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Finite size effects on grain boundary structure and precipitate composition

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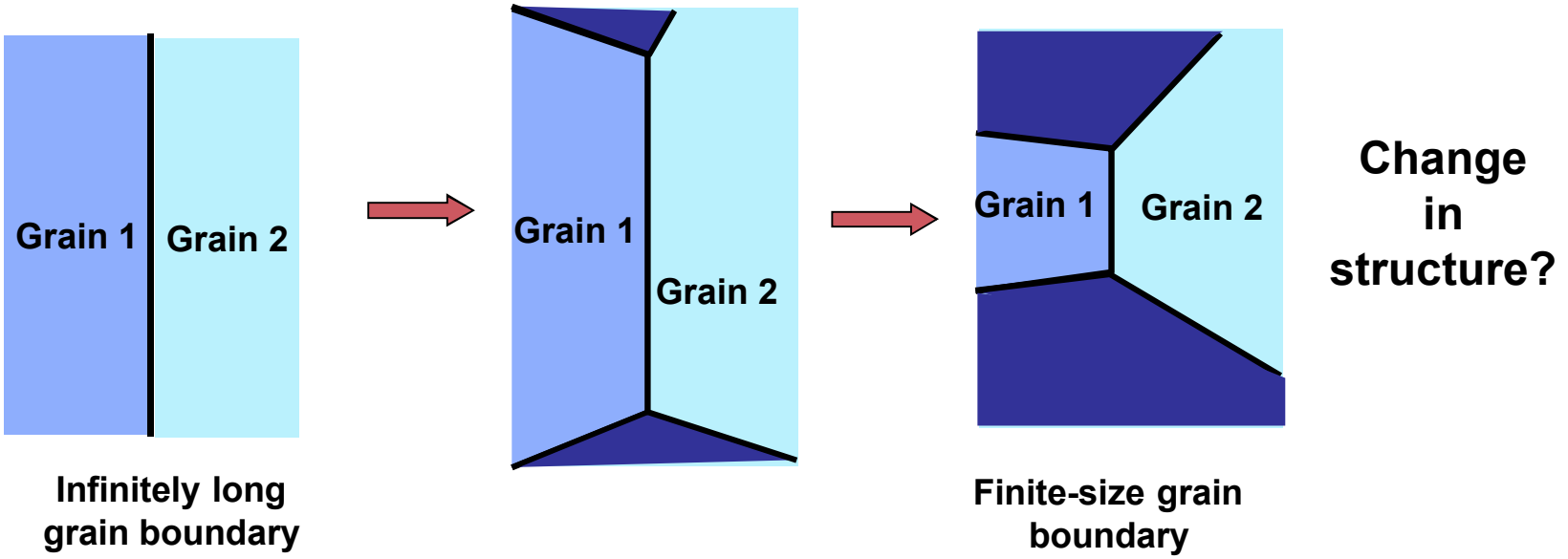
Internal interfaces: relationships between structure, chemistry and topology

- **Complexity** of interfaces
  - 3D objects, homophase/heterophase, chemistry, defects, strains, …
- **Atomistic mechanisms** controlling the structure of interfaces
  - High spatial and chemical **resolution** tools
    - Transmission electron microscopy
    - Atom probe tomography
  - Extract **quantitative** information from observations to validate **theoretical** predictions
    - Controlled model systems
    - Detailed understanding of physical atomic phenomena

- **Two examples**:
  - Homophase interfaces: Grain boundary structures
  - Alloy structures: Precipitate structures in Al-Ag alloys

Finite size effects on the structure of grain boundaries

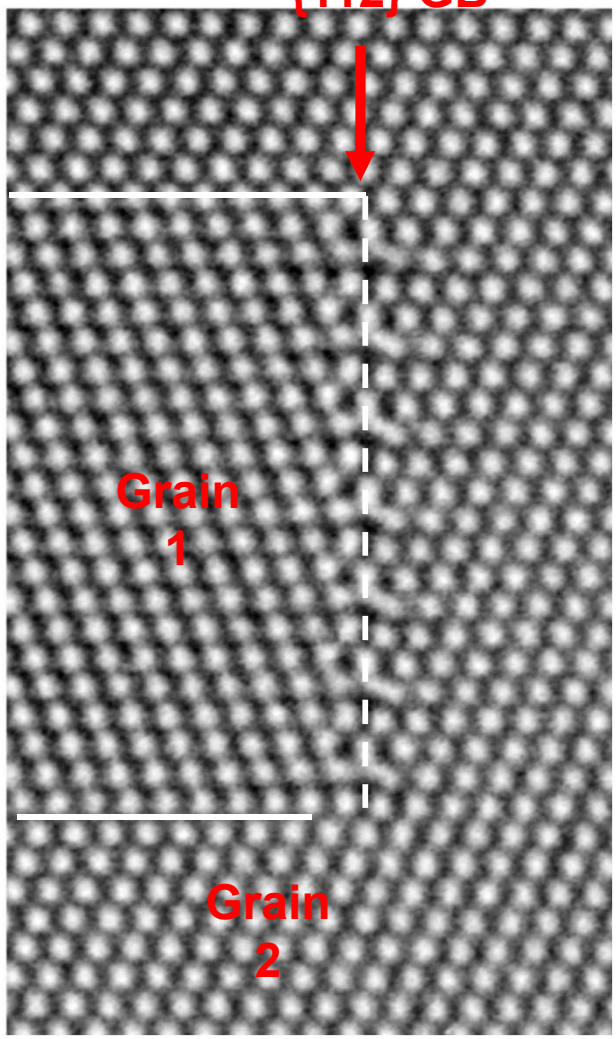
Acknowledgements: John C. Hamilton, Douglas L. Medlin and François Léonard



Challenge: how to quantify the roles of atomic relaxation and elastic interactions

→ **Combination of systematic experimental observations, continuum modeling and first-principles calculations.**

