# Nanostructure Studies of early

# Decomposition Stages in Aluminum Alloys

- Motivation: early precipitation stages unclear

--> e.g. negative effect by RT storage (AA6xxx T6)

--> e.g. FeCu: Reactor steel

Hasegawa/Nagai group - Japan

- 1906 --> new material:

Duralumin (A. Wilm)

- 1919 first Airplane of metal:

Junkers F13

- 100 years later: very little known

on structure of early precipitations


T.E.M. Staab

universitätbonn

# Motivation Aluminium: AA6xxx alloys

- Aluminium --> important material
  - car and airplane production
  - construction material

AA6082

AA6061

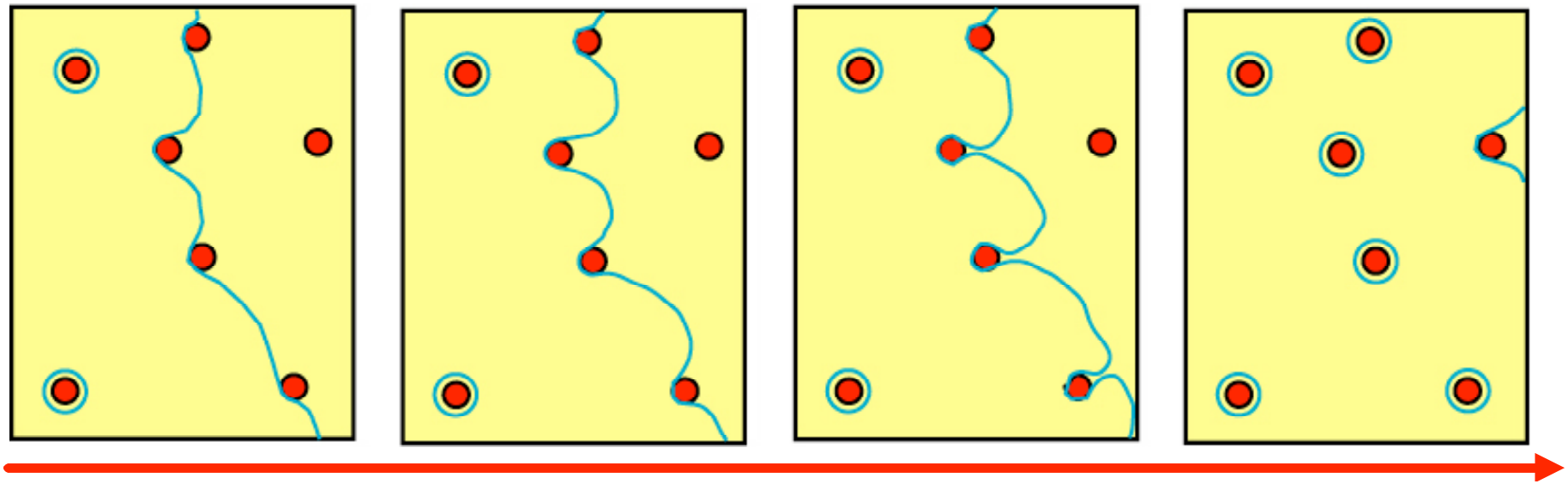

AA6013

older aircrafts: AA2024

- pure Al: light but weak (yield point: 4MPa)
- Precipitation of alloying atoms --> hardness (yield point: 70MPa)
- Final strength after T6 treatment: 180°C 4h for AlMgSi-alloys
  - depends on storage time at RT ==> UNWANTED ! ! !
- Goal: Microscopic understanding (atomic level)

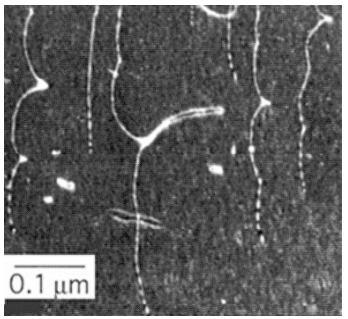
# Precipitation Hardening

- Overcoming obstacles of radius R:
  - particle cutting $\sim R^{1/2}$
  - go around --> Orowan-mechanism $\sim 1/R$



Tension $\sigma$

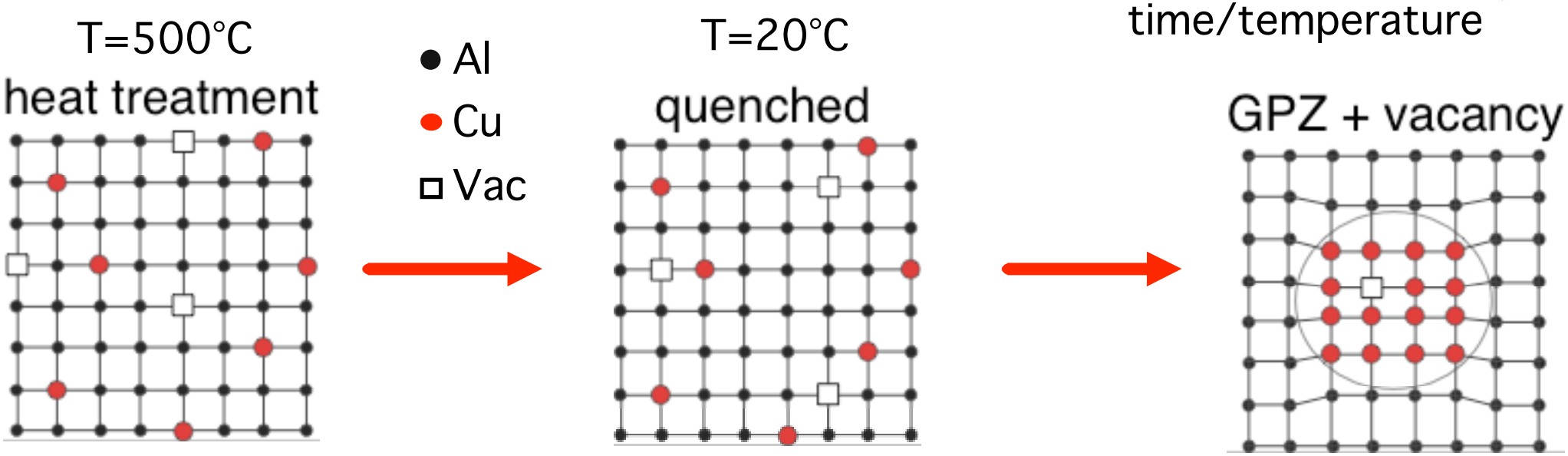
- Precipitation hardening: Temp./Time-regime
- optimizing particle size & particle distance
  ---> tailoring of the material



# Precipitation Hardening - example: Al-Cu

- Solution treatment --> quench --> GP1 --> GP2 (Θ'') --> Θ' --> Θ

time/temperature




- GP-Zones: A. Guinier & G.D. Preston 1938

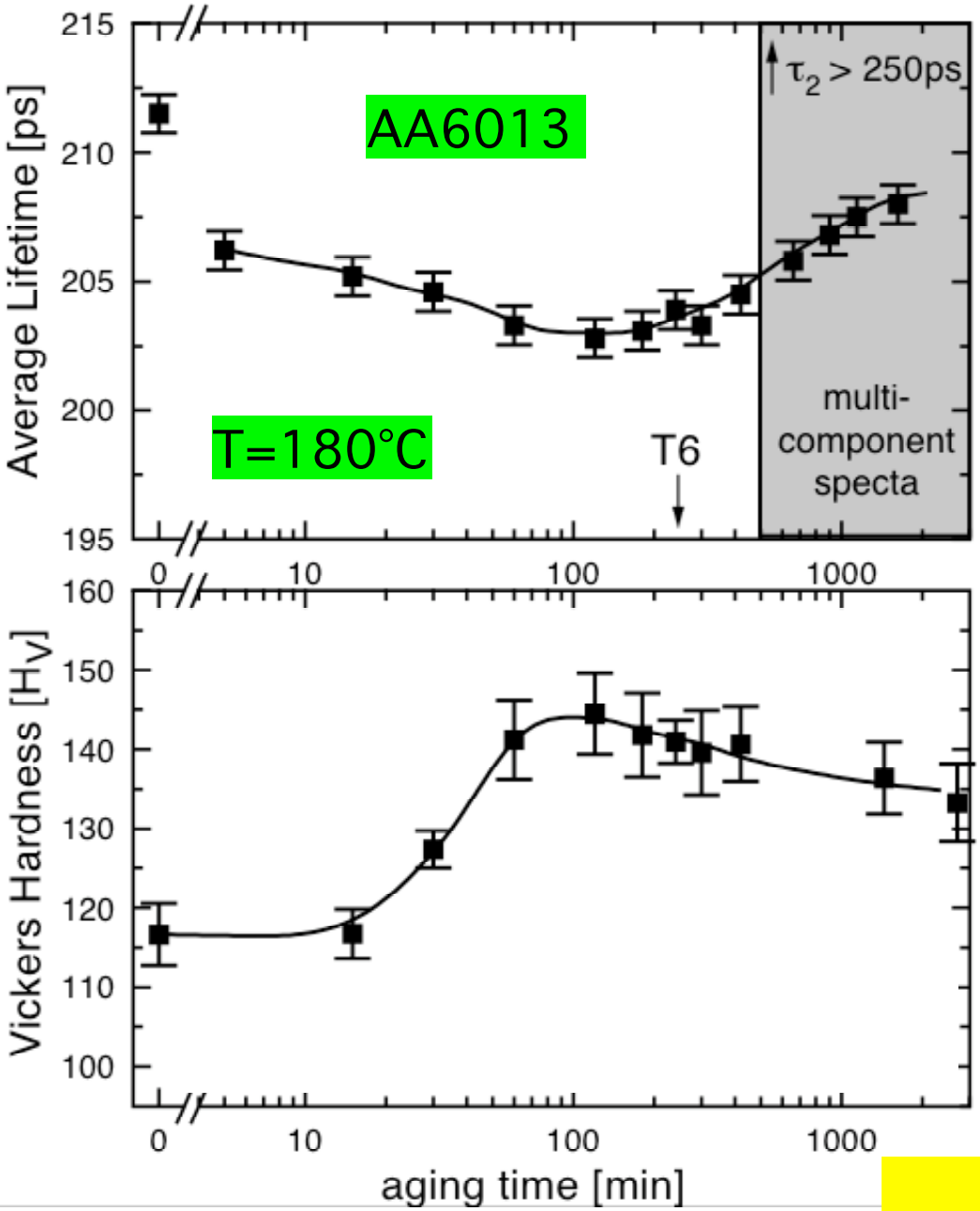
  --> Agglomerates of Cu on Al {100}

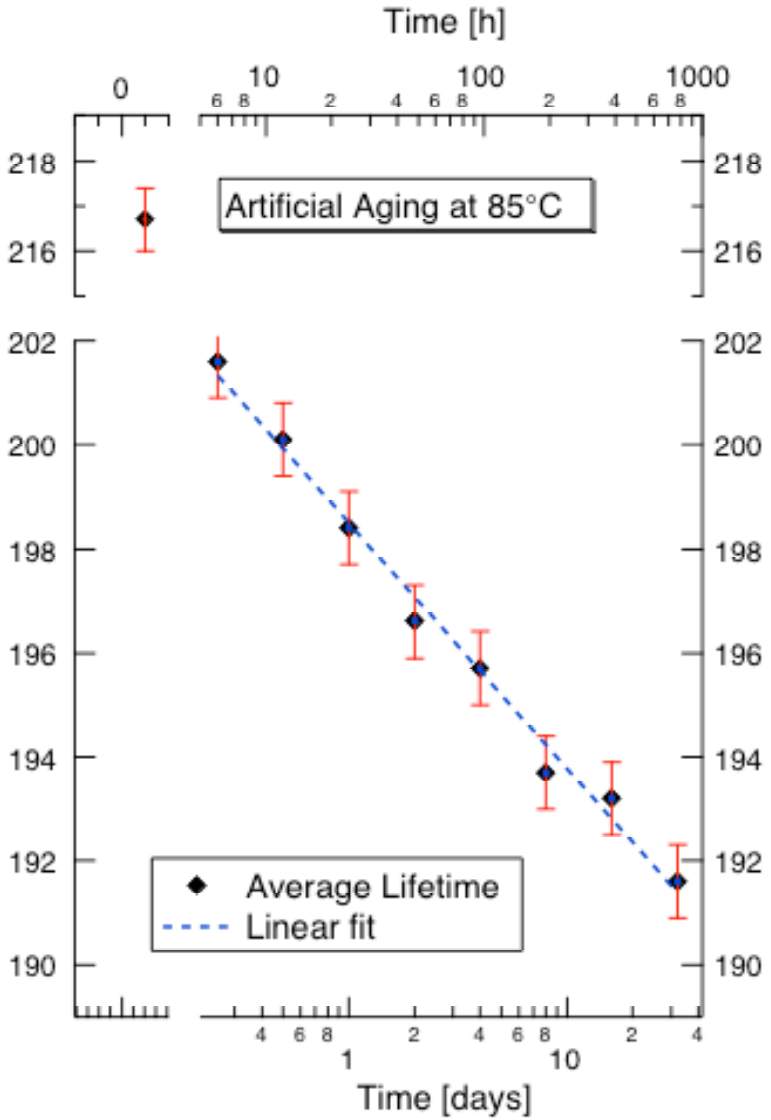
- $10^{-5}$ vacancies
- $10^{-2}$ Cu atoms


A. Guinier, Un nouveau type de diagrammes de rayons X, *Comptes Rendus* **206** (1938) 1641-1643

G.D. Preston, The diffraction of X-rays by age-hardening aluminum copper alloys, *Proc.Roy.Soc.* **A167** (1938) 526-538

