Marcin Kędzierski

Amorphous Phase Separation as a Precursor for Nanocrystallization

WYDZIAŁ FIZYKI
POLITECHNIKA WARSZAWSKA

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Presentation outline

- Theoretical preliminaries
  - Fick's law
  - Regular solution model
  - Phase separation
  - Amorphous phase -> structure & technology

- Experiment & data analysis
  - DSC
  - WAXS
    - Mean grain size
    - Crystalline volume fraction
  - SAXS:
    - Exponential amplification in the early stage
    - Scaling in the intermediate and late stages
    - Pair distribution function based on experiment and simulation

Fick’s law

$$j = -D\frac{d\phi}{dx}$$

Fick's law

$$j = -D\frac{d\phi}{dx} \longrightarrow j = -M\frac{d\mu}{dx}$$

Regular solution model

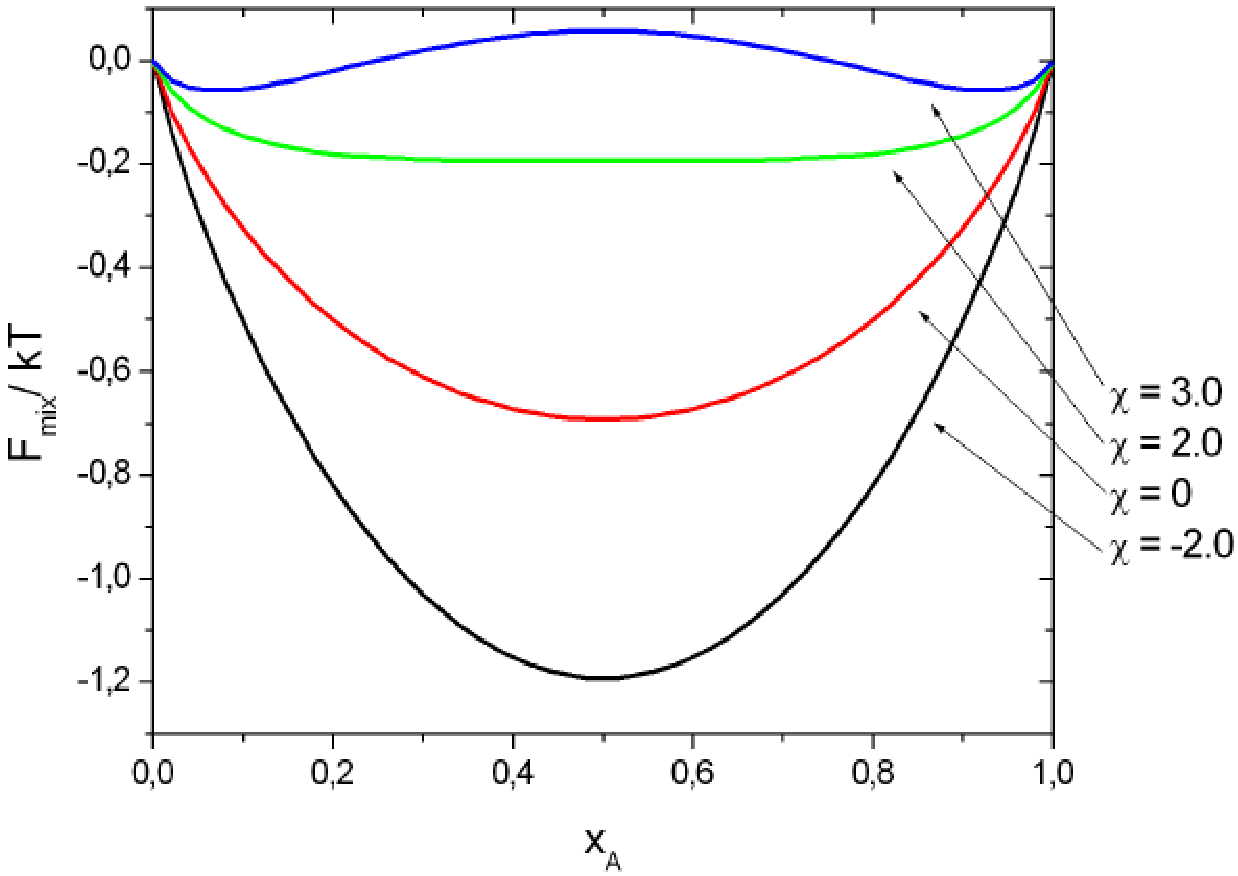
$$S_{mix} = -k\left(x_A \cdot \ln x_A + x_B \cdot \ln x_B\right)$$