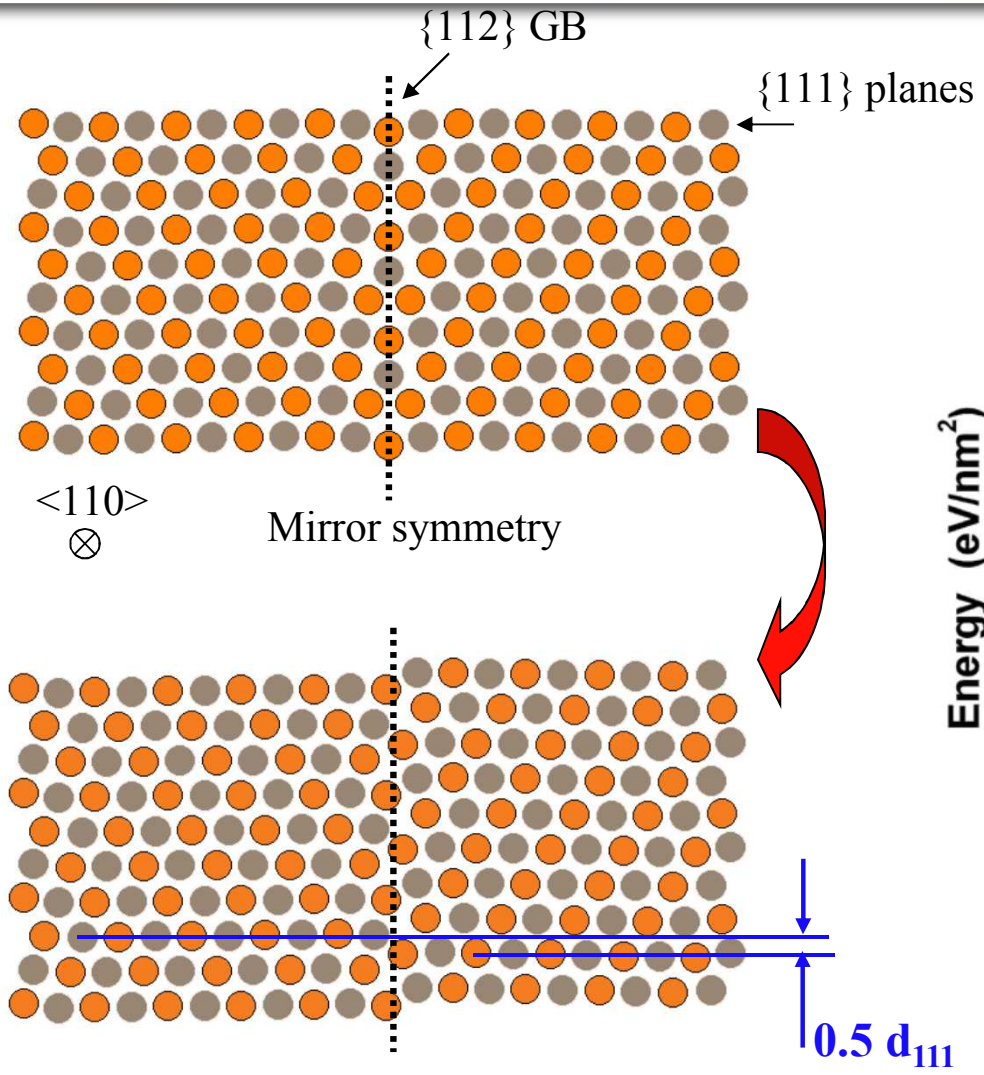
The {112} twin boundary



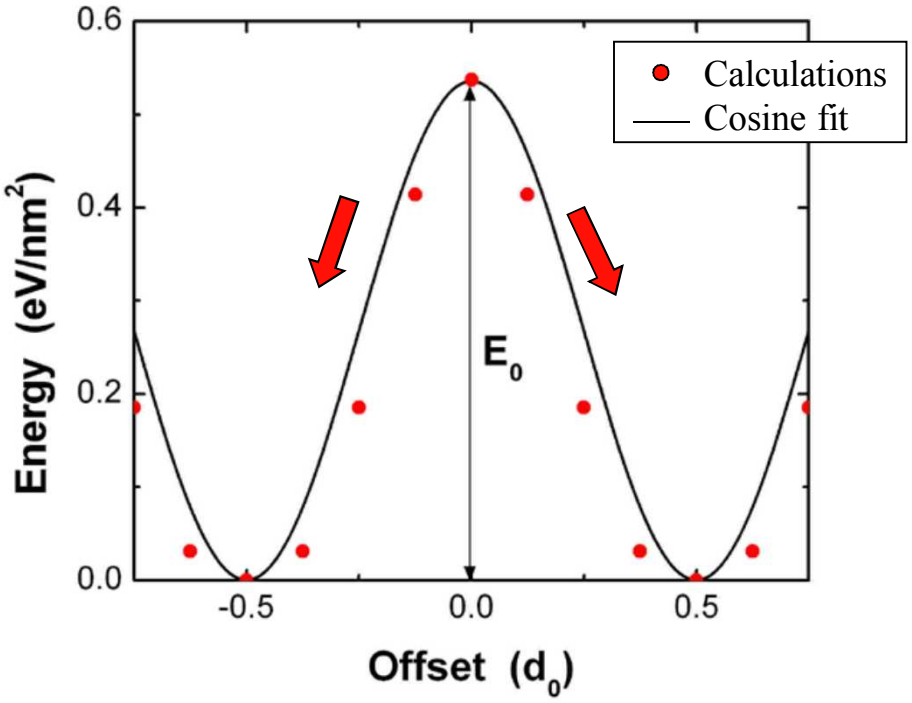
- **Simple structure previously studied**
  - For instance, in Al: Medlin et al. (1993)
- Conflicting report in the literature about the structure
  - Au: Ichinose and Ishida (1985)
  - Au: Krakow and Smith (1987)
  - Al: Penisson, Dahmen, Mills (1991)
- Relevant for nanocrystalline and grain boundary engineered materials