# Positron Results: PALS



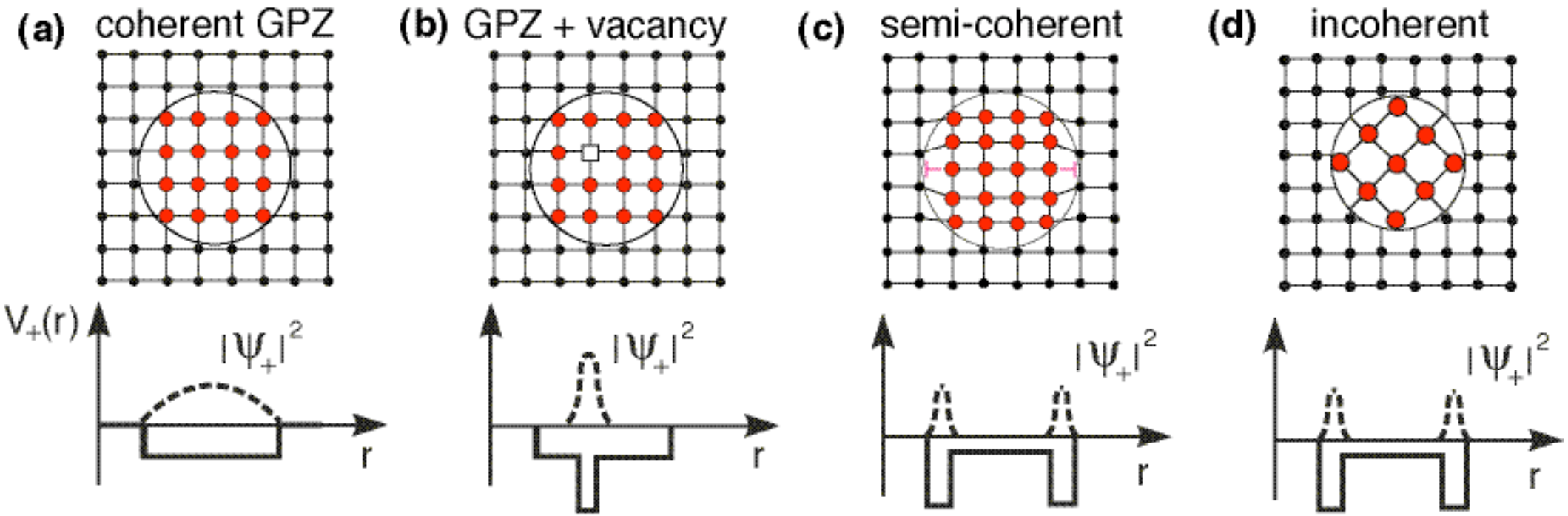

AA2024: AlCuMg

as-quenched: $\tau_{av}$ = 210 ... 220ps

# Precipitates: Positron Trapping

- Aging: coherent ---> semi-coherent ---> incoherent

time/temperature




G. Dlubek, O. Brümmer,J. Yli-Kauppila, P. Hautojärvi , Positron Experiments on the Formation and Growth of Guinier-Preston Zones in AlZn Alloys, *J.Phys.F: Metal.Phys.* 11 (1981) 2525-2537

- coherent GPZ: size > 1nm --> positron trapping
- BUT: most interesting very early stages: 1-5 atoms

# Early precipitations: failed methods

- TEM/HRTEM --> only precipitations > 2nm
- electrical resistivity --> too unspecific
- DSC --> no microscopic information
- XRD --> not sensitive during the first 10 hours (AlCu)
- 3DAP --> no atomic resolution: only larger clusters > 1nm

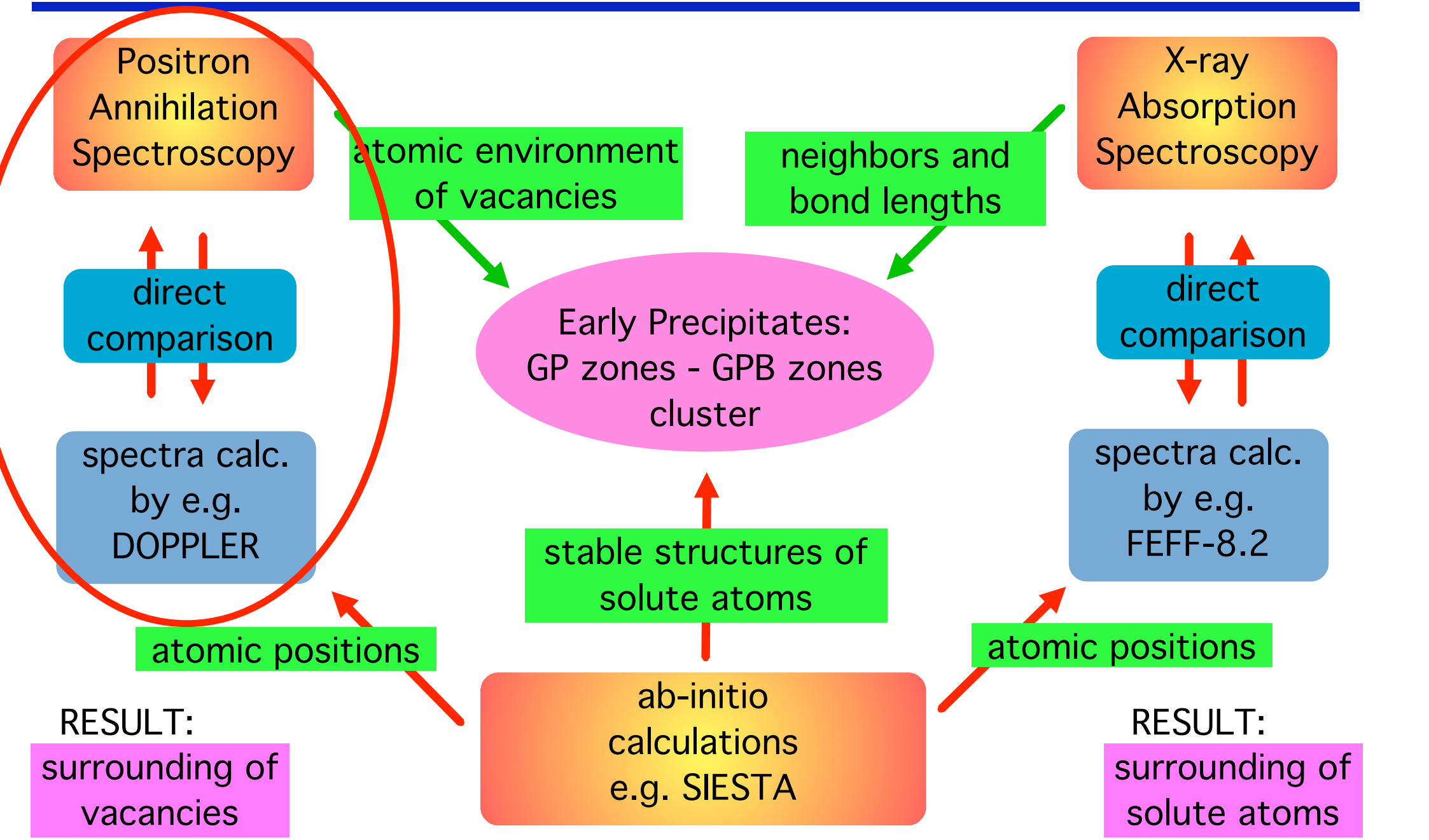
AA6082

## What we need:

- information on local atomic environment of Cu or Mg or Si
- what is the role of quenched-in vacancies?

## Our goal: a microscopic understanding on the atomic level

# Our Multi-Disciplinary Approach



# Numerical Method: SIESTA

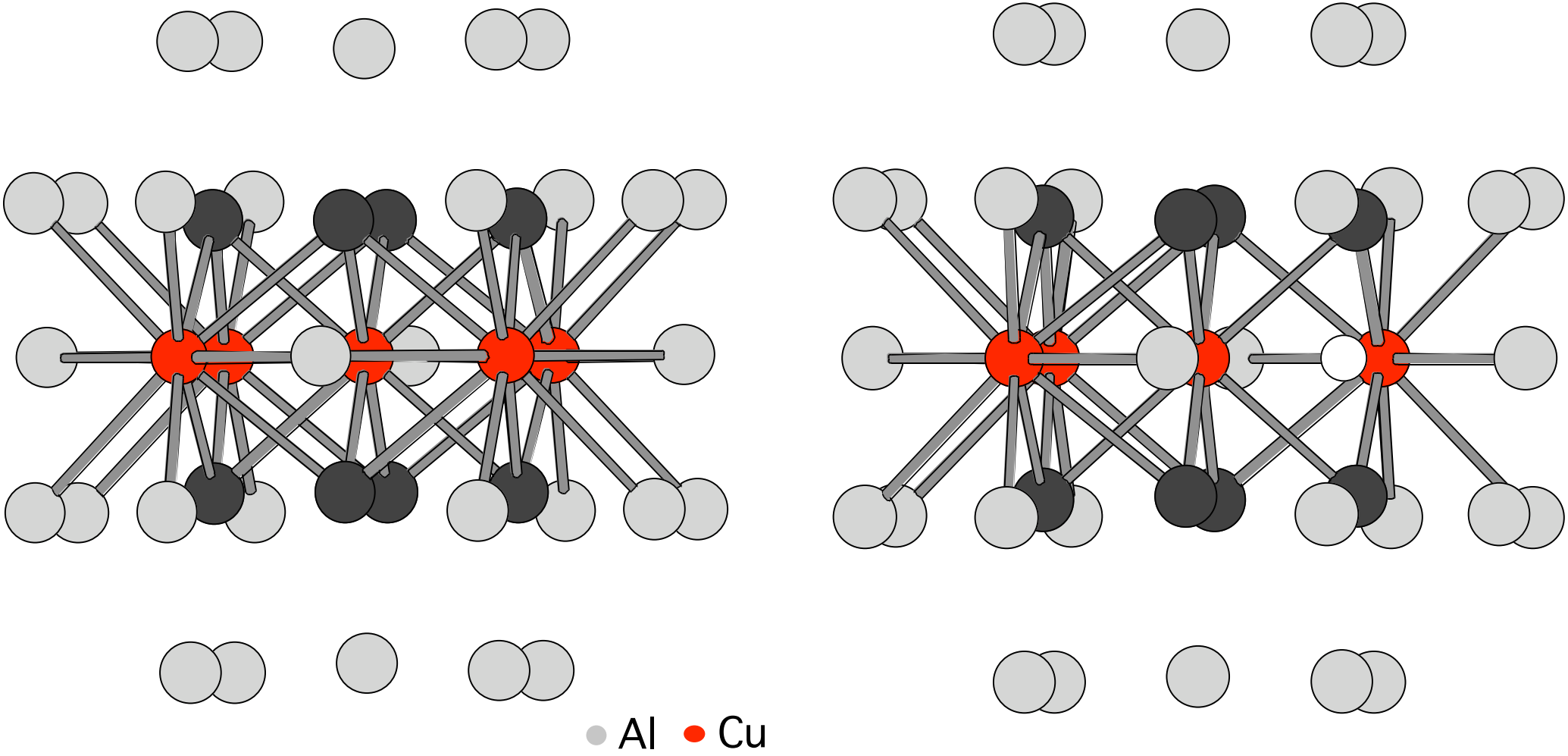
- SIESTA ab-initio code

Spanish Initiative for Electronic Simulations with Thousands of Atoms

- Kohn-Sham Density Functional Theory
- Pseudopotential approximation
- LDA/GGA


- Calculation of properties:
  - --> total energy
  - --> electron density
  - --> atomic positions
  - --> ...
- Better understanding of materials
  - on a microscopic scale (atomic level)

