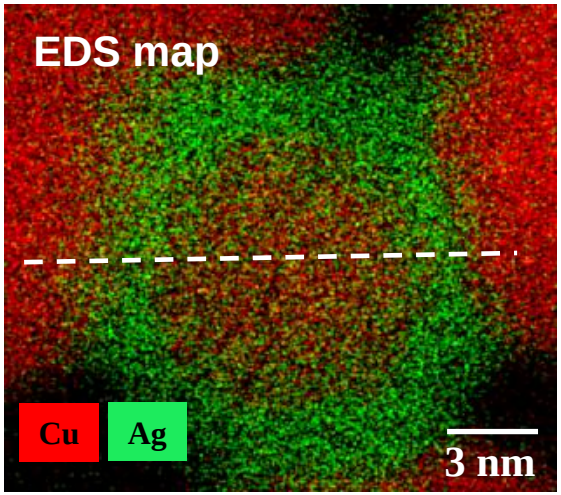
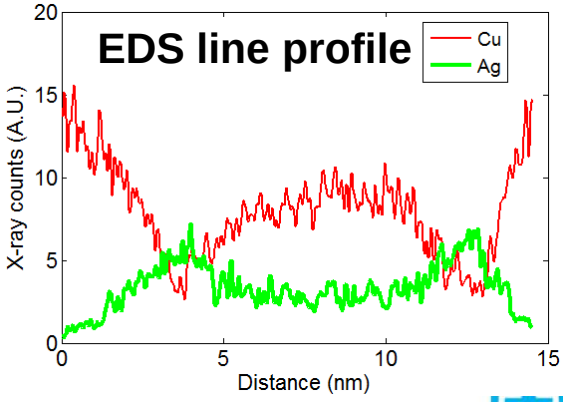
Cu/Ag NPs interact at temperatures as low as 150°C and form a Cu-core/Ag-shell structure



Cube-on-cube orientation relationships between Cu-core and Ag-shell







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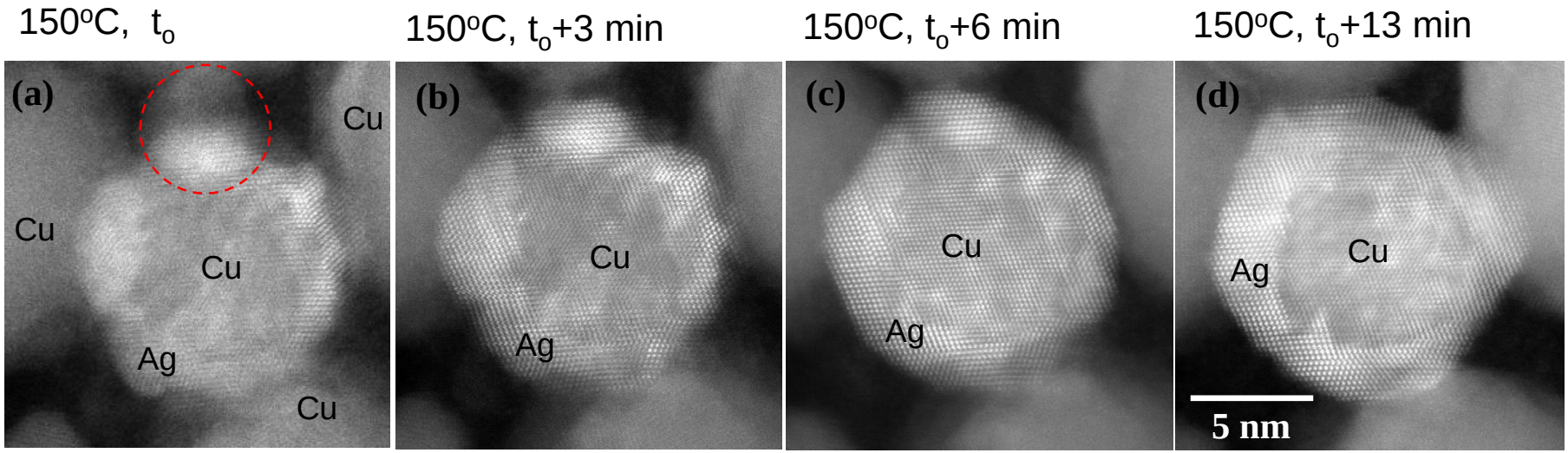

- Electron beam was off during the heating!
- The core/shell structure appears to be stable as long as no new interactions are initiated with neighboring NPs.