Vapor Deposited
Au thin film on <101> NaCl

Plane offset at the infinitely long Σ3 {112} boundary

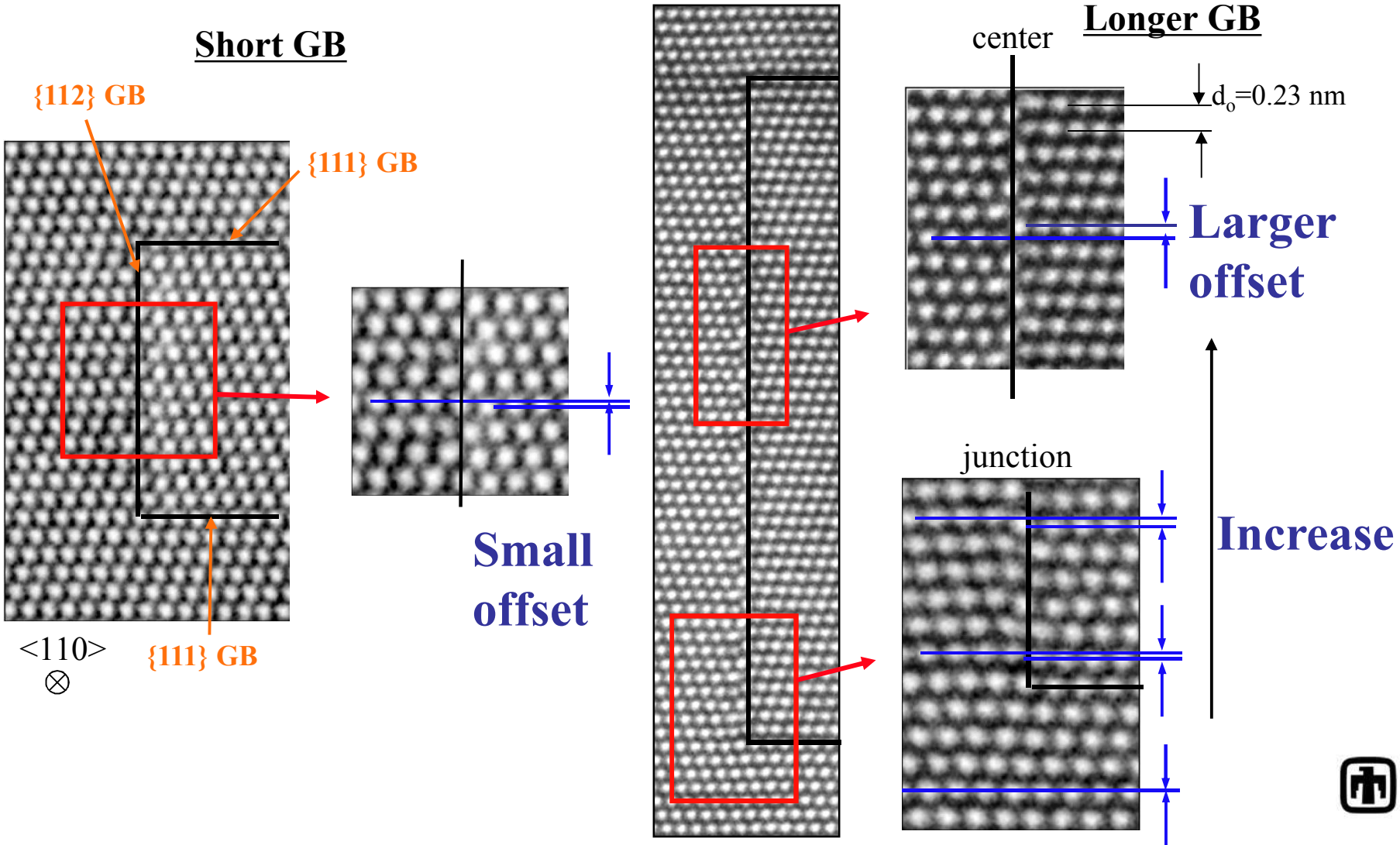


First-principles calculations of GB energy

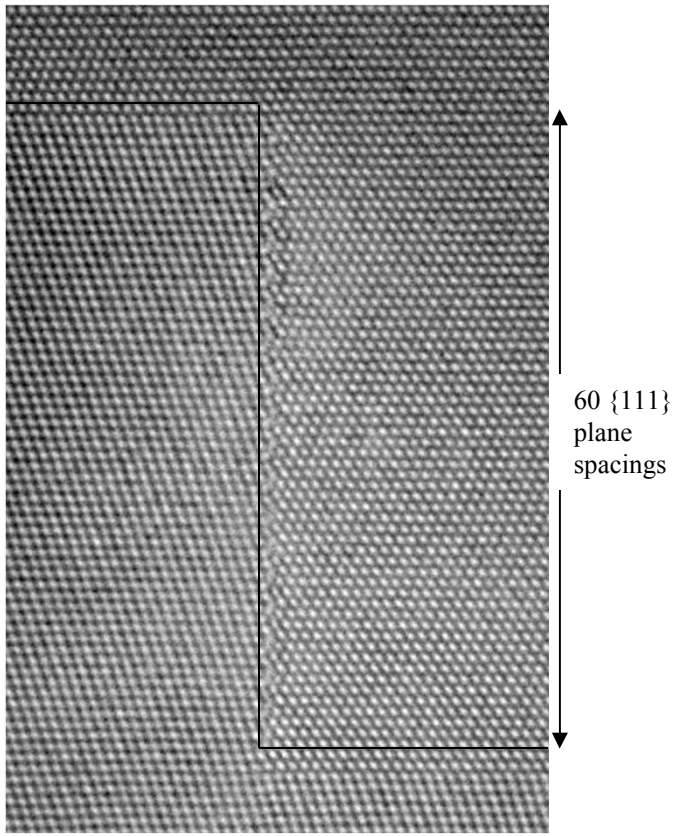


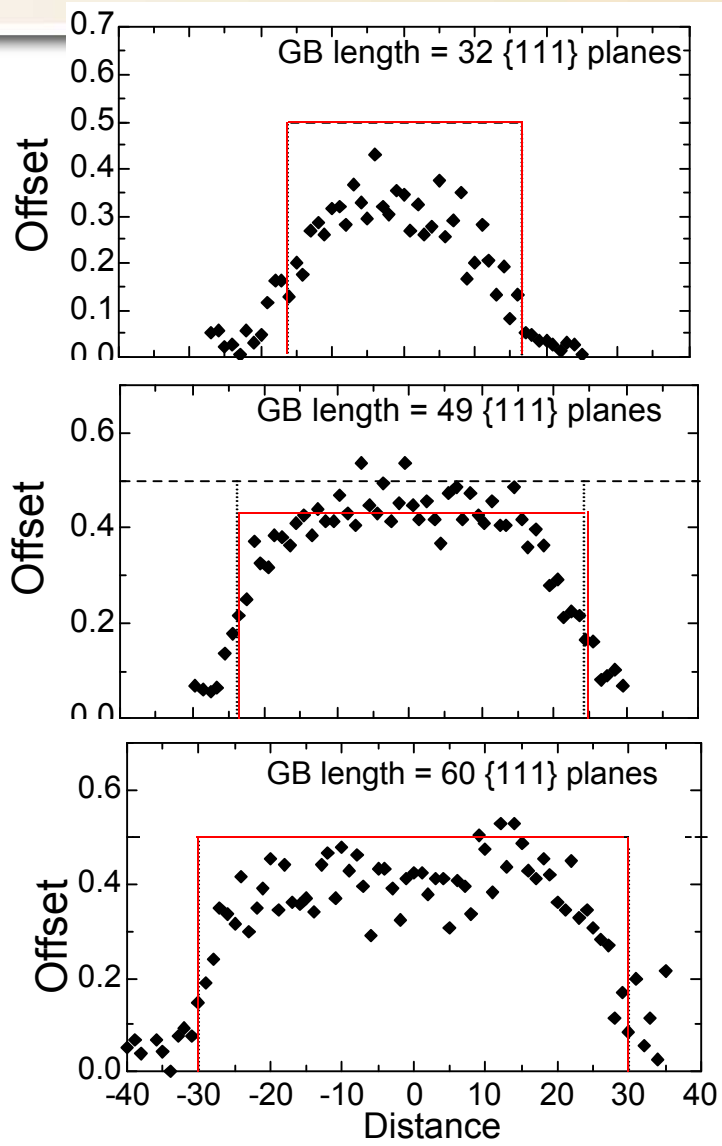
$E_o = 0.5$ eV/nm^2

Offset changes with GB length and location at {112} GB



Offset profiles: length dependence

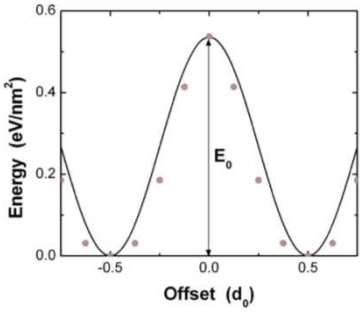




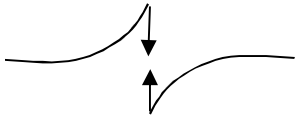
Modeling of the offset along the boundary

- Offset energy

$$E_{offset} = \frac{E_o}{2}\int_{length}\cos\left[\frac{2\pi\phi(y)}{d_o}\right]dy$$



- Elastic energy (restoring force)



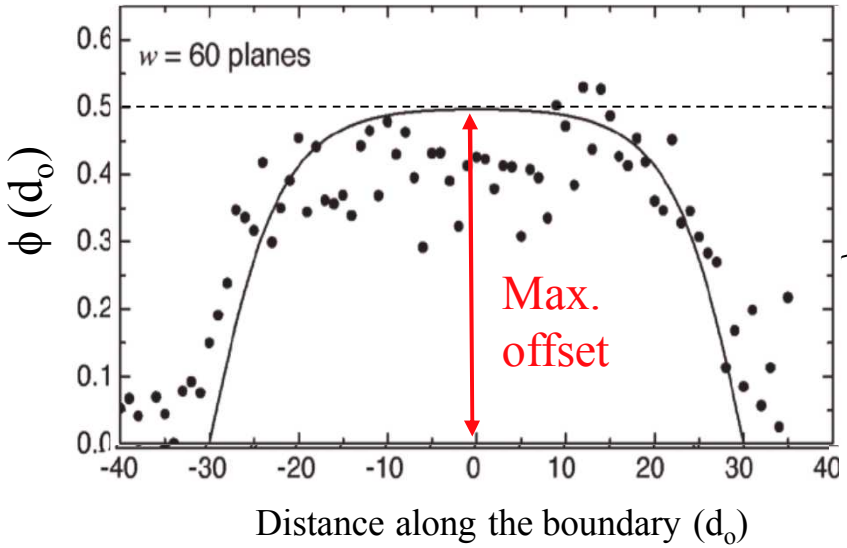
$$E_{elastic} = \frac{\pi G d_o}{2(1-\nu)}\int_{length}\left|\nabla_y\phi\right|^2 dy$$

Profile obtained by minimization of the energy of the boundary: $\frac{\delta E}{\delta\phi} = 0$

Offset profile along the boundary, $\phi(y)$, is solution of the equation:

$$-\frac{2\pi}{d_o}\sin\left(\frac{2\pi\phi}{d_o}\right) - \lambda\nabla^2\phi = 0$$

with $\phi = 0$ at $y = \pm w/2$ and $\lambda = \frac{2\pi G d_o}{(1-\nu)E_o}$



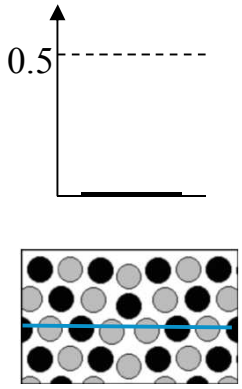
Best fit to the experimental profile for the parameter, λ