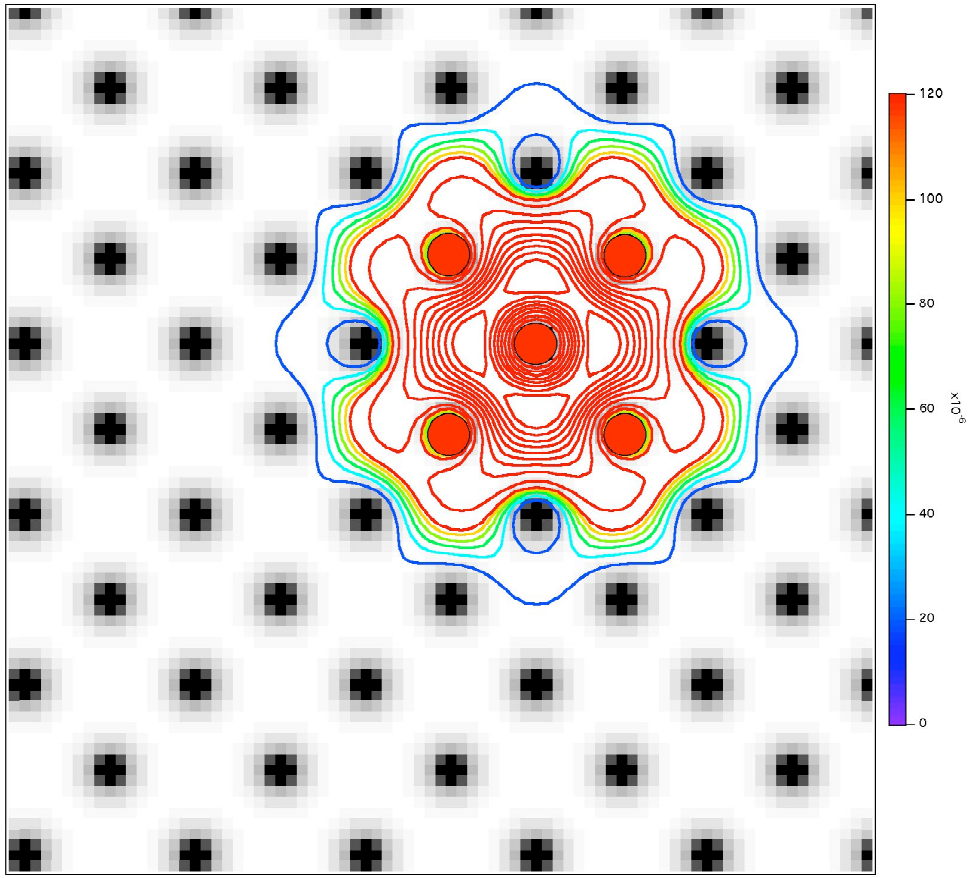
# Atomic Structure: Pre-GPZ

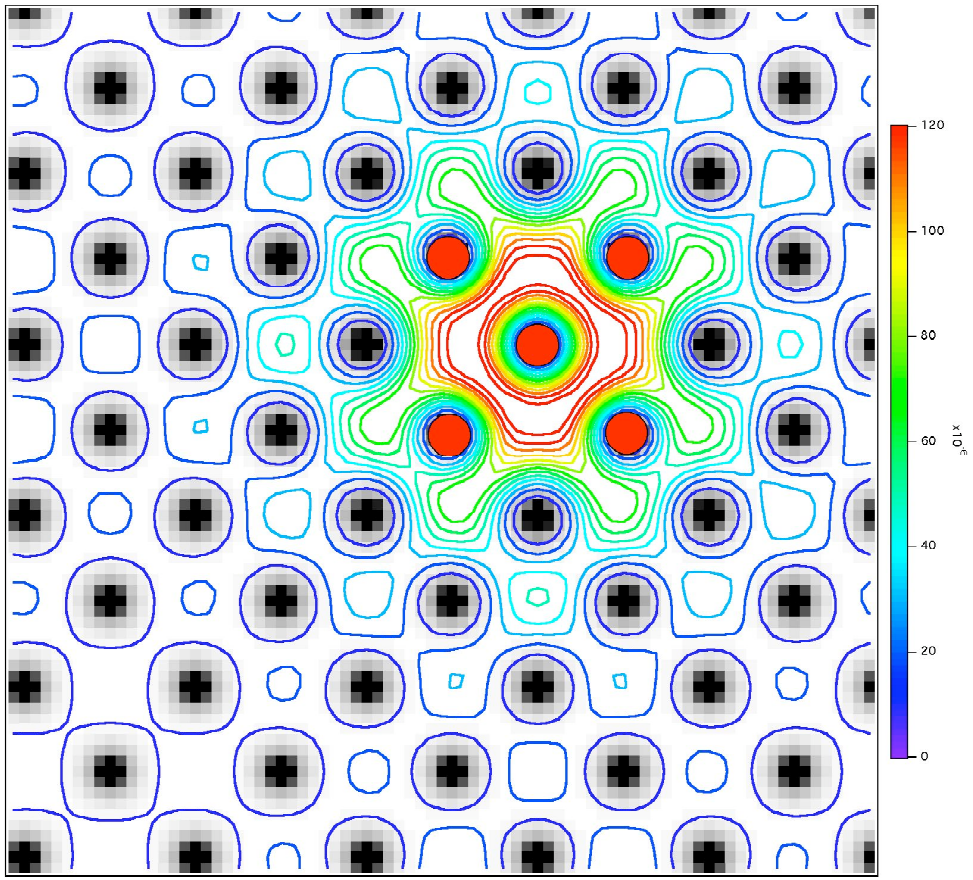



- 5 Atom pre-GPZ: size: 0.42 x 0.6 nm --> with and without vacancy

# Positron Trapping to pre-GPZ

- 5 Atom pre-GPZ: size = 0.42 x 0.60 nm ($\tau_{bulk}$(Al) = 168ps)



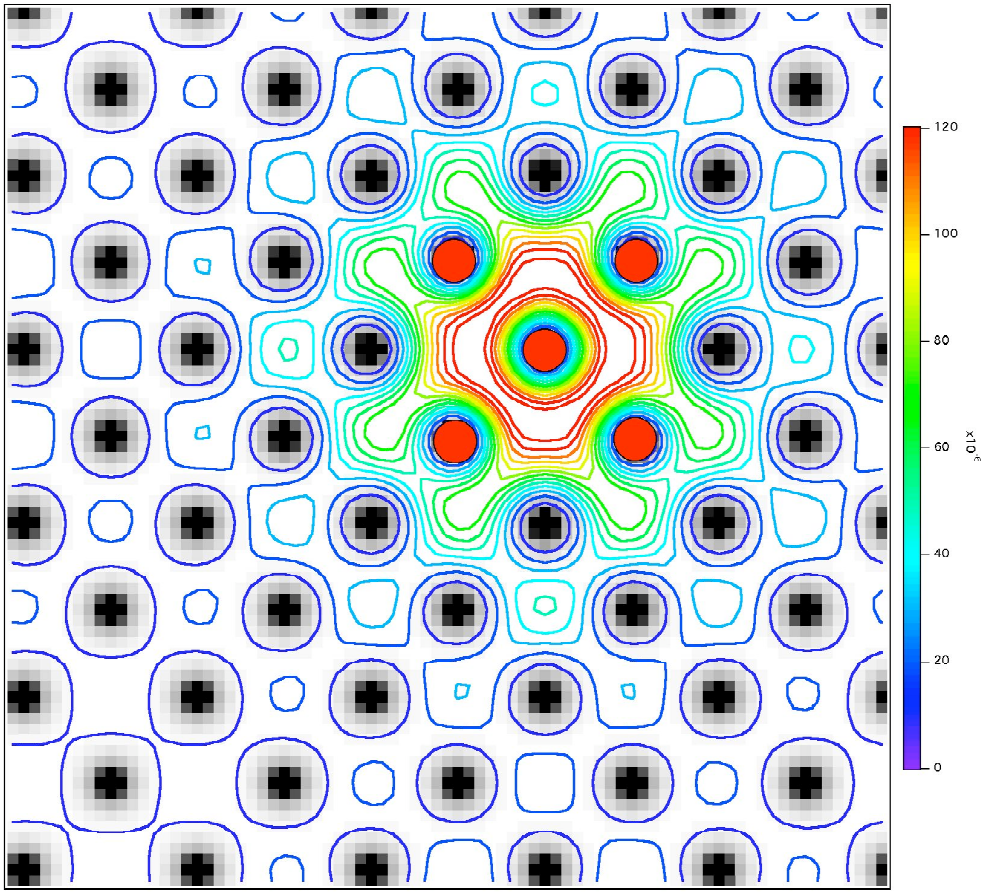



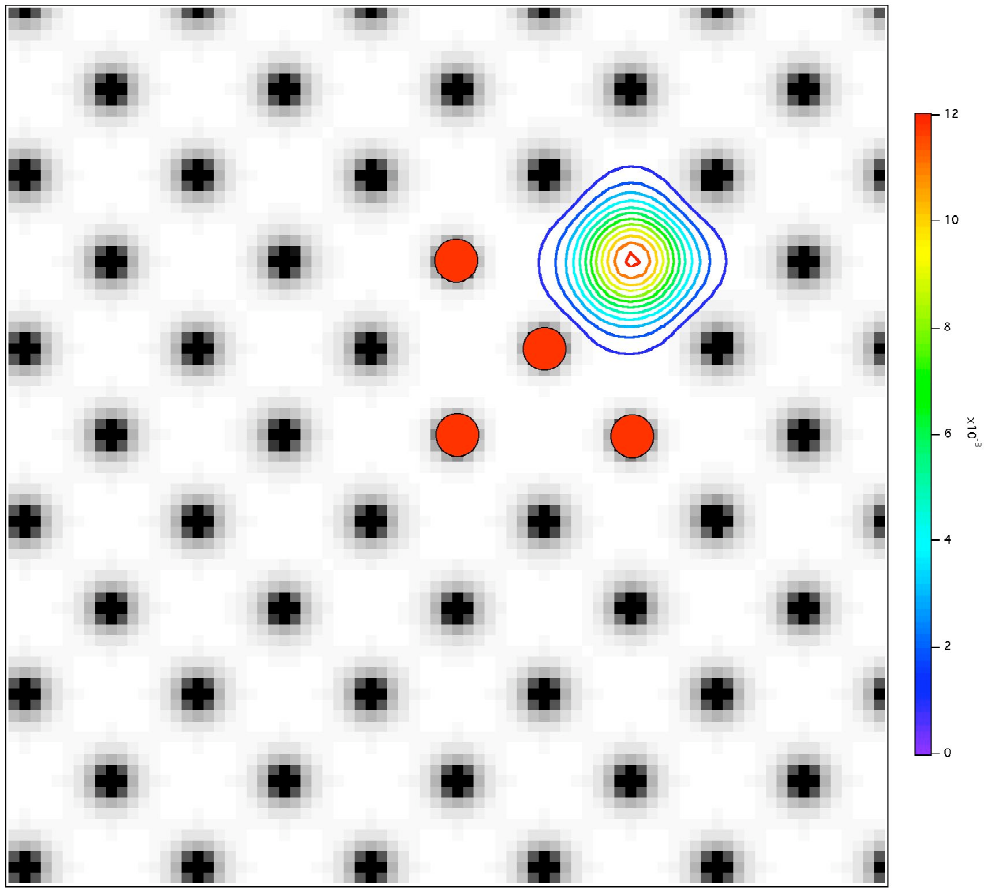

unrelaxed: 158ps

relaxed: 167ps (+10ps)

# Positron Density - Trapping

- 5 Atom pre-GPZ: size = 0.42 x 0.60 nm ($\tau_{vac}$(Al) = 236ps)



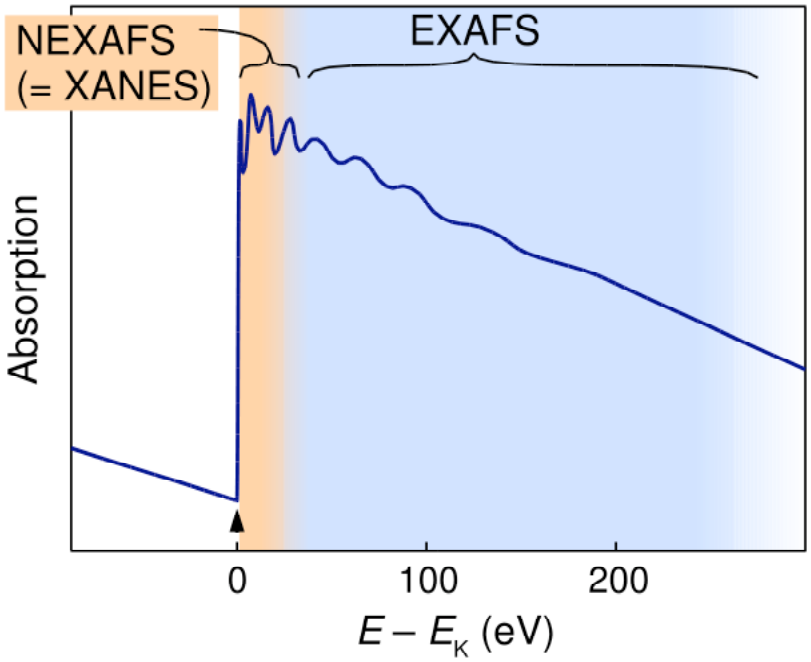




SIESTA relaxed: 167ps (+10ps)

SIESTA relaxed: 217ps (-22ps)

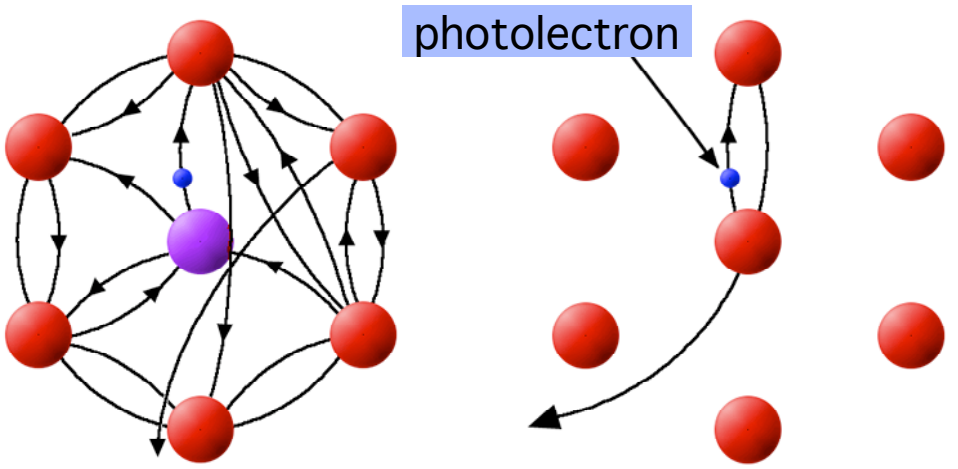
# X-ray Absorption Fine Structure (XAFS)

- XANES/EXAFS
  - --> element specific: K-edge
  - --> uses synchrotron radiation
  - --> measurement in fluorescence




- highly sensitive to:
  - --> bond angles
  - --> bond length
  - --> atomic surrounding

- Better understanding of
  - - atomic arrangements in small precipitated clusters in a matrix