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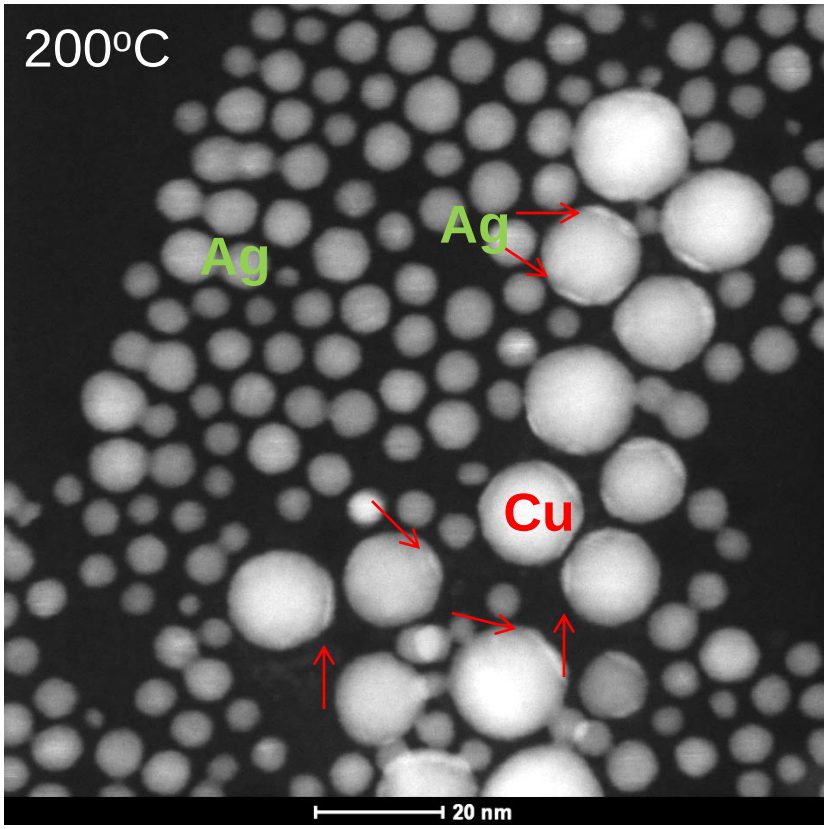
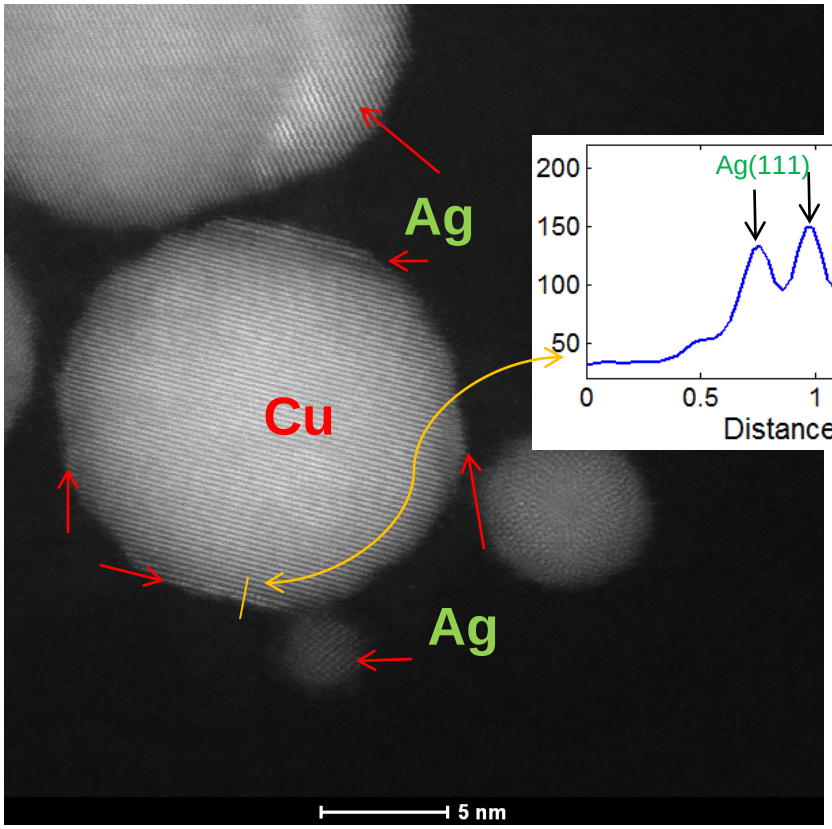
Initial Ag/Cu Interaction