⇩

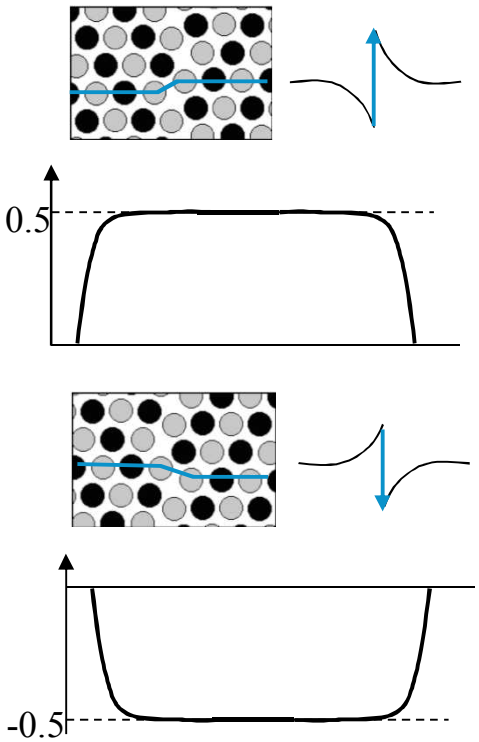
Experimental measurement of the energy barrier:
$E_o = 0.50 \pm 0.24$ eV/nm²

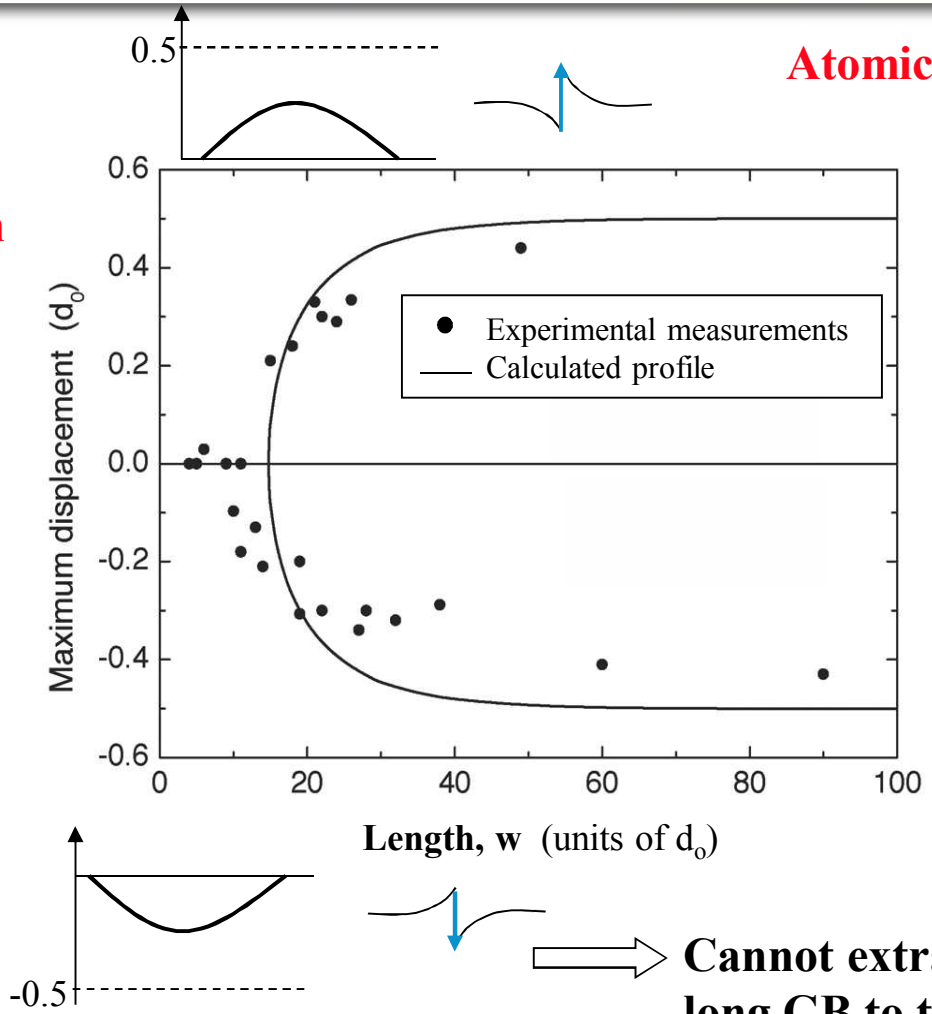
Elastic interactions leads to a structural transition

Elastic strain energy



Atomic relaxation





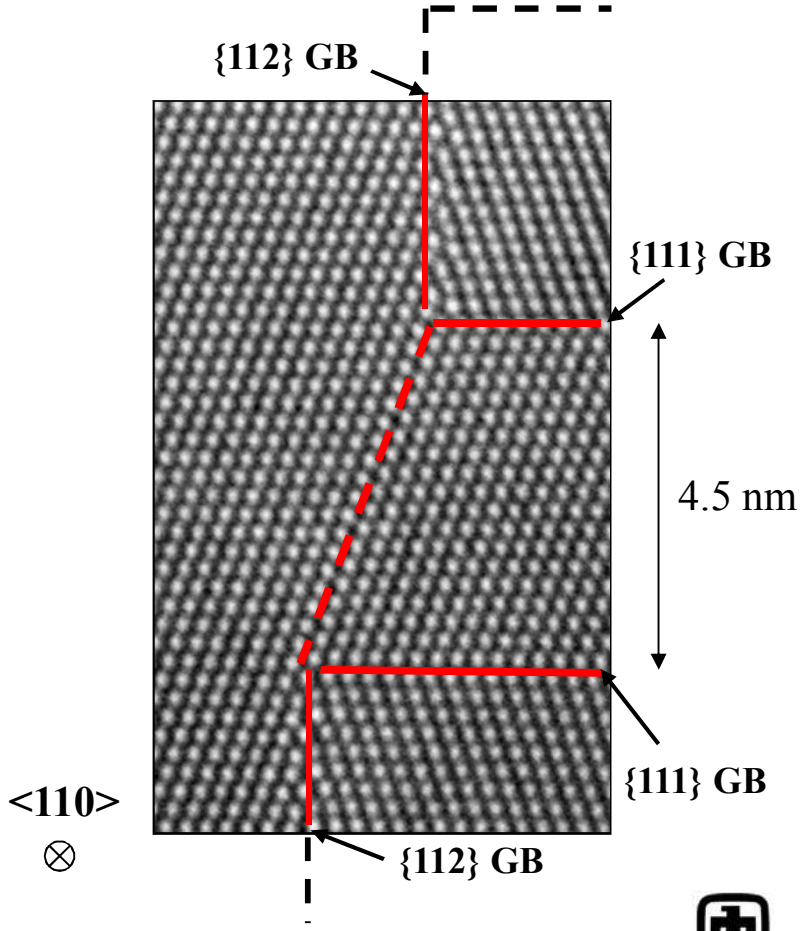
Cannot extrapolate structure of infinitely long GB to that of nano-length GB

E.A. Marquis, J.C. Hamilton, D.L. Medlin, F. Léonard Phys. Rev. Letters (2004)