# Comparison: EXAFS <--> SIESTA

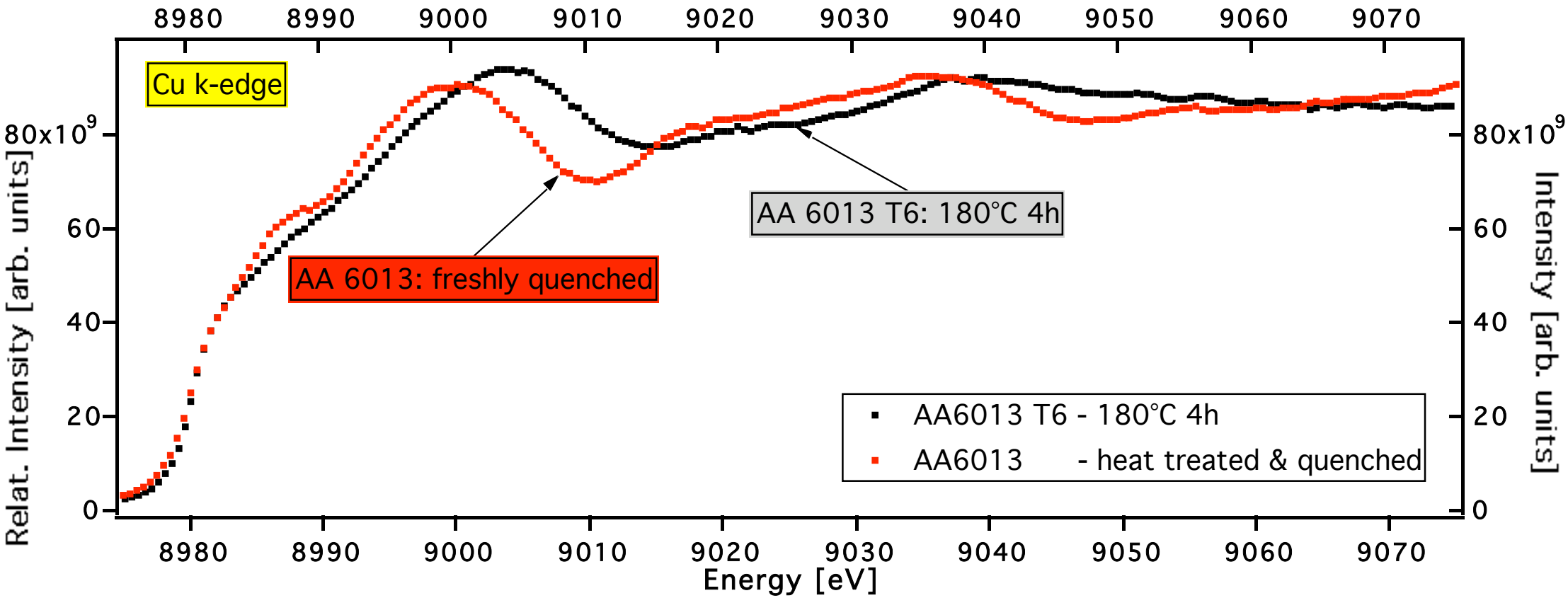
- testing SIESTA (DZP-Basis - 108 atoms)
  vs. EXAFS (literature)
  --> atomic distances around:
  Cu and Mg

| Element | atomic dist. [pm] EXAFS | | atomic dist. [pm] SIESTA |
|---|---|---|---|
| Mg | 293 | (Raoux 1981) | 290 |
| Cu | 279 | (Lengeler 1980 - 0.5at%) | 280 |
| Cu | 273 | (Fontaine 1979 - 2.5at.%) | 273 (Cu-pair) |
| Al-Al | to compare: | | 286.3 |

# XANES at the Cu K-edge: AA6013

- AA6013 AlMgSiCu-alloy
  --> T6: 180°C 4h & freshly quenched

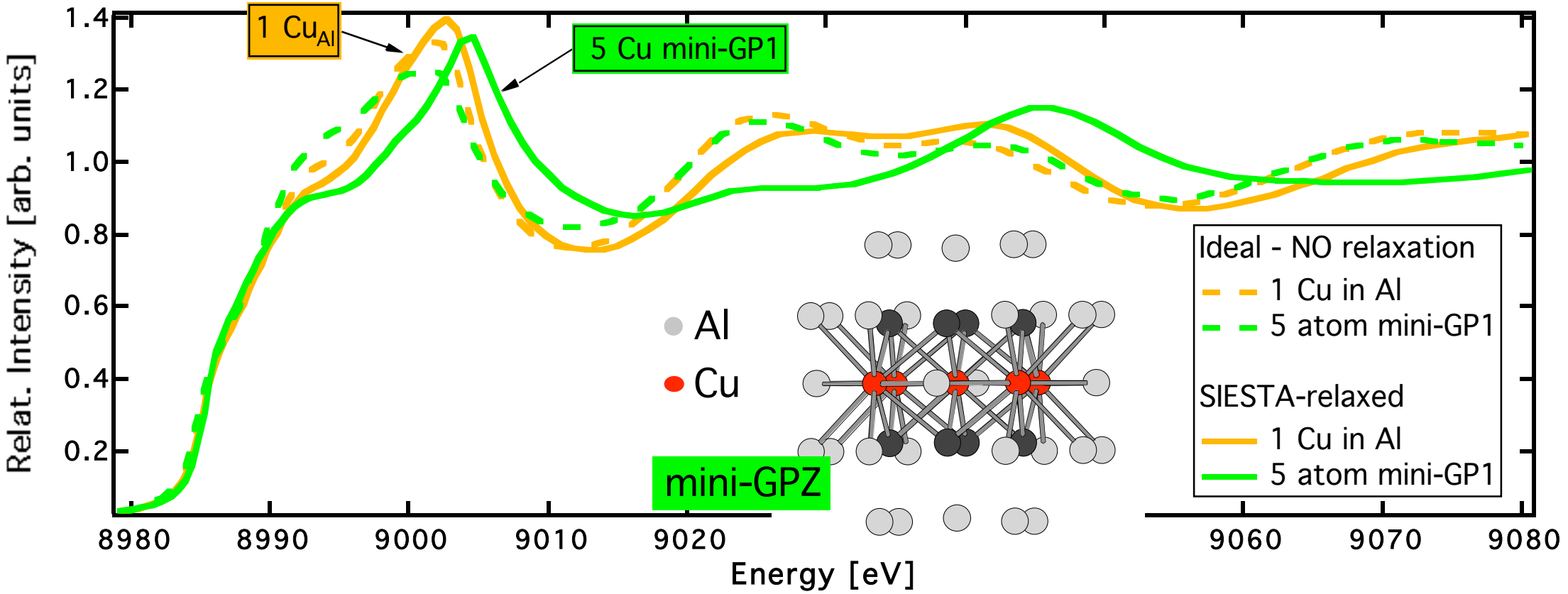
T.E.M. Staab, M.Haaks, C.Zamponi, H.Modrow, K. Maier. *pss Rapid Research Letters* **1** (2007) 172-174




- qualitative & quantitative differences in experimental data

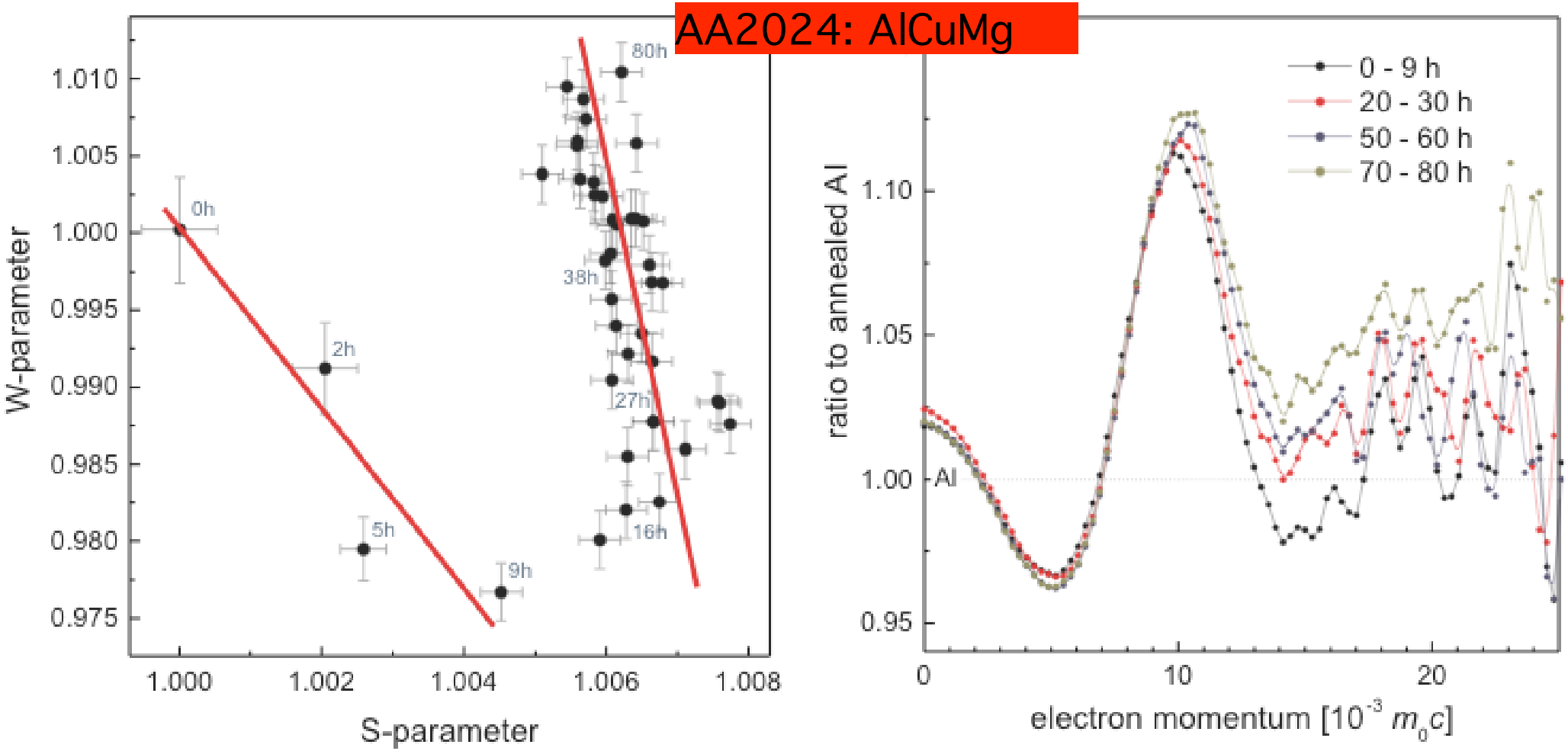
# XANES at the Cu K-edge: FEFF-8 Calc.

- comparison: relaxed atomic positions <--> ideal positions (SIESTA)
  --> e.g. Cu-Al distances change: > 2.5% of bond length




- significant differences ==> use relaxed atomic positions !!

# Positron Results: Doppler broadening

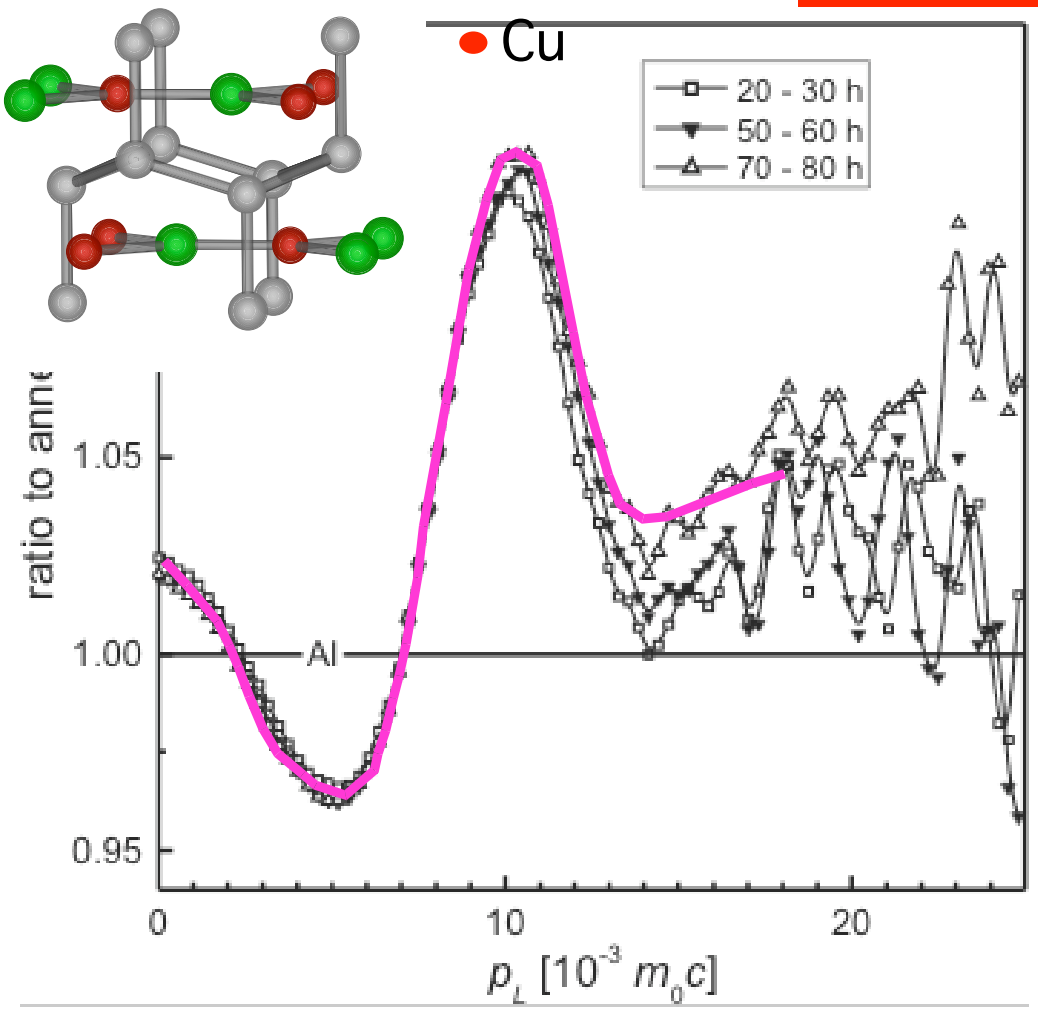


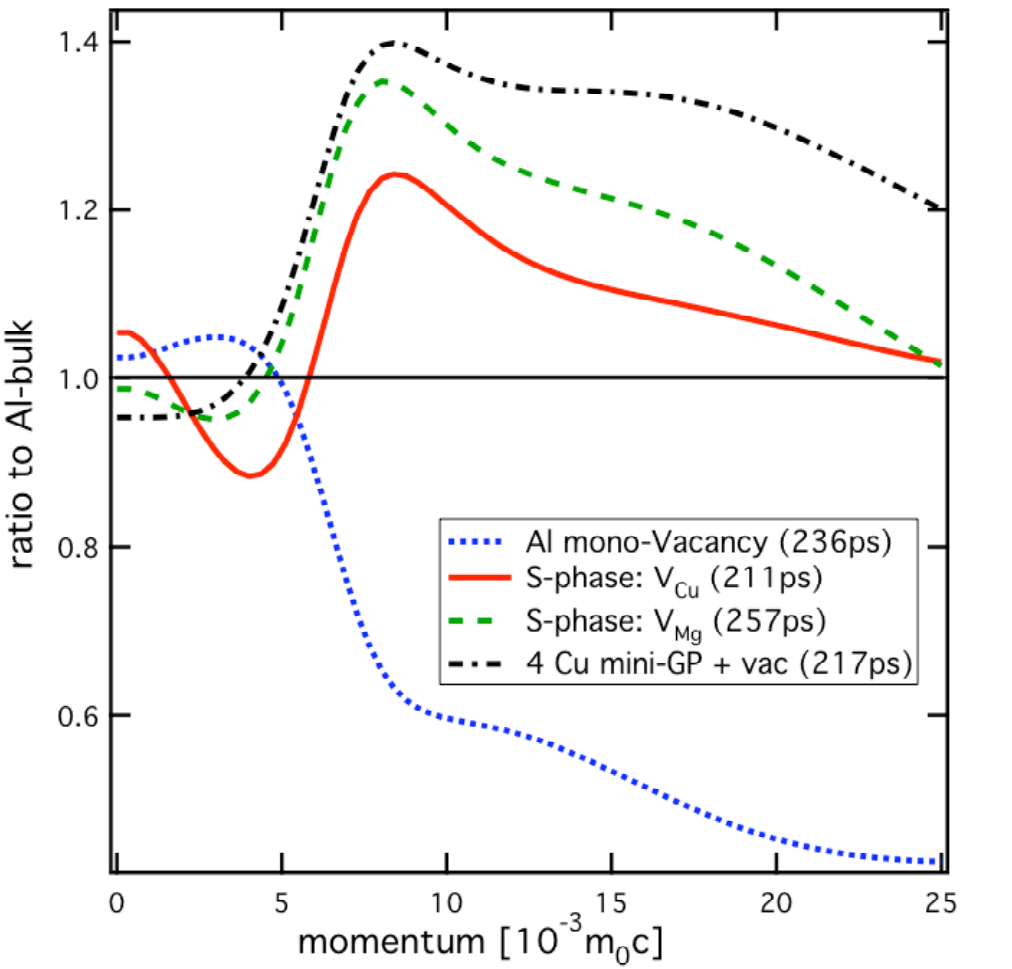

- well known results --> BUT: atomic structure of pre-GPZ?