– Ag wetting on Cu {111} surface, and forming Ag{111}/Cu{111} type of epitaxial layer.

– Ag layers can be as thin as ~2-3 monolayer {111} Ag.





Small NPs are Ag (~6 nm)

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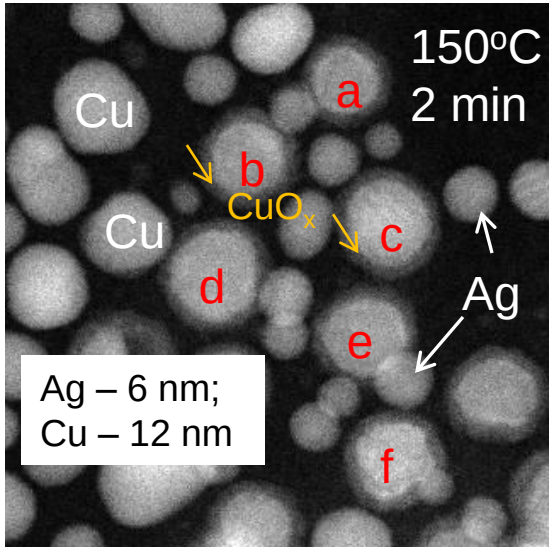
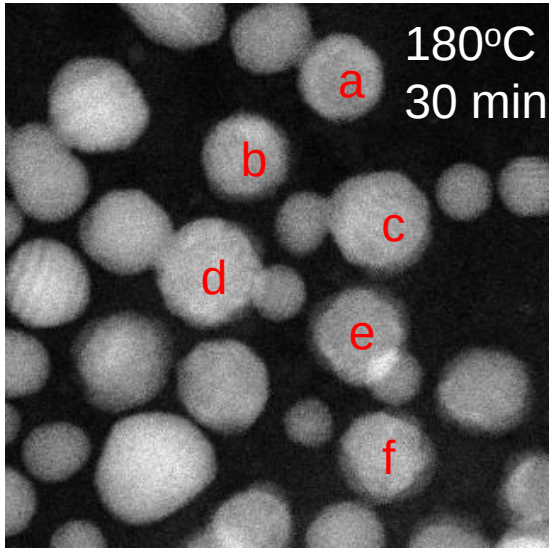
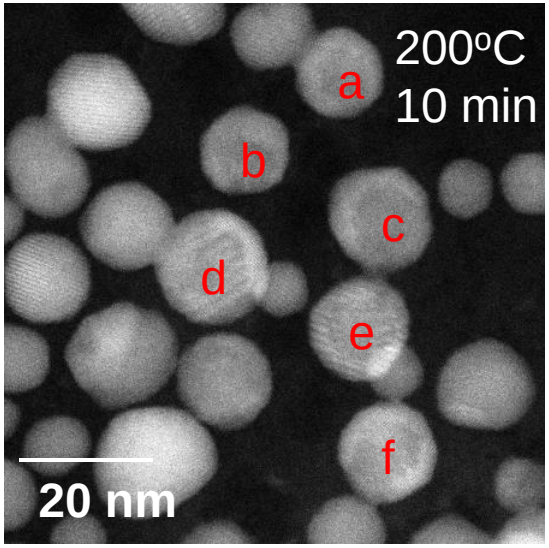
Effect of Cu oxide layer on Cu/Ag NP interaction

- **The presence of Cu oxide layer on Cu NPs makes the Cu/Ag core-shell formation process longer**