Summary: Grain boundaries at the atomic scale

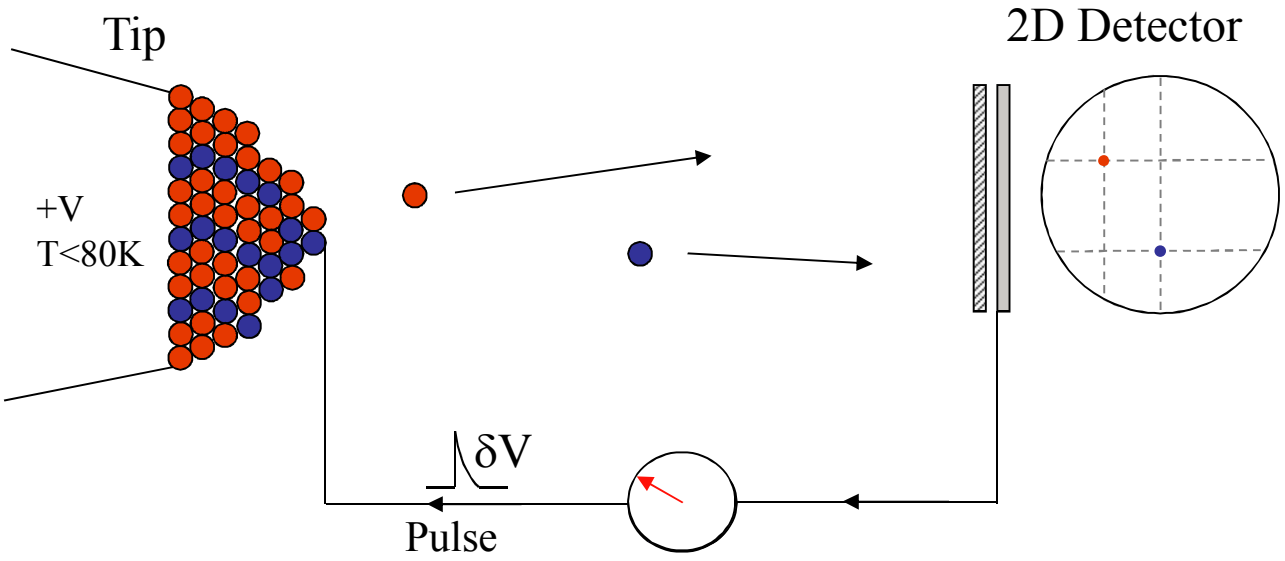
- From bi-crystal experiments to **real** materials…
- **Quantitative** study of grain boundary structures using TEM
- **Size** effect: Compromise between elastic energy and atomic relaxation

- Step towards the understanding of dislocation interactions with grain boundaries
  - Dislocation and GB interactions
  - Structure, deformation, stability of nanocrystalline materials



Atom Probe Tomography: atom by atom volume analysis

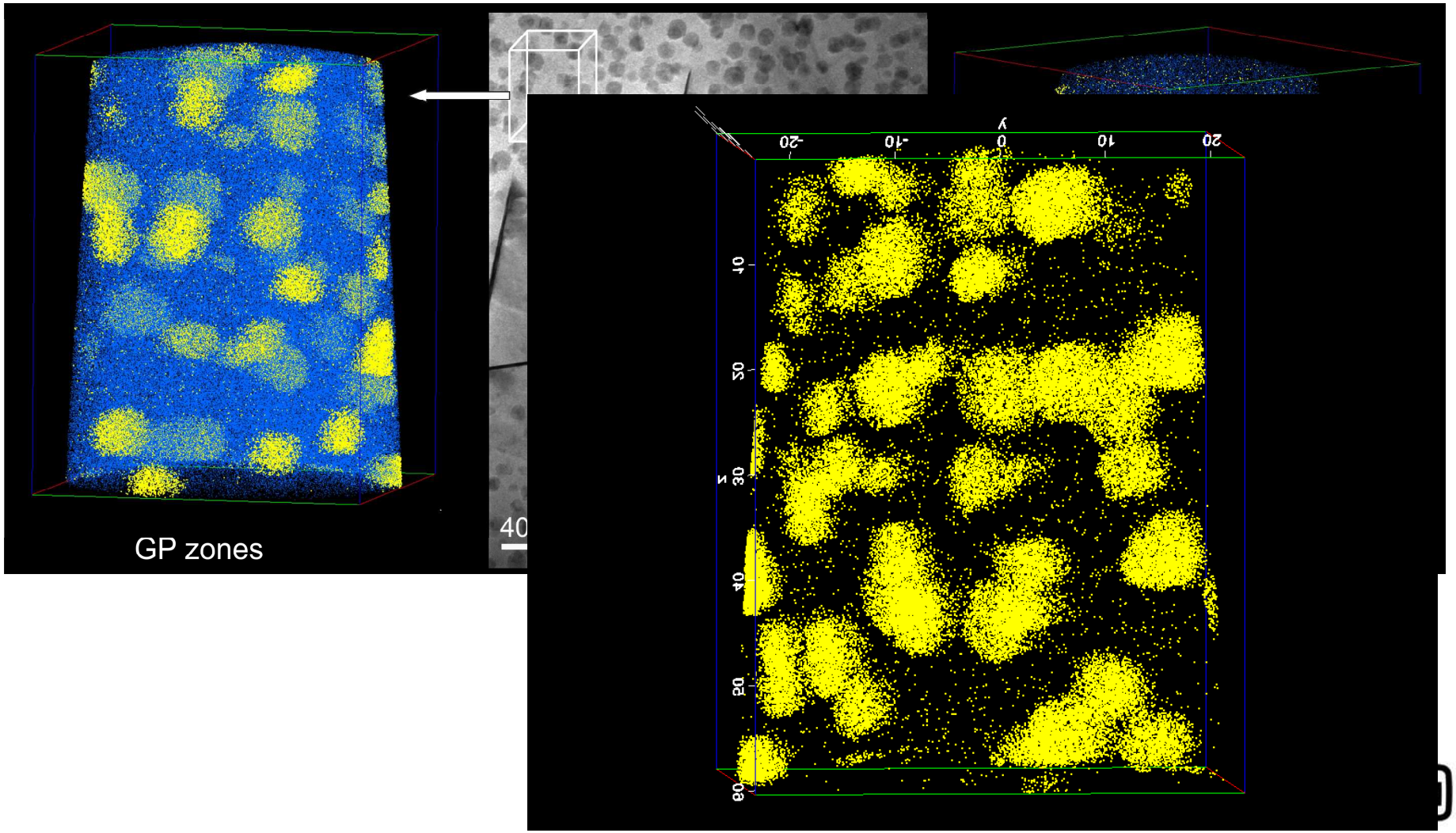
Time-of-flight mass spectrometry



Sequence of evaporation:
depth information

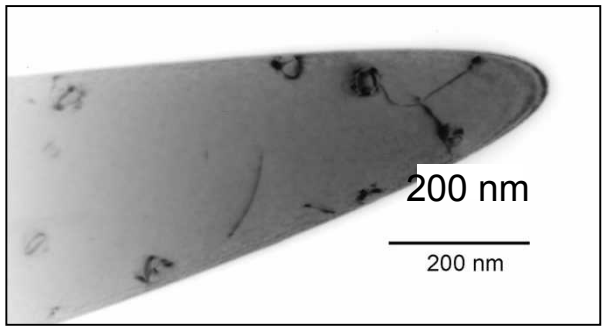
- Spatial resolution: 0.1-0.2 nm depth, 0.3-0.5 nm lateral
- 50-60% efficiency

3D reconstructions



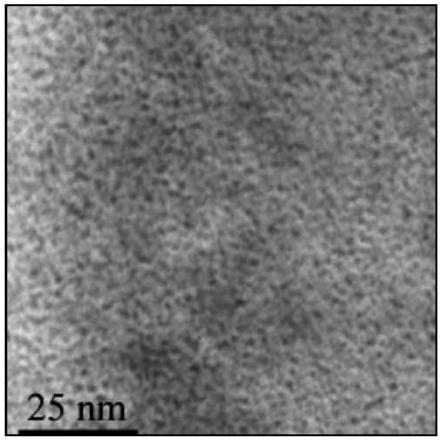
Alloy structures

- Understanding the solute distribution, solute interactions with defects, and temporal stability: **Atomic scale structure AND chemistry**
- Interfaces
  - Precipitate/matrix