# Comparison: Exp. <-> Calculation

S-phase: $Al_2MgCu$ ● Al ● Mg ● Cu

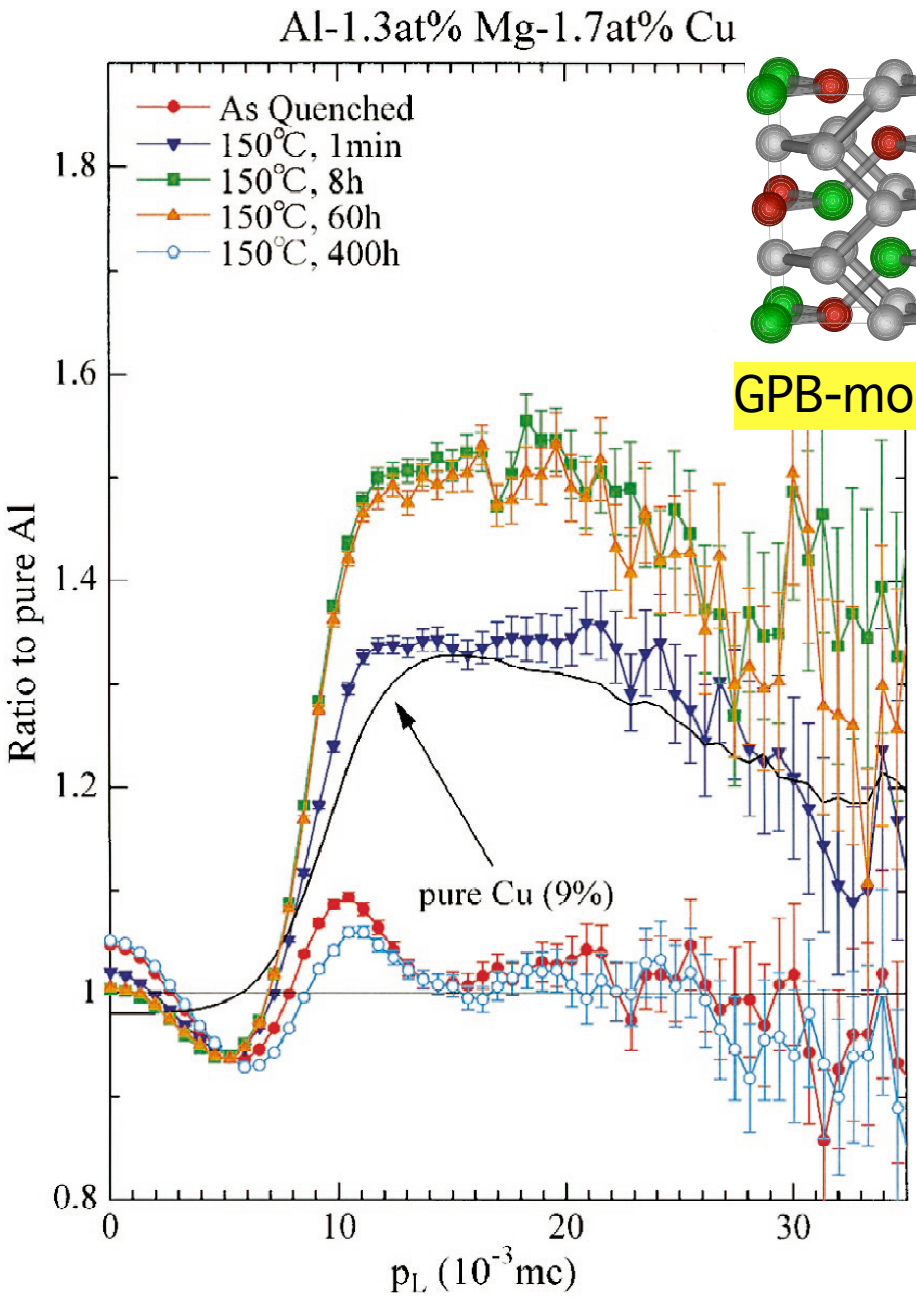
AA2024: AlCuMg

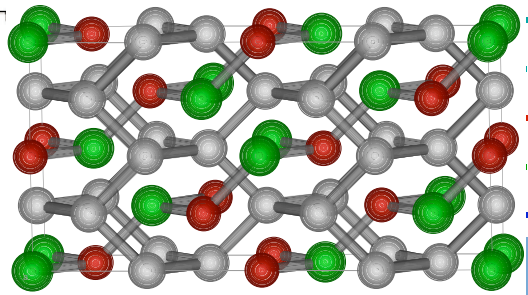


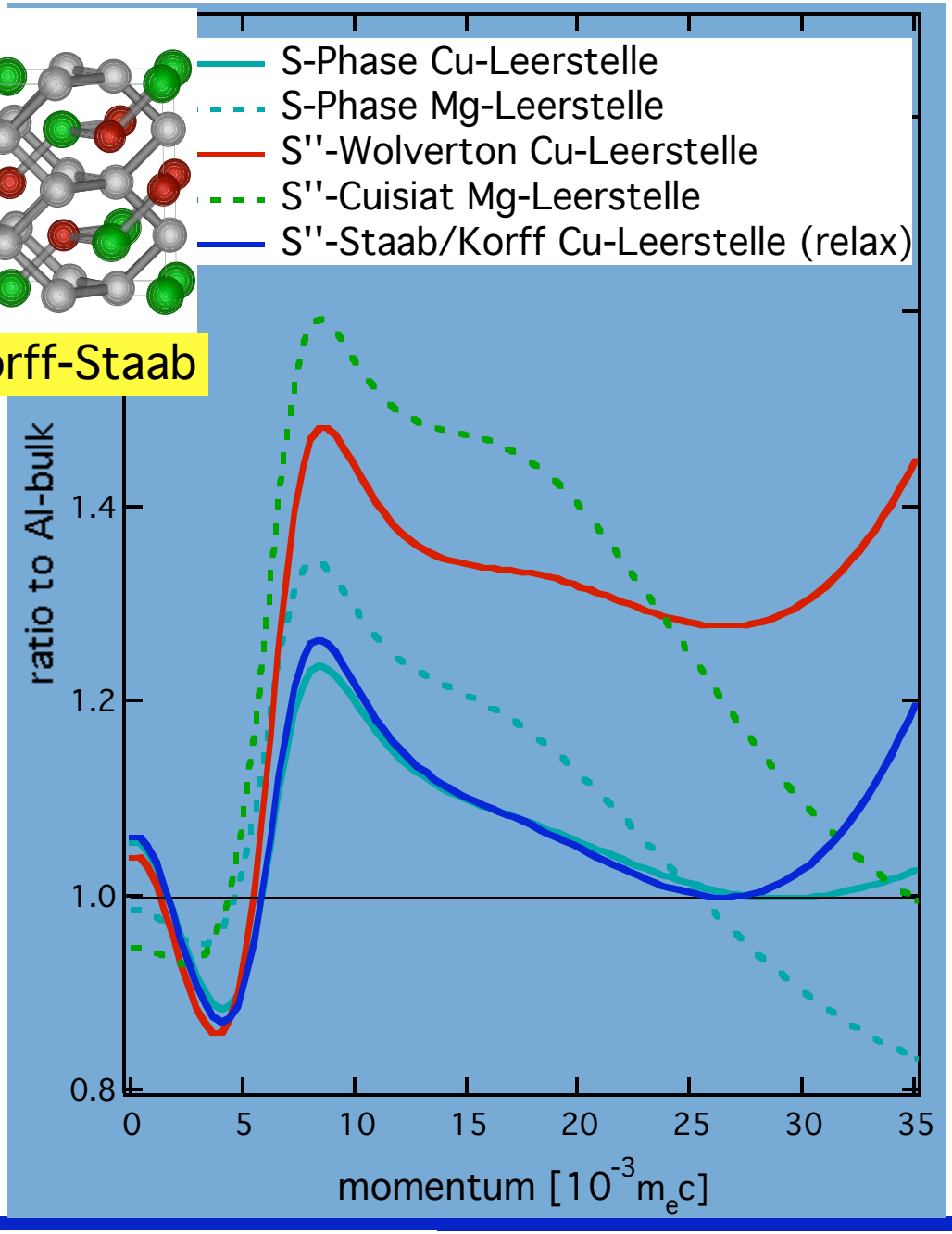

- ~~isolated vacancy~~ & ~~pre-GP zone~~ --> S-phase-like ($Al_2MgCu$): $V_{Cu}$ ~~$V_{Mg}$~~