Cu NPs can be partially oxidized before the Cu/Ag interaction

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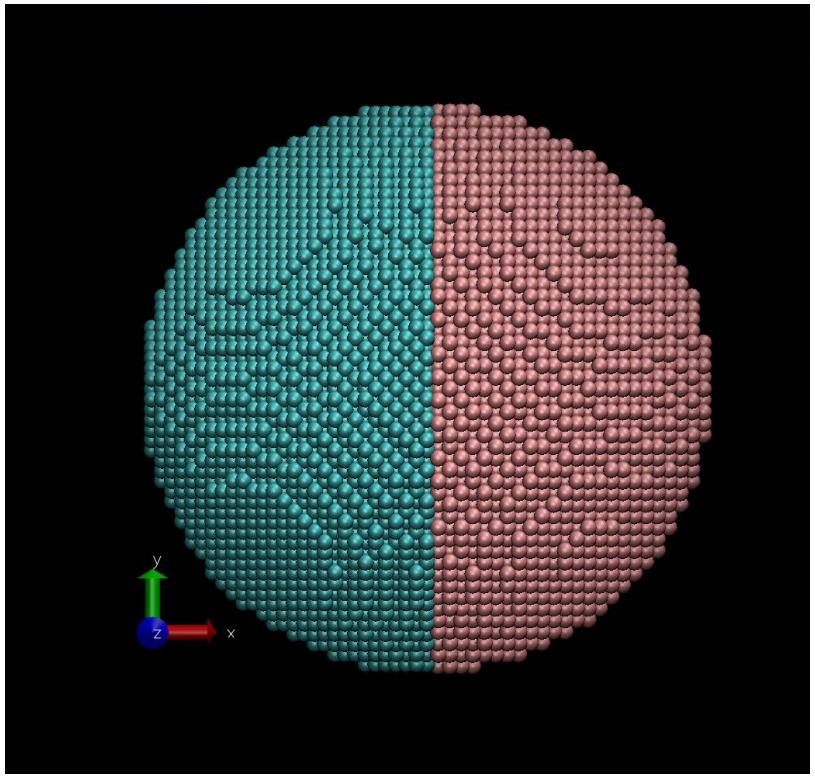
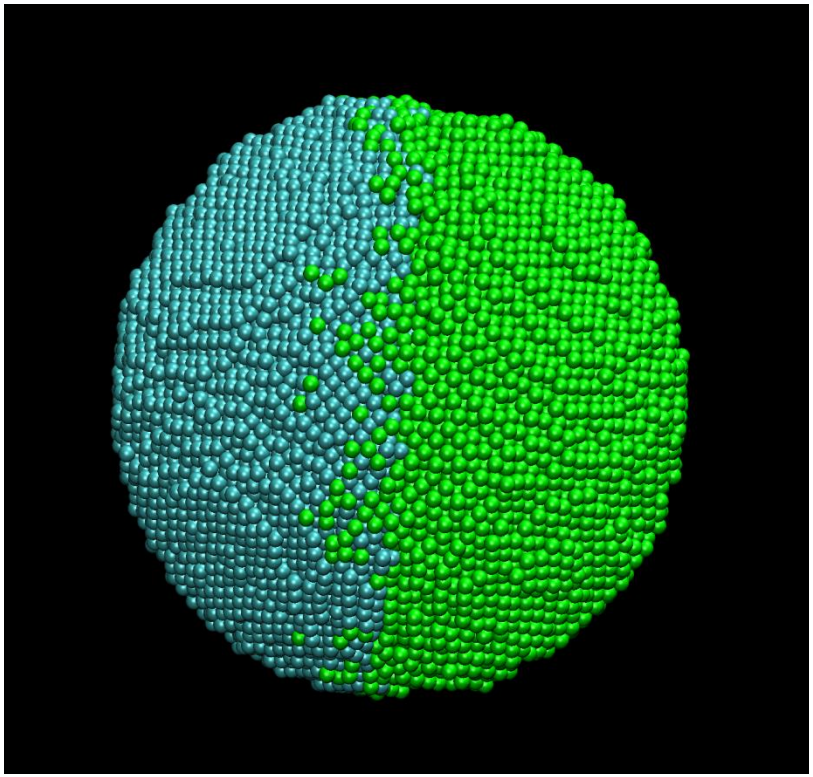
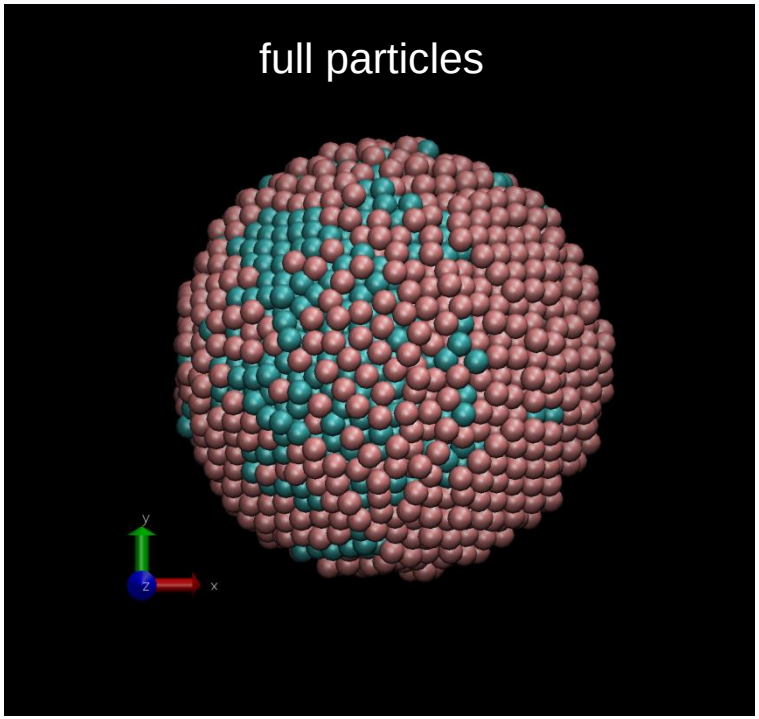
Simulation Results