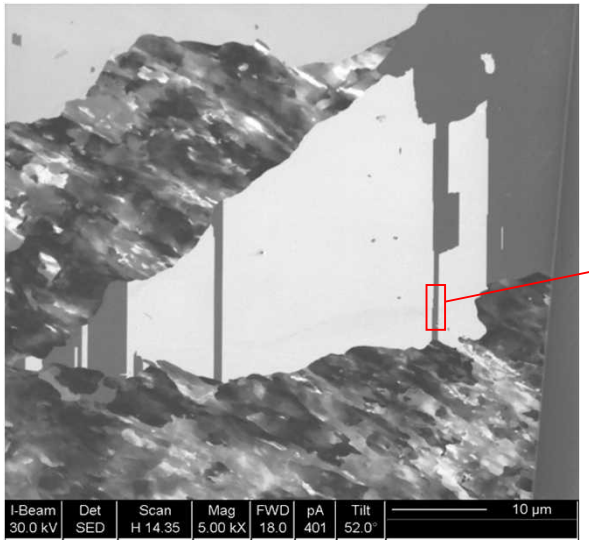


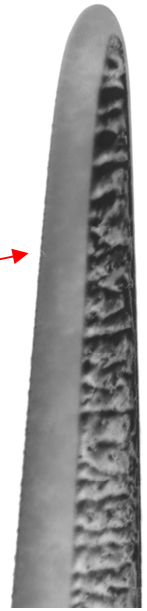
- Solute interactions

clusters



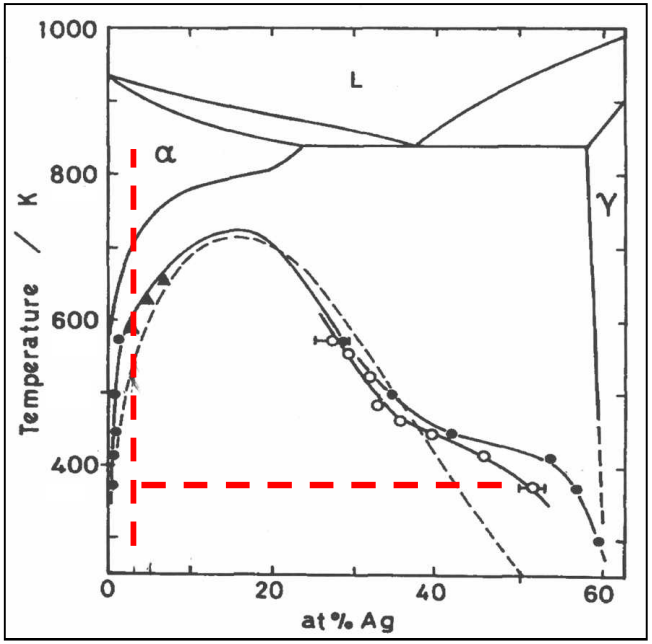
Grain boundaries

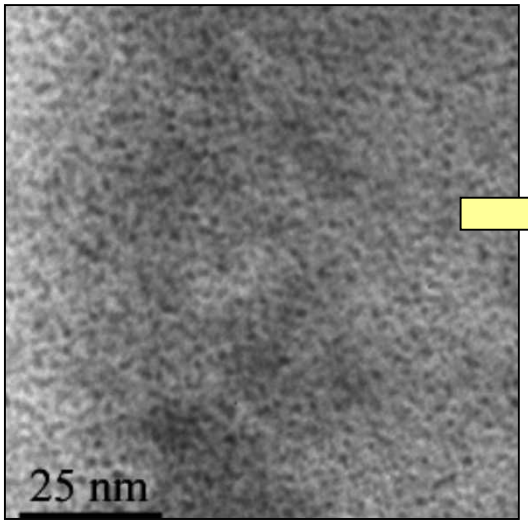




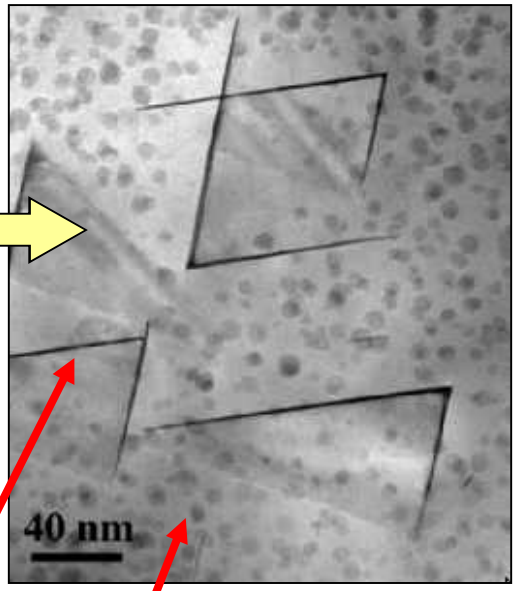
Structure of GP zones in Al-Ag alloys

Acknowledgements: Norman C. Bartelt and François Léonard





As-quenched



130°C-450hrs

γ'

GP zones

Solid-solution → GP zones → γ' → γ

Spherical

Plates (coherent)

Plates (Ag_2Al) (semi-coherent)

How does the structure evolve?

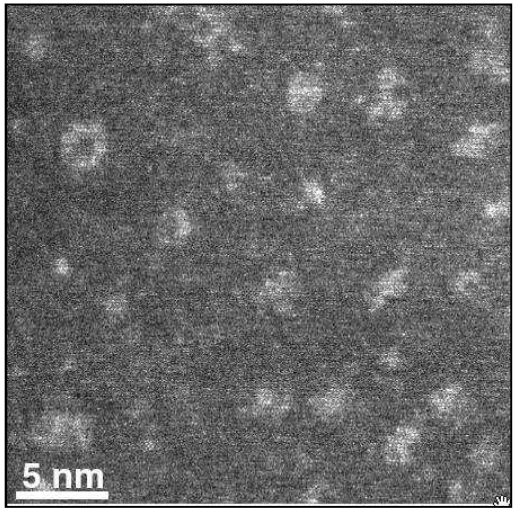
A very studied system yet with unanswered questions

- Guinier, **1942**: First evidence for GP zone formation in Al-Ag alloys

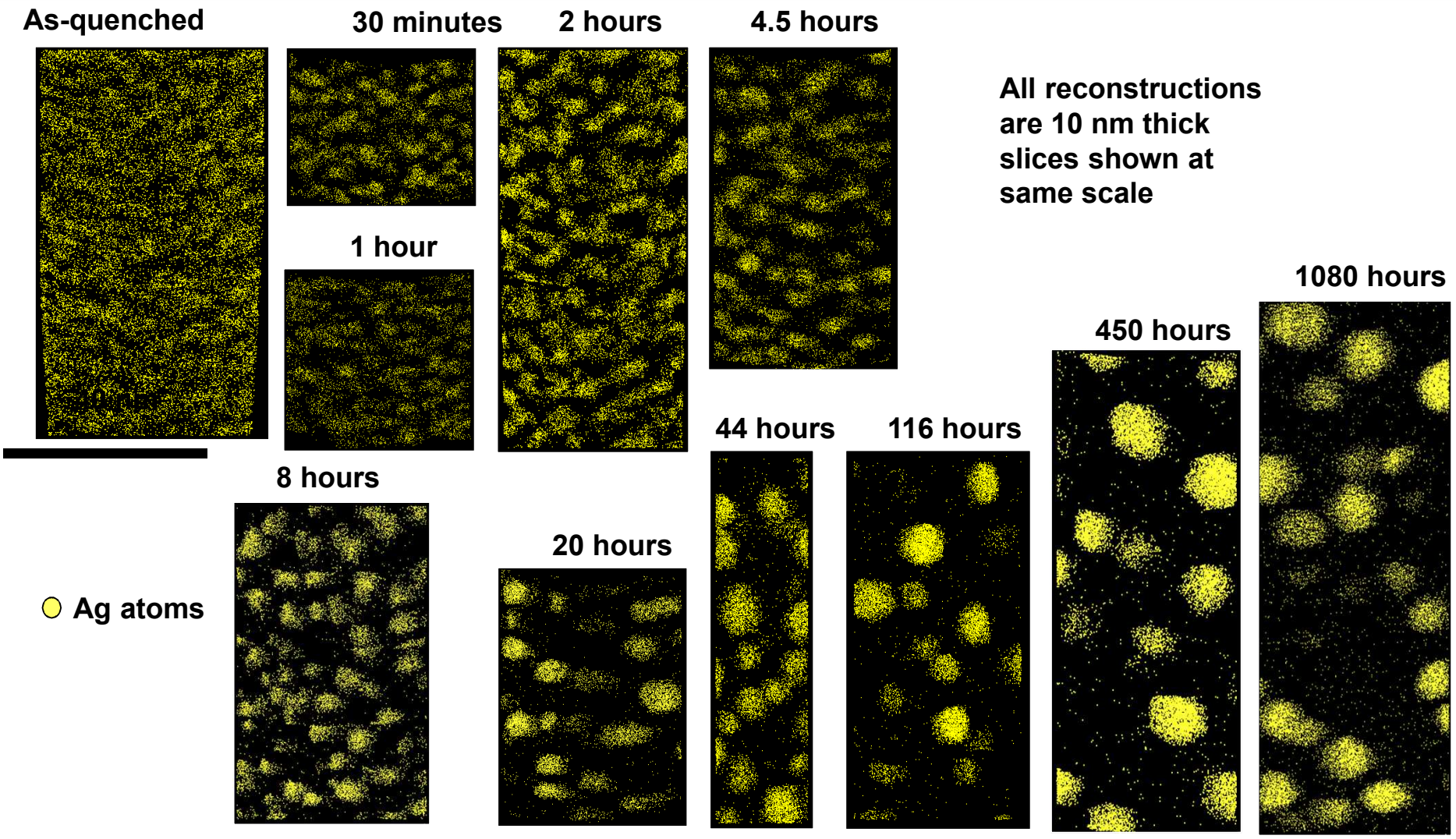
  (Phys. Radium, Paris 8, 124 (1942))
- Since then, many studies leading to various theories on the structure of GP zones:
  - Ag rich shell structure?
  - Ag depleted shell structure?
  - Uniform structure?