# Calc. compared to Nagai/Hasegawa



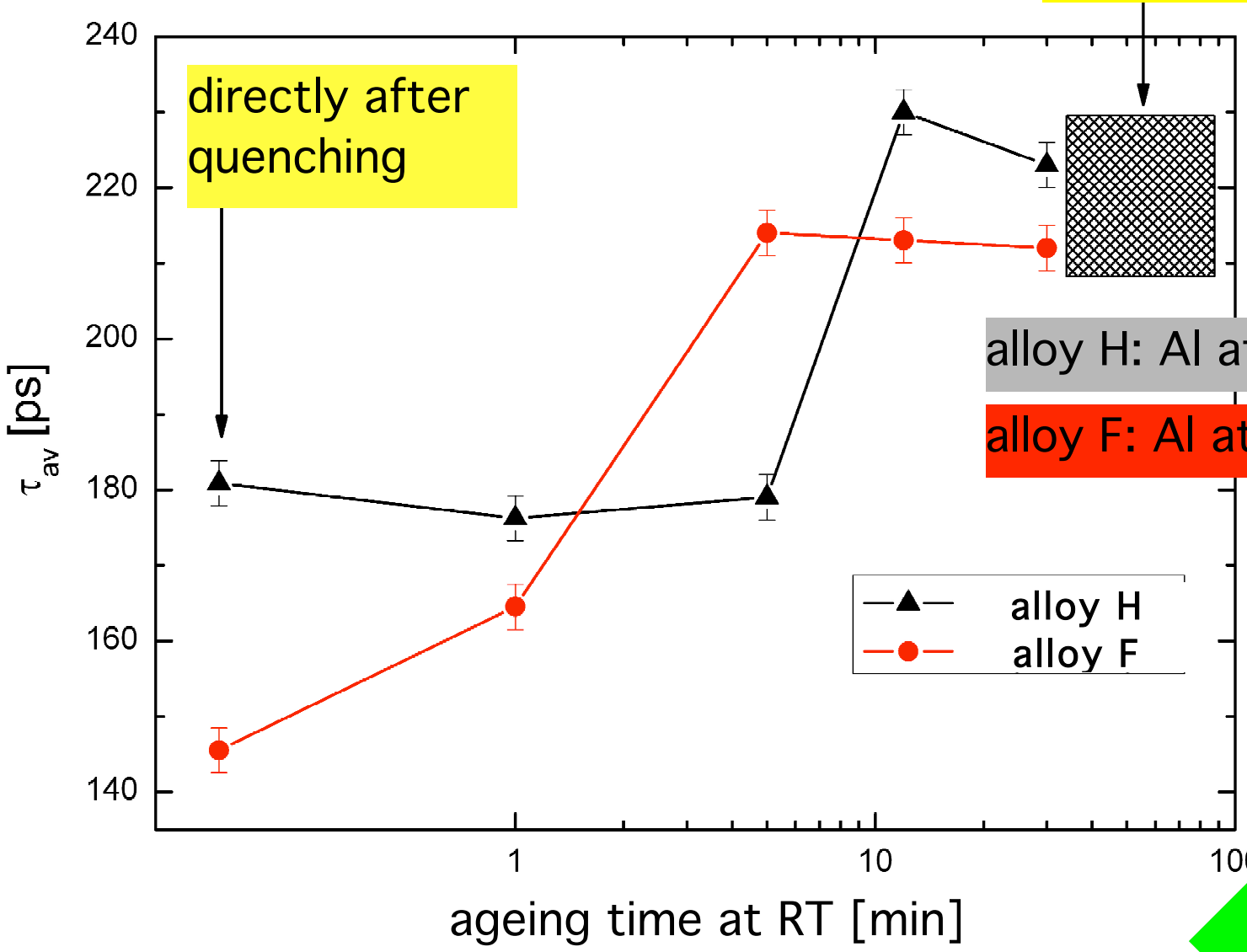
GPB-model:Korff-Staab



# Very early precipitation stages

Al-MgSi alloys: pure elements

known from literature



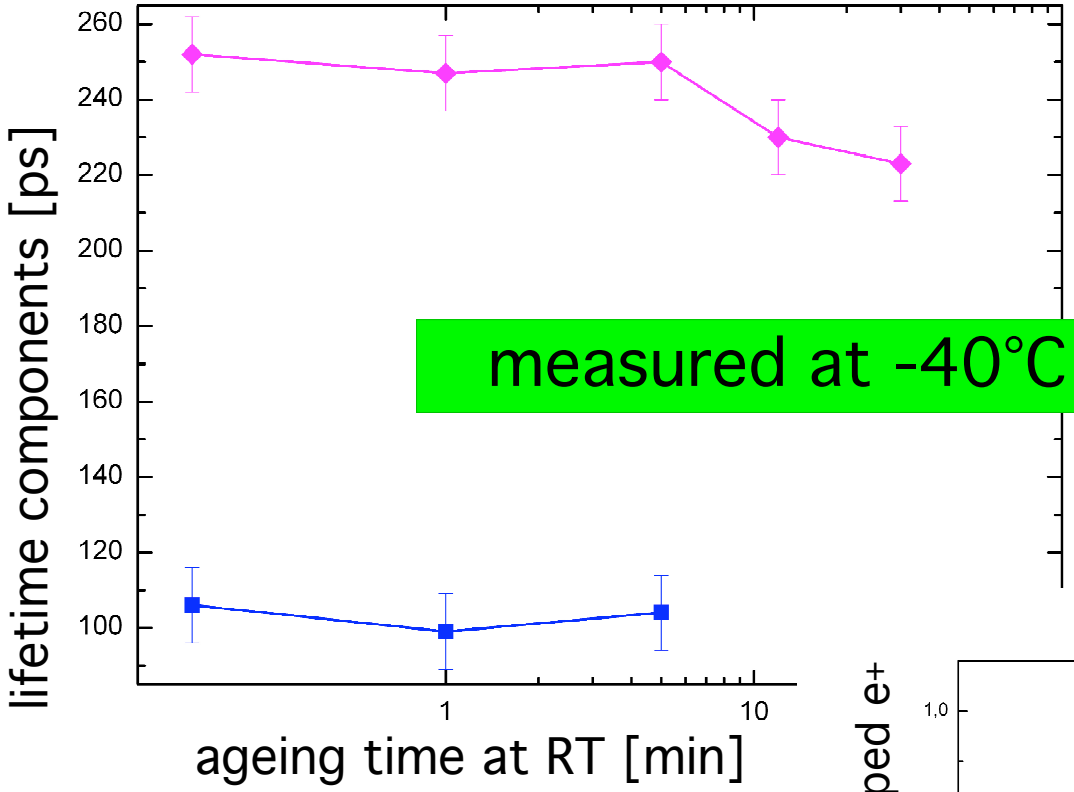

alloy H: Al at.% 0.42Mg 0.41Si

alloy F: Al at.% 0.69Mg 0.77Si

measured at -40°C

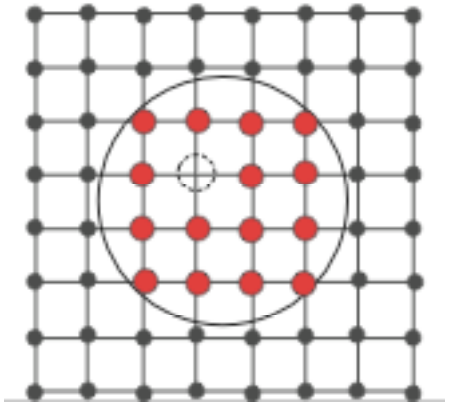
# Early precipitation stages: explanation