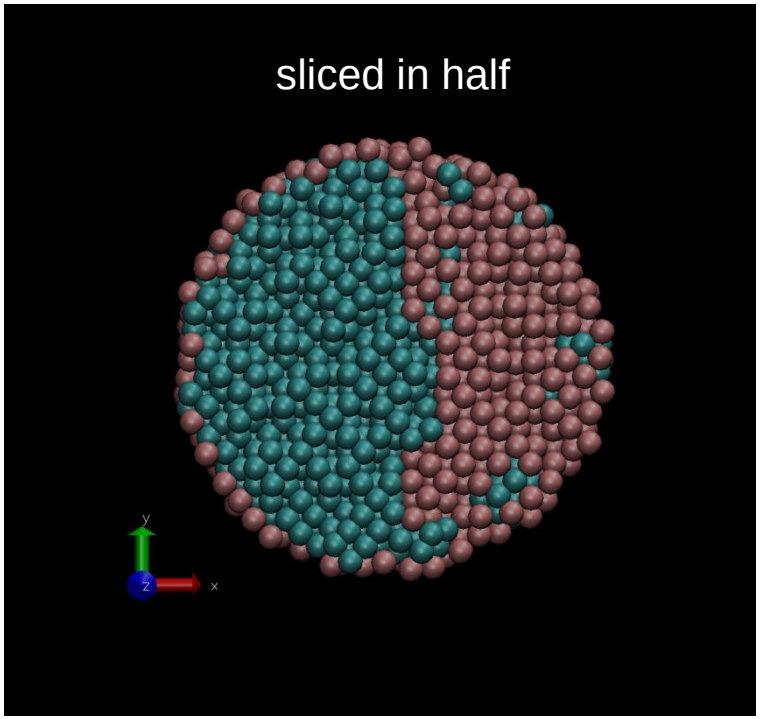




- 10nm Janus nanoparticles (left half Cu, right half Ag)
- At 800K (below eutectic) for < 1 ns

Monte Carlo Simulations





- Simulation is not real time, but can be slow
- Randomly pick two particles to swap (with small translation)
- Accept move if energy is lower, or according to Boltzmann
- 5nm particle after 20M steps