Guinier, Mat. Sci. Forum (**1996)**:
"Two models are possible:
i) the spherical zones of uniform radii are arranged like the molecules in a liquid or
ii) the zone is complex, made of central sphere enriched in Ag, surrounded by a depleted shell. The choice between the two models is **ambiguous**."

Shell structures?
Erni et al., 2004 using STEM

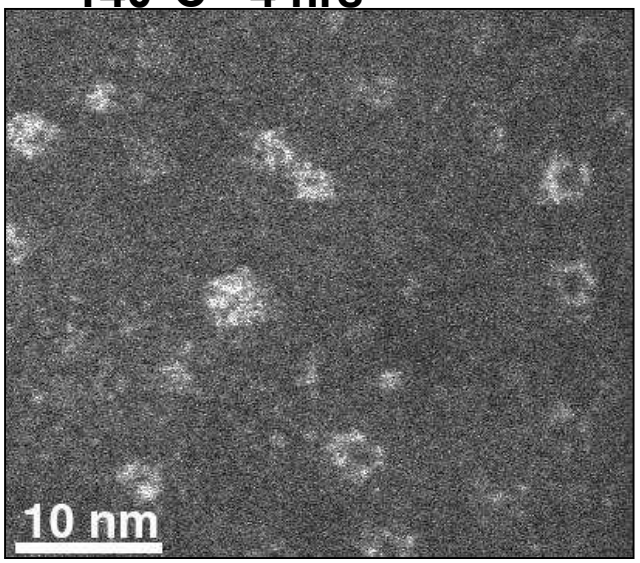


Time evolution at 130°C



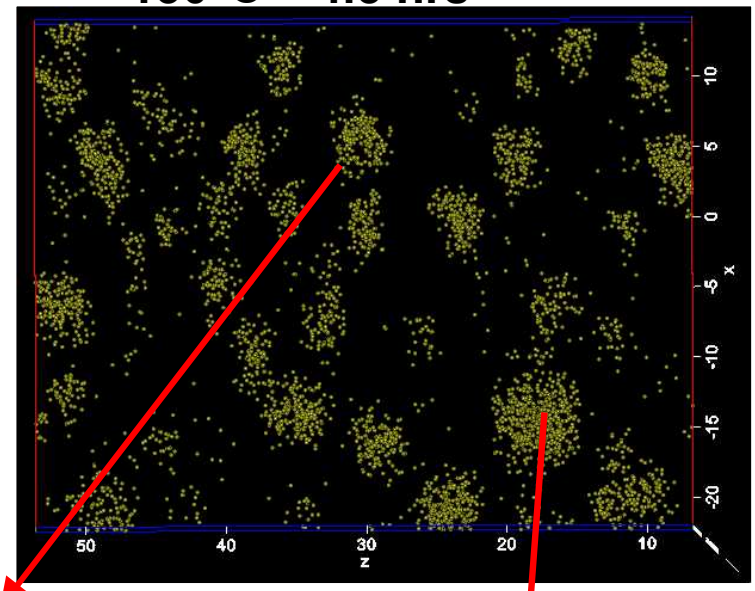
Early times: Fluctuations in an evolving system

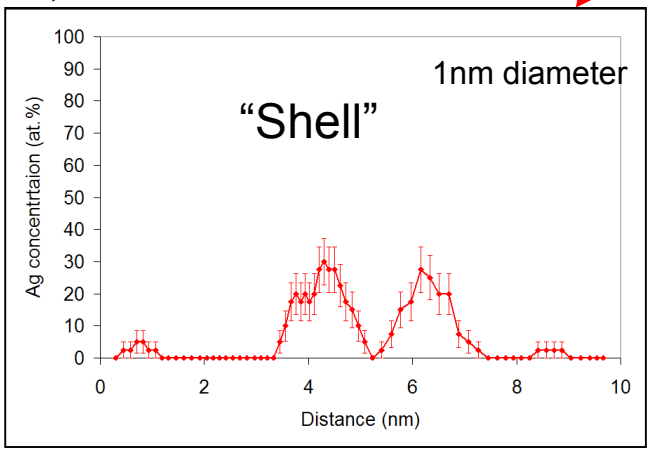
140°C - 4 hrs

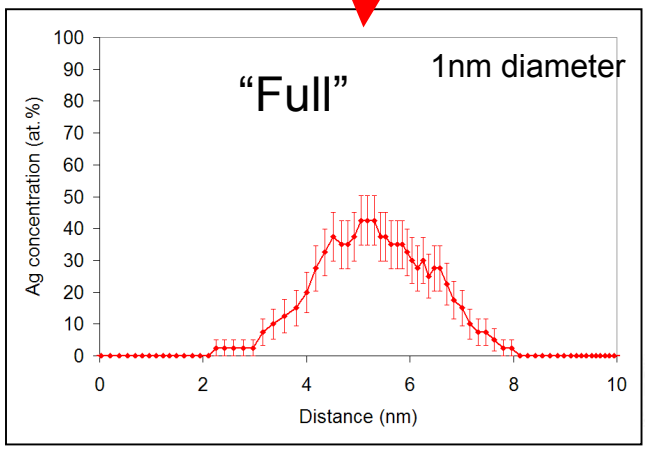


From R. Erni, H. Heinrich, G. Kostorz, Phil. Mag. Letters 81 (2003)