Al-MgSi alloy H: 0.42at.%Mg 0.41at.%Si

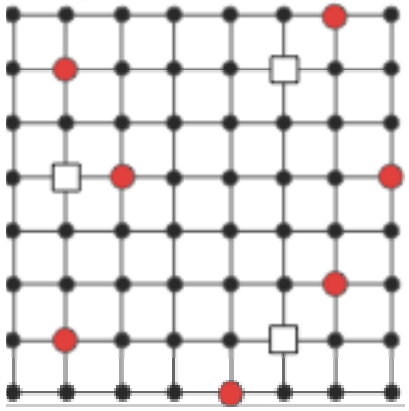


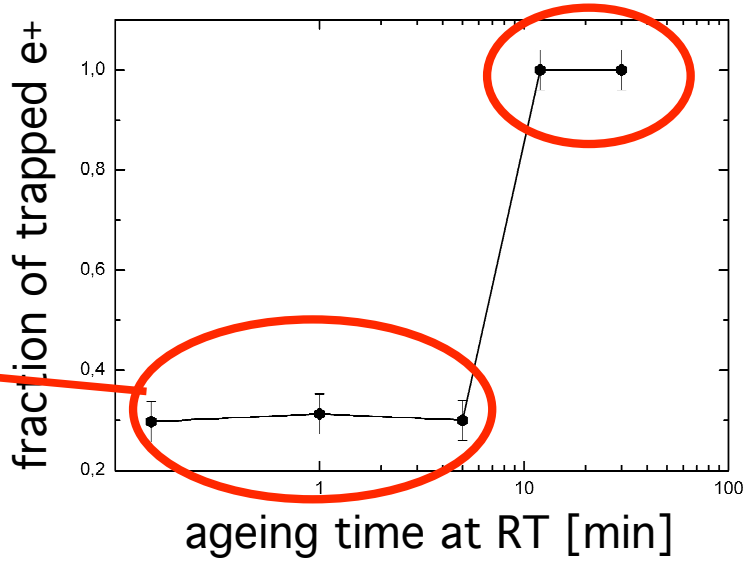

measured at -40°C

GPZ + vacancy

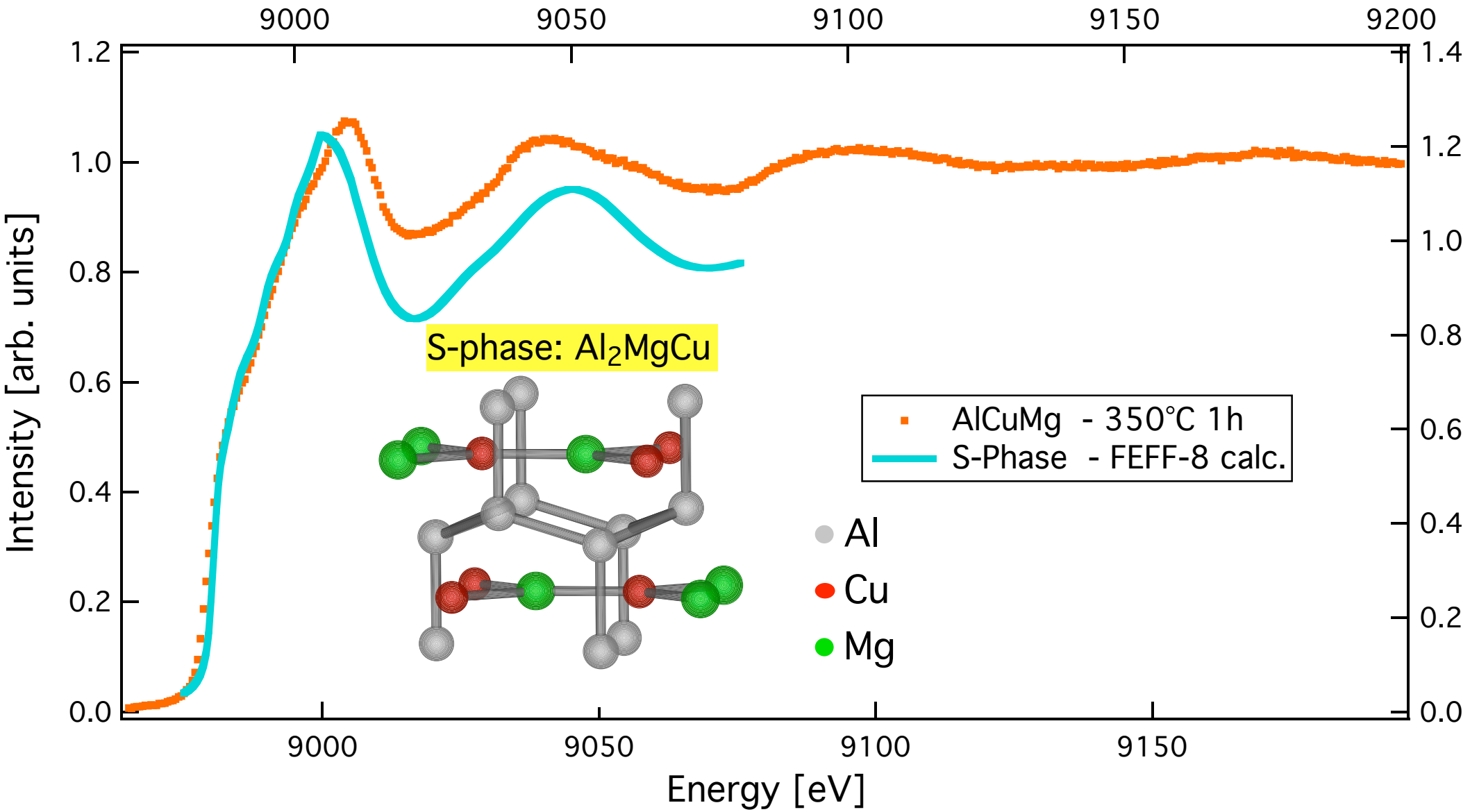


quenched

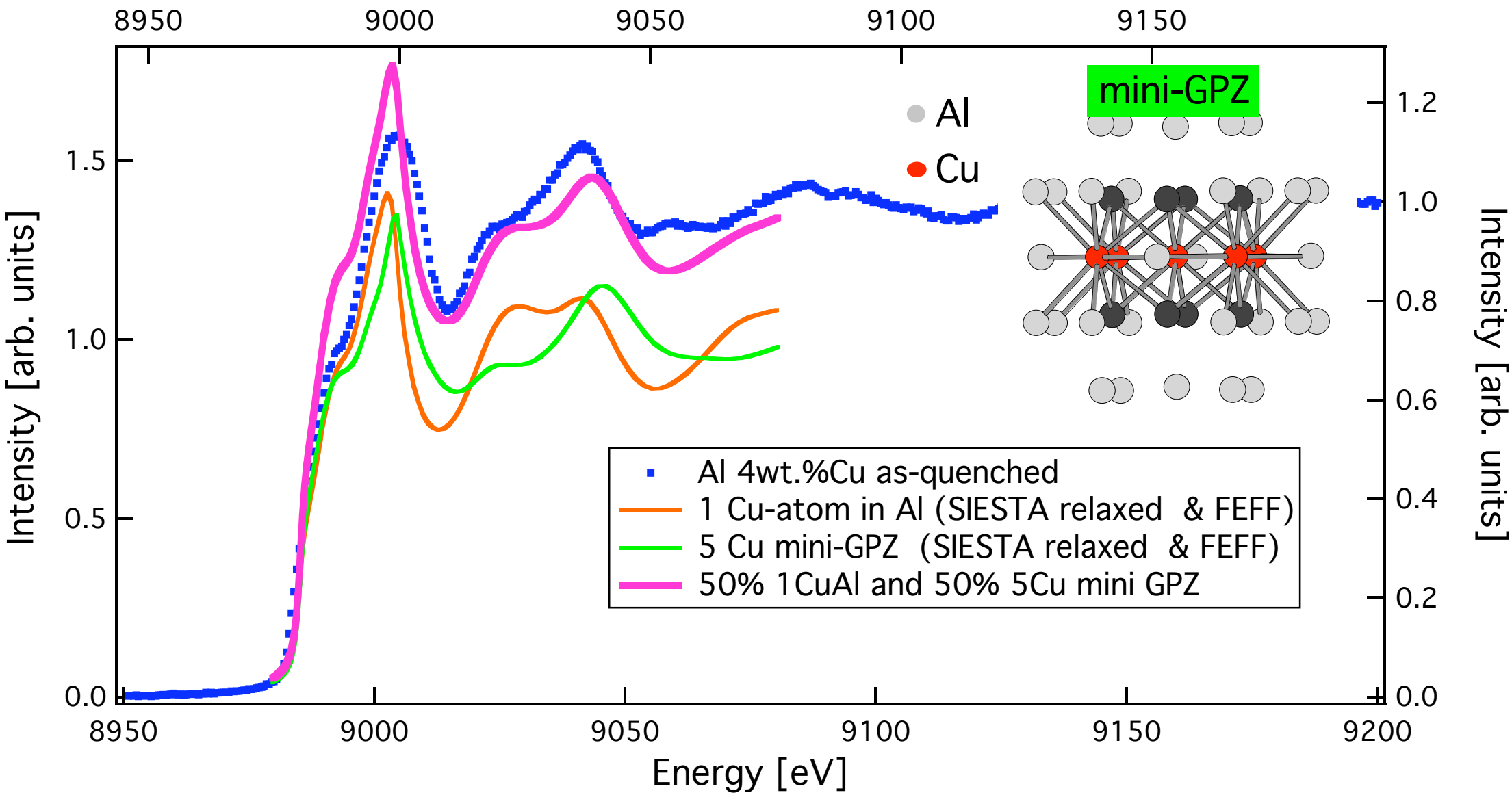




# FEFF-calc. vs. experiment: S-phase

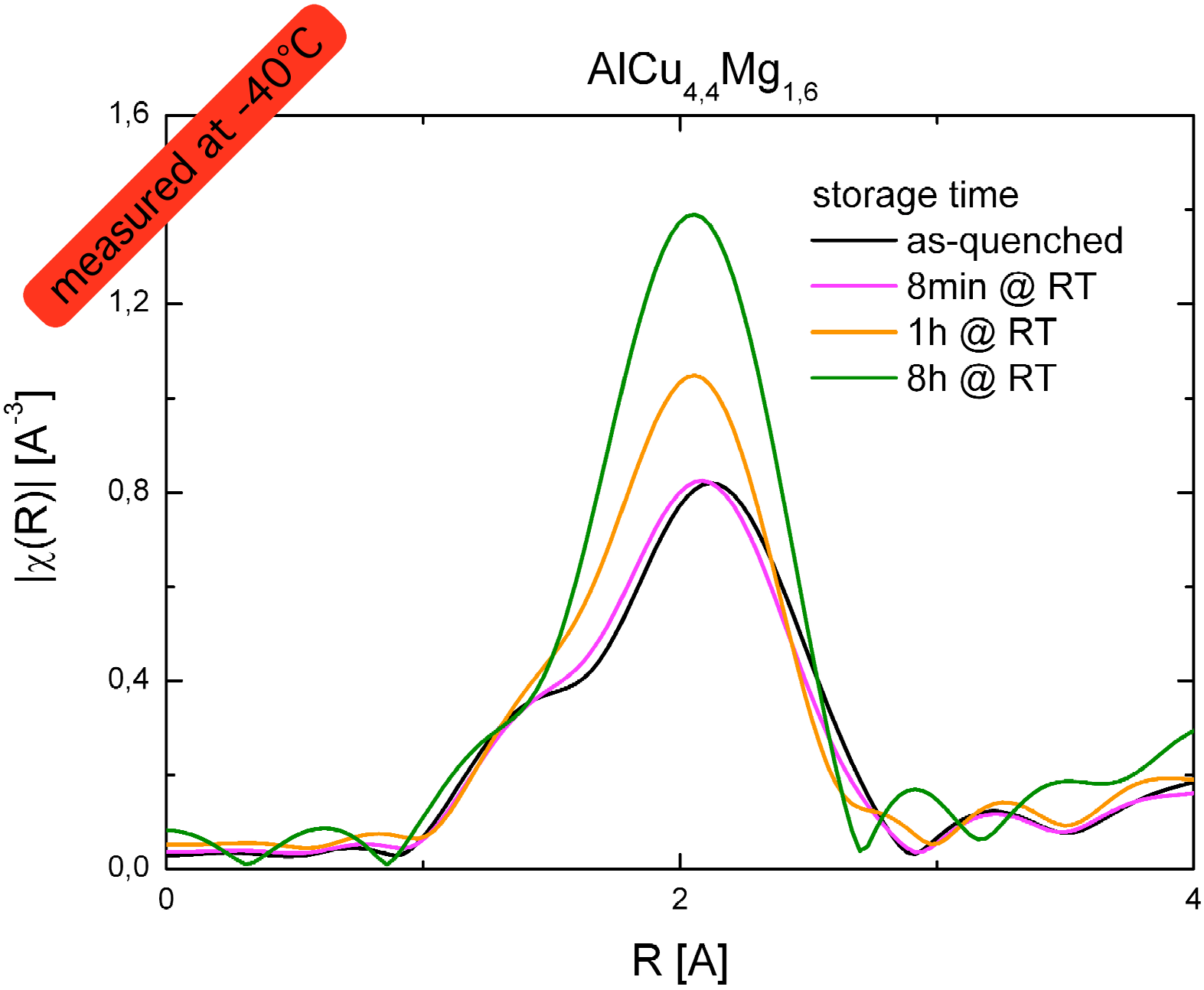


# FEFF-calc. vs. experiment: atoms or GPZ




- as-quenched ==> small cluster & isolated Cu atoms

# XANES at the Cu K-edge: - Early stages



# Conclusions & Outlook

- Atomic environment around vacancies: PAS / CDB / HMA
  --> Cu and Mg substitional or in complexes with Mg(Cu)/Si
  --> pure AlCu: P. Folegati, I. Makkonen, M. Puska et al. 2005-2007

- Atomic environment around selctive elements: XANES / EXAFS
  --> valuable tool for characterizing sub-nano-clusters in Al
  --> local atomic structure with FEFF-8 --> atomic relaxations

- XAFS & PAS need atomic positions by ab-initio calculations

- Early precipitations in AlMgSi/AlCuMg (<20min) --> new physics

- Future: binary alloys (AlCu, AlMg, AlSi) --> gauge methods

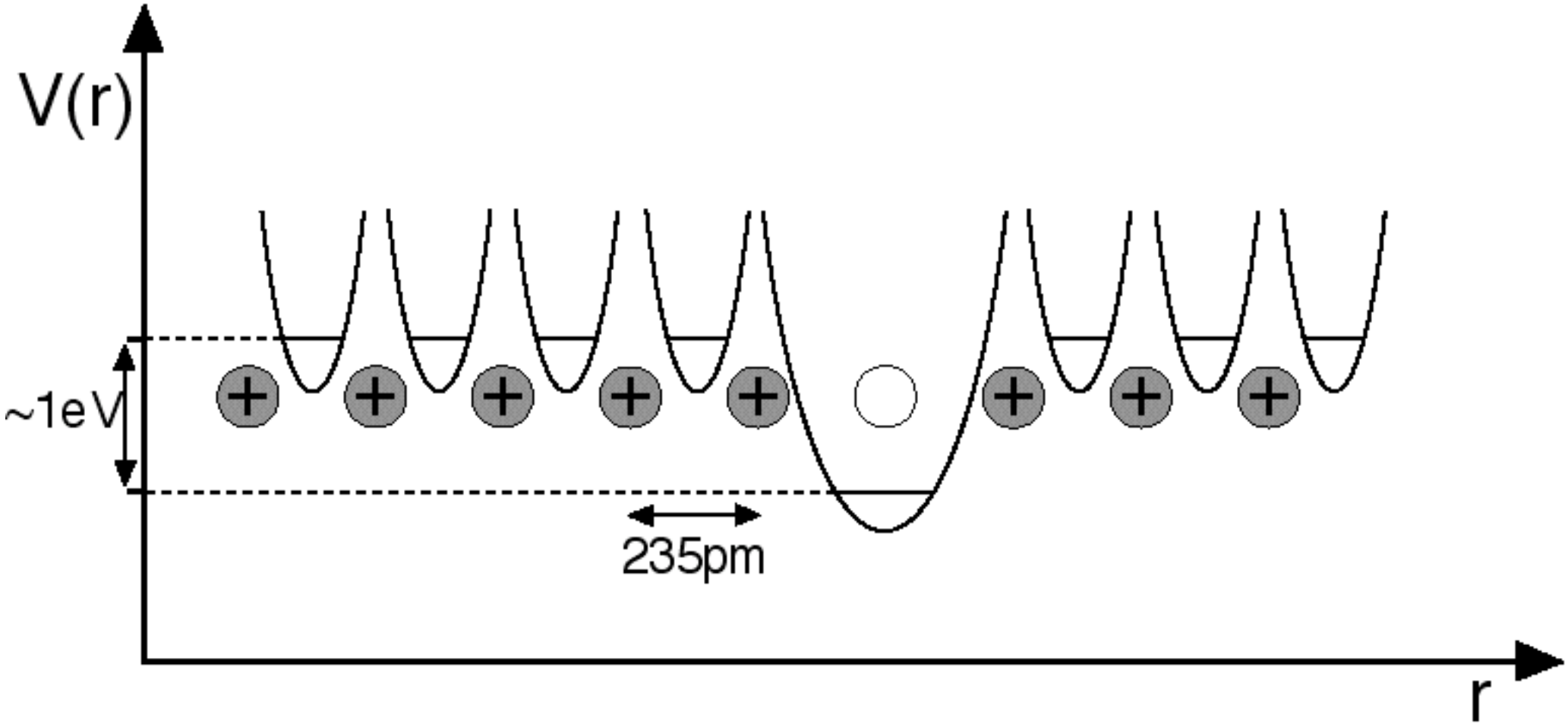
- Better characterization of technical alloys (AA6xxx, AA2xxx)

# Fin

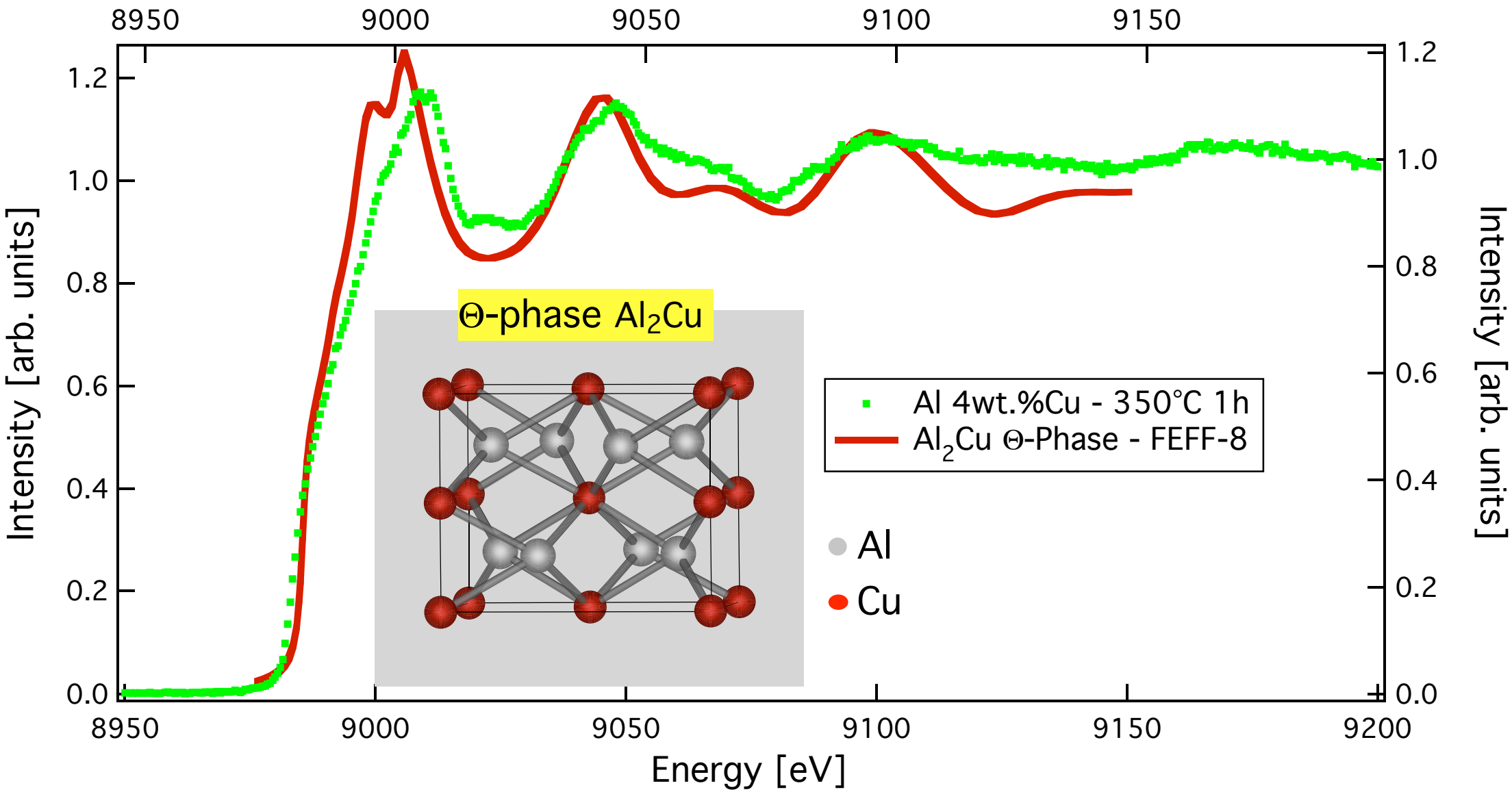
Thank you
for your attention!!!

# Positron Annihilation Spectroscopy

- Sensitivity --> vacancy-like defect & dislocations
  - $1\times10^{-7}\ldots5\times10^{-4}$ vacancies per atoms & $5\times10^{8}\ldots1\times10^{11}$ cm$^{-2}$