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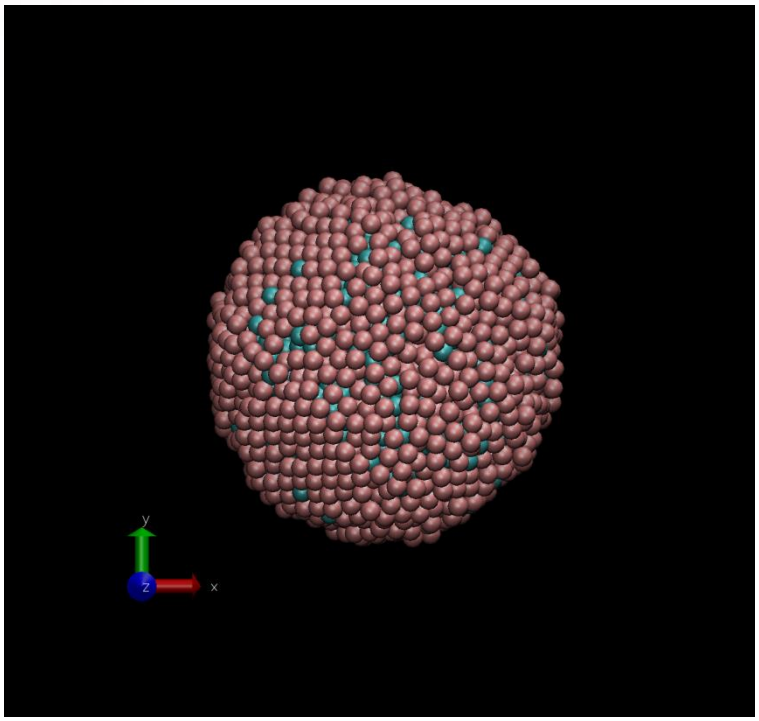
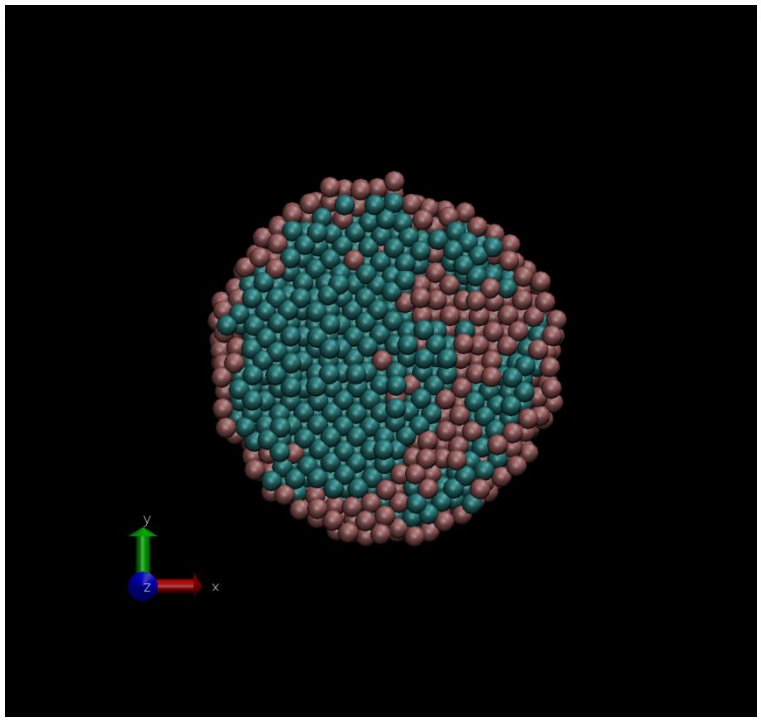
Longer Time Results

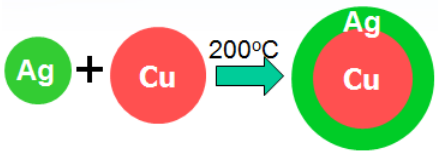




- 5nm, after 60M steps
- Shell is clearly favored at 800K

Conclusion

- Ag (~6nm) and Cu (~12nm) NP interactions at elevated temperatures (150°-300°C) lead to formation a 3-D epitaxial Cu-core/Ag-shell structures.



- The interaction takes place initially by Ag wetting Cu along its {111} surfaces and forming an Ag {111}/Cu{111} epitaxial interface.
- The Cu-core/Ag-shell structure appears to be a thermally stable structure for the Cu-Ag nano alloys.
- The observation is possible only after avoiding the effect due to irradiation of electron beam.
- The new structure can be only explained as a nano-effect related to the large surface-to-volume ratio of the particles, and potentially could be exploited for several technological applications.

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