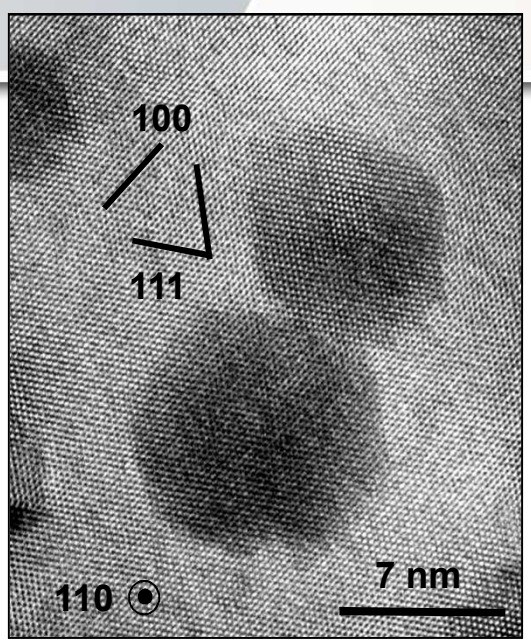
130°C – 4.5 hrs







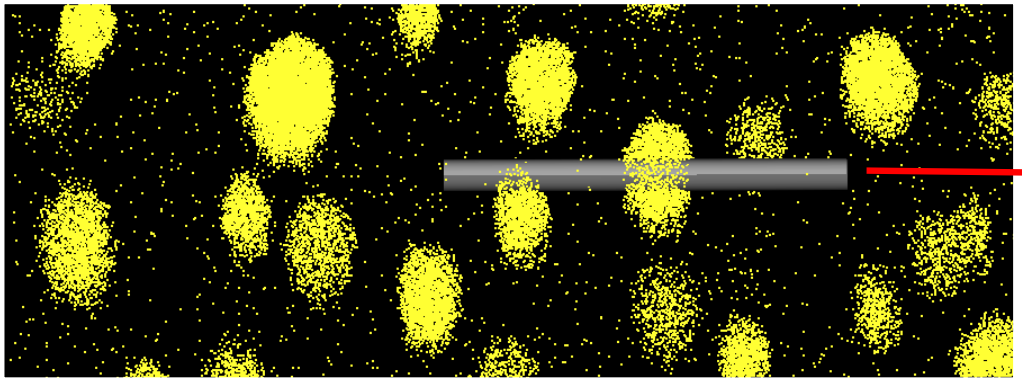
Steady state structure



- After **long** aging times:
  - Faceted GP zones
  - Uniform composition inside the zones
  - All zones have same composition

130°C- 450 hours

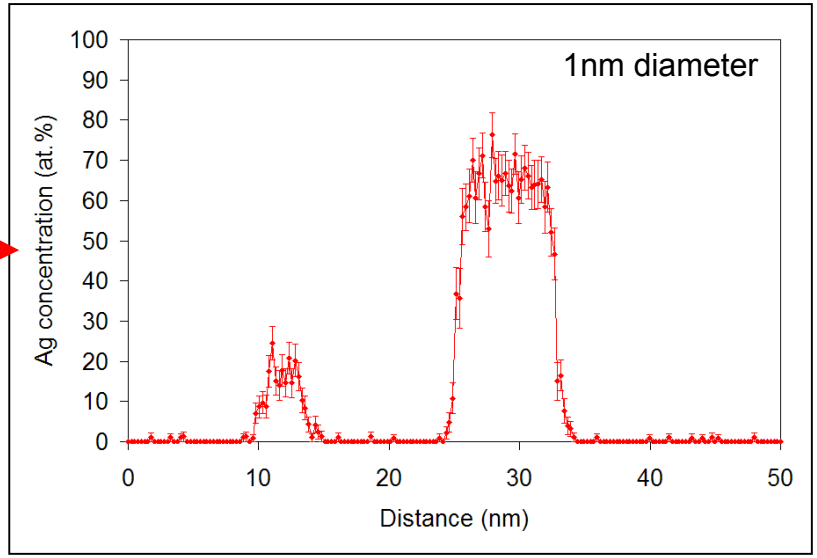
Reconstruction: 20nm thick slice



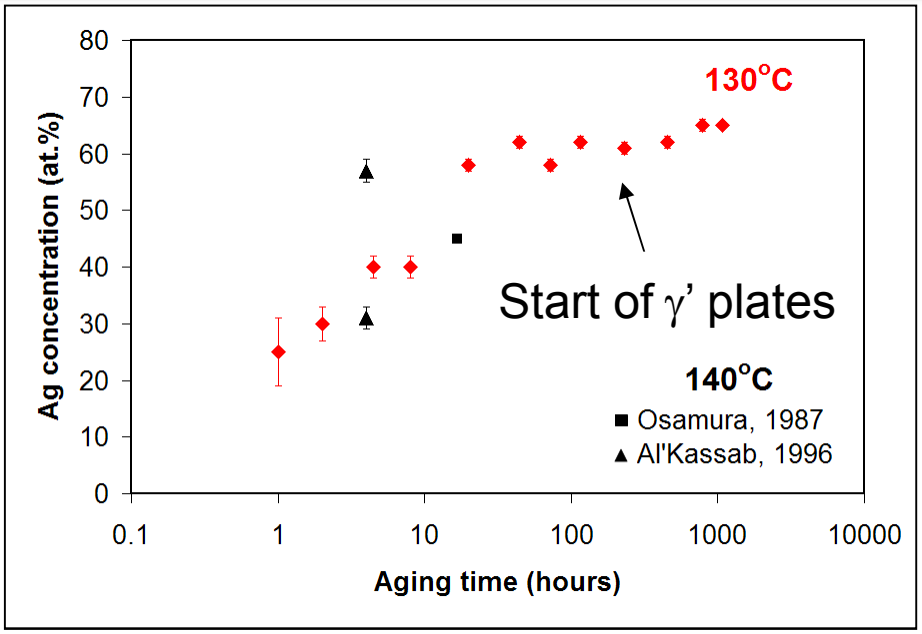
40 nm

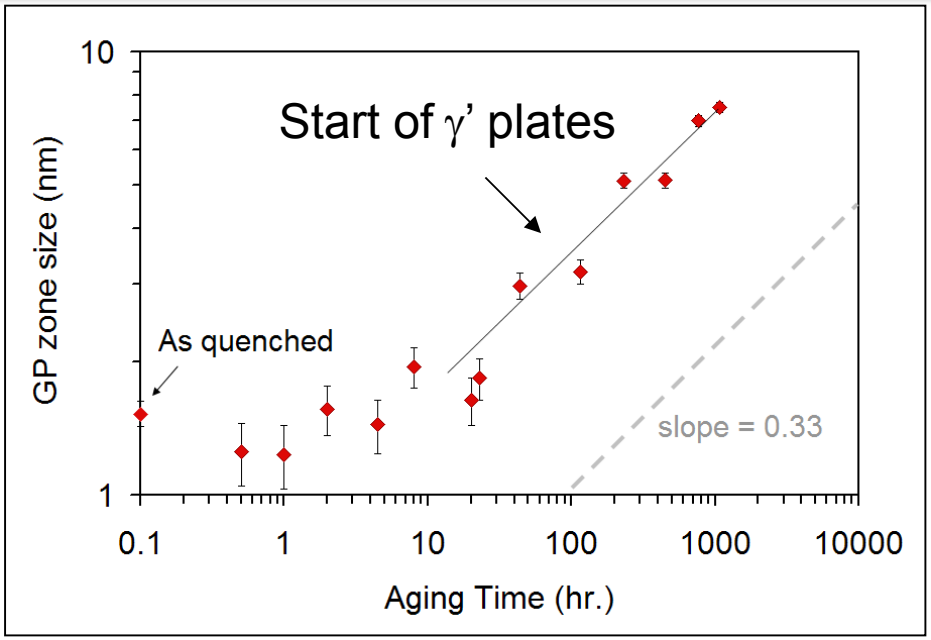
● Ag atoms

Concentration profile



GP zones change over time





- 2 regimes
  - Concentration increase and wavelength constant
    - Spinodal decomposition?
  - Coarsening beyond ~20 hours → Vacancy-solute interactions?

Conclusions and outlooks

- Understanding **alloy structures** at the **atomic scale**
  - **Integration** of theoretical and experimental approaches
    - Tools to extract **quantitative** information from measurements
    - Combination of complementary **experimental** techniques
      - **Atom Probe Tomography**
      - TEM
    - Combination of complementary **theoretical** techniques
      - First principles calculations, continuum modeling, ...
    - New insights into the atomic mechanisms involved in alloy systems
      - Solute-solute, solute-defect interactions
      - Kinetic pathways
      - Equilibrium structures