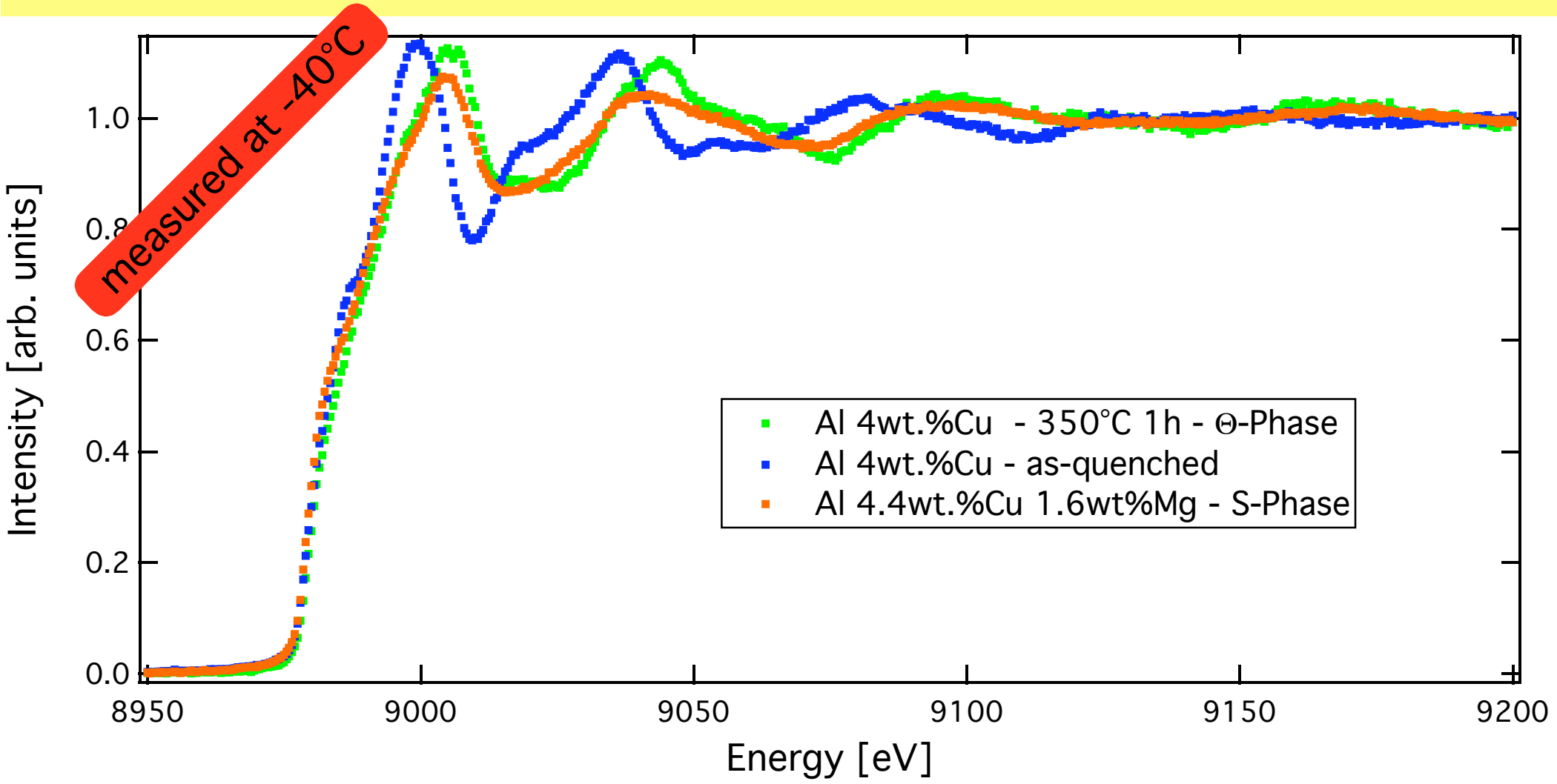


# FEFF-calc. vs. experiment: Θ-phase

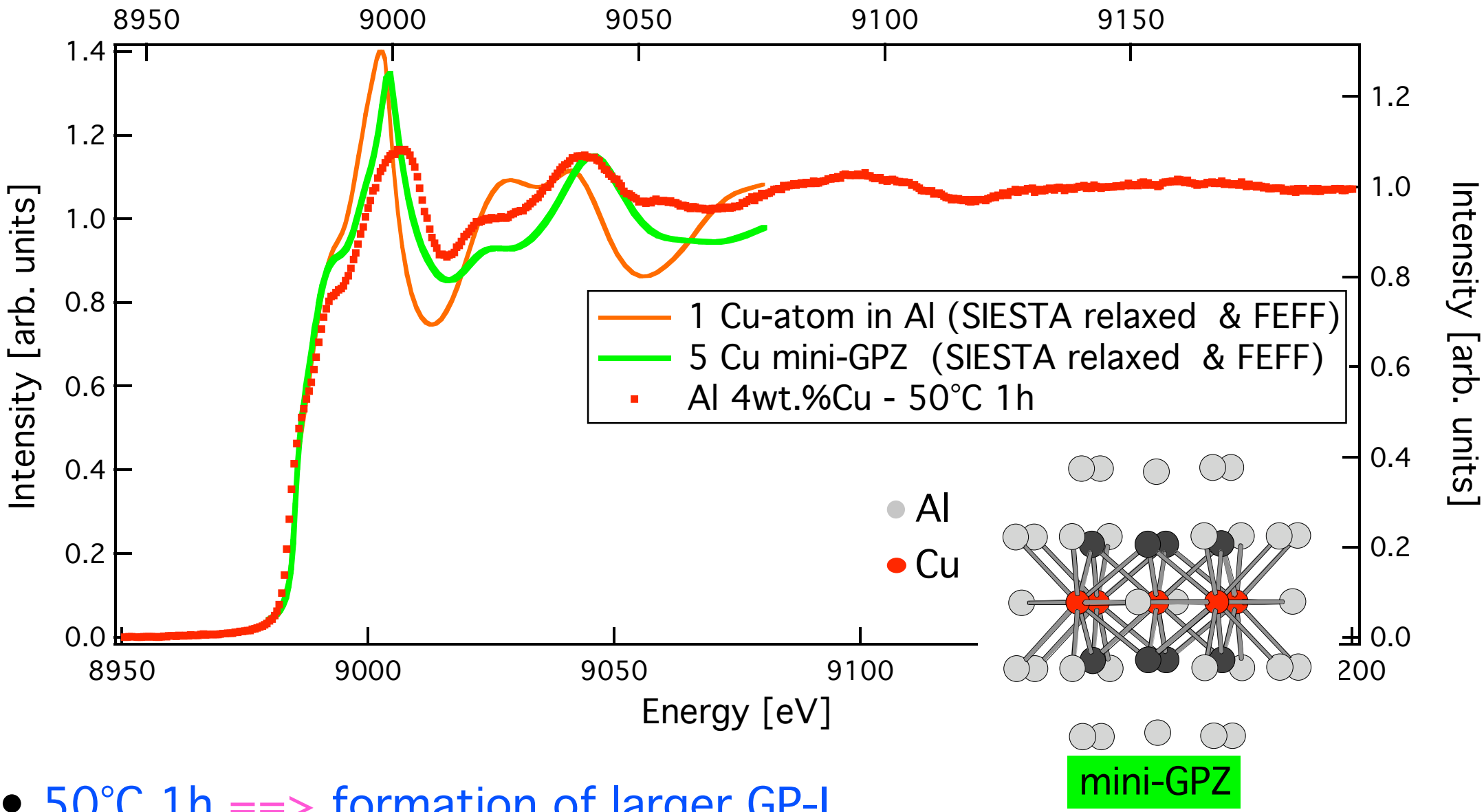


# XANES at the Cu K-edge: AlCu / AlCuMg

- AlCu: SSS --> quench --> GP1 --> GP2 (Θ'') --> Θ' --> Θ
- AlCuMg: SSS --> quench --> cluster --> GPB -->S'' --> S'/S



# FEFF-calc. vs. experiment: larger GPZ?




- 50°C 1h ==> formation of larger GP-I

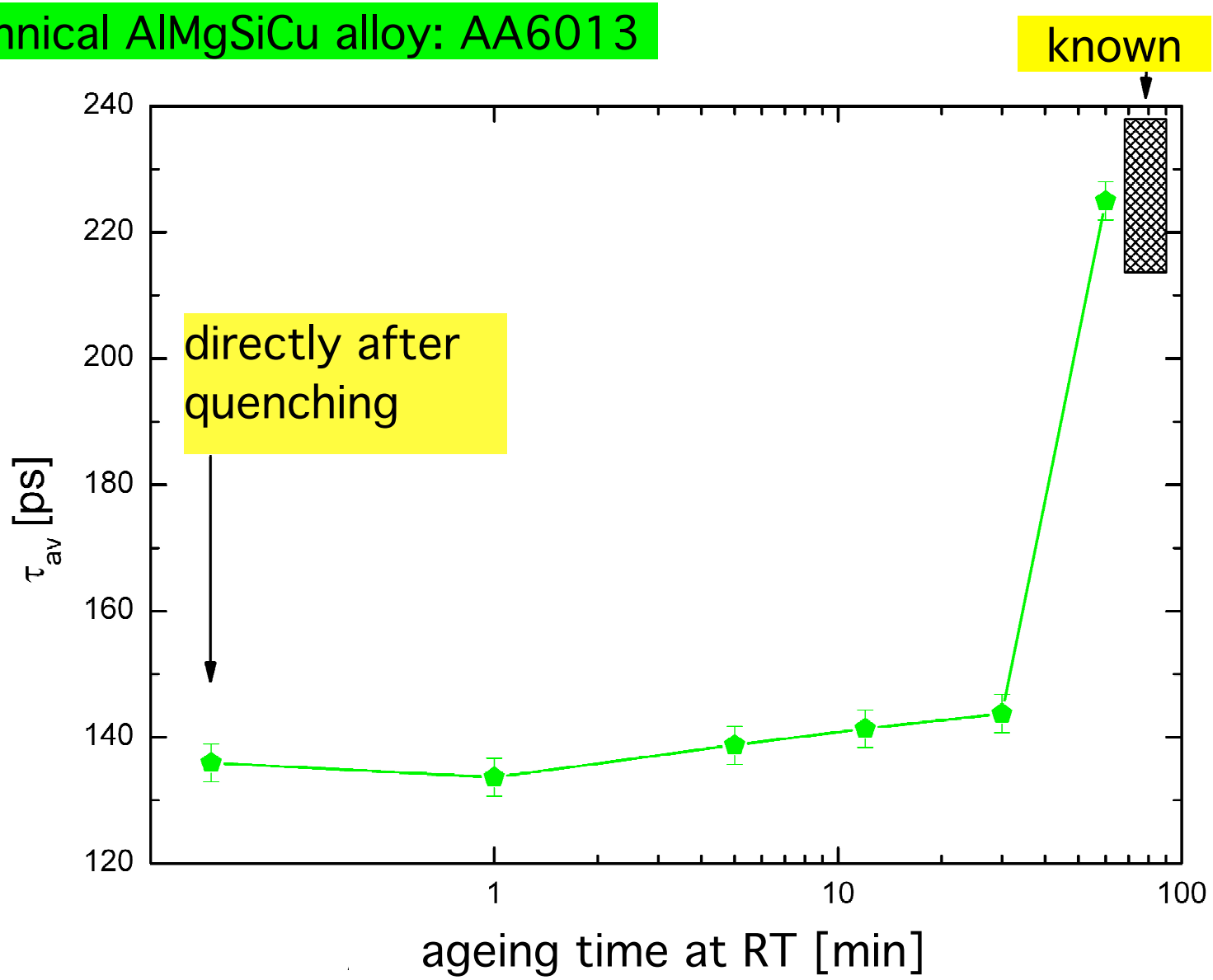
# Pure Elements

- testing SIESTA (pseudo potentials) DZP-Basis
  - --> lattice constant $a_0$
  - --> bulk modulus B
  - --> vacancy formation energy $E_F$

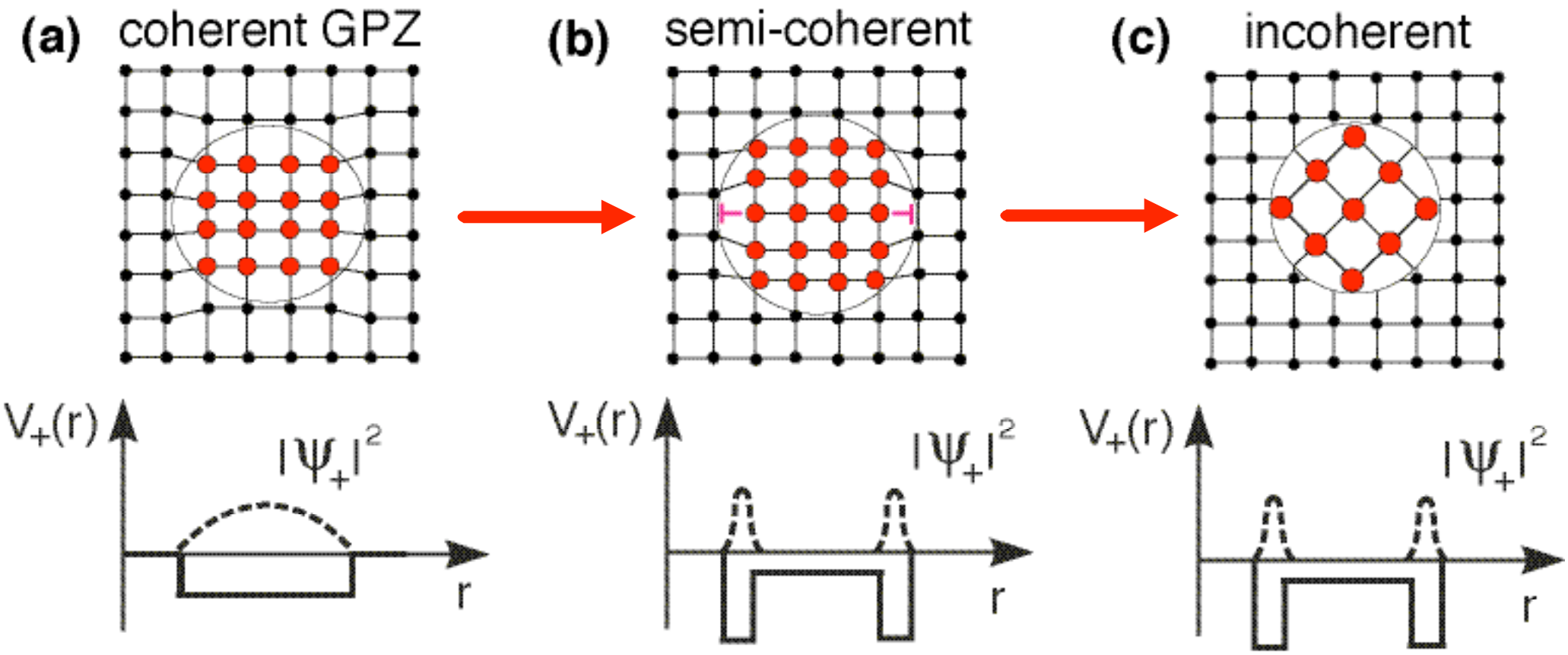
| Element | $a_0/a_0$(exp) | c/a | B/B(exp) | $E_F$(calc) | $E_F$(exp/cal) |
|---|---|---|---|---|---|
| Al | +0.86% | --- | -26% | 0.60 | 0.67 (0.6) |
| Mg | +0.64% | -0.7% | +29% | 0.97 | 0.9 |
| Si | +0.9% | --- | -12% | 4.0 | (3.7) |
| Cu (DZ) | -1.5% | --- | +19% | 1.1 | 1.28 |

# Early precipitation stages: tech. alloys

Technical AlMgSiCu alloy: AA6013



# Precipitates: Positron Annihilation




R. Krause, G. Dlubek and G. Wendrock. *Cryst. Res. Technol.* **20** (1985) 1495

- GPZ: size > 1nm --> positron trapping
- BUT: most interesting very early stages: 1-5 atoms