$$U_{mix} = kT \cdot \chi x_A x_B$$

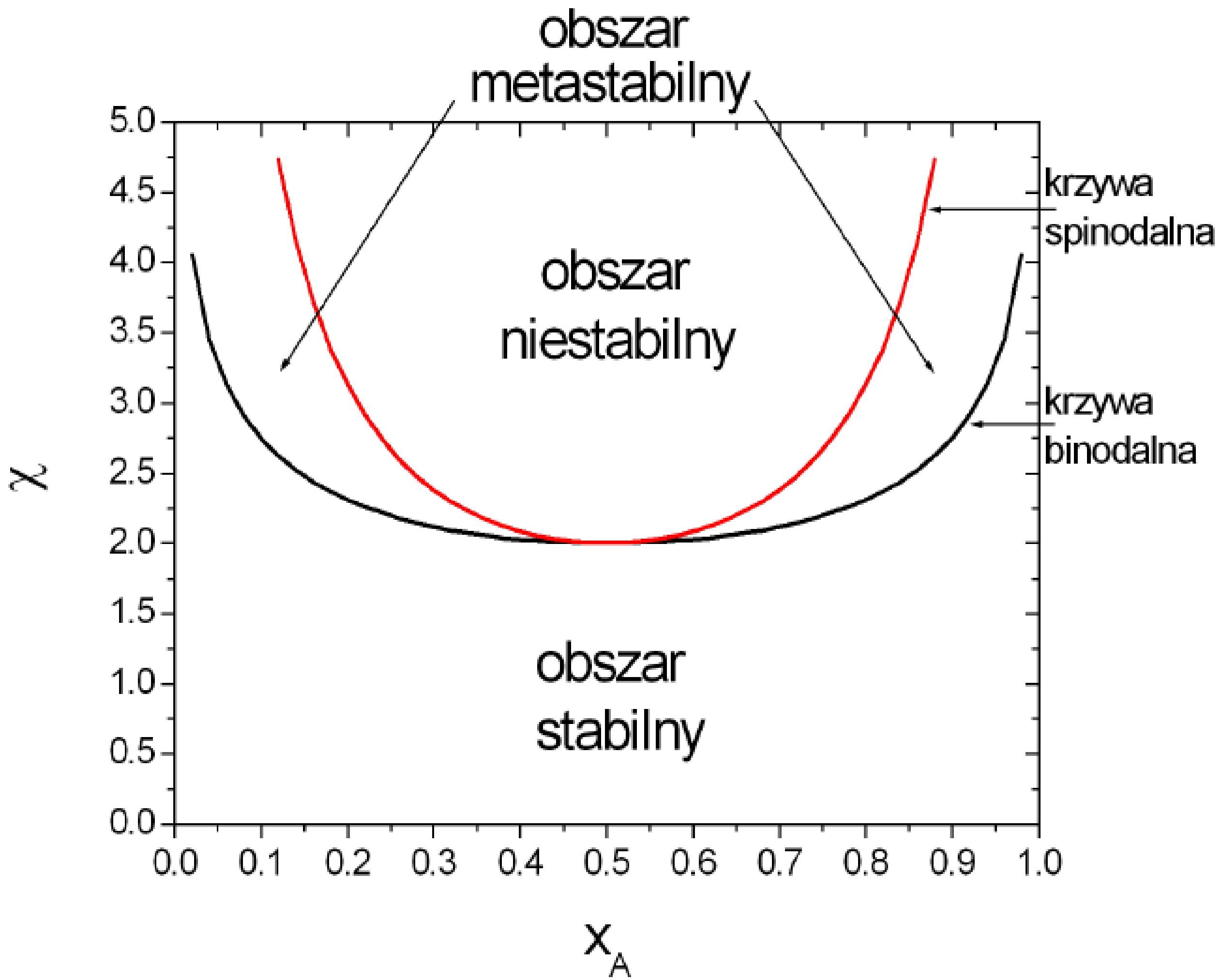
$$\chi = \frac{Z}{2kT}\left(2\varepsilon_{AB} - \varepsilon_{AA} - \varepsilon_{BB}\right)$$

$$\frac{F_{mix}}{kT} = x_A \ln x_A + x_B \ln x_B + \chi x_A x_B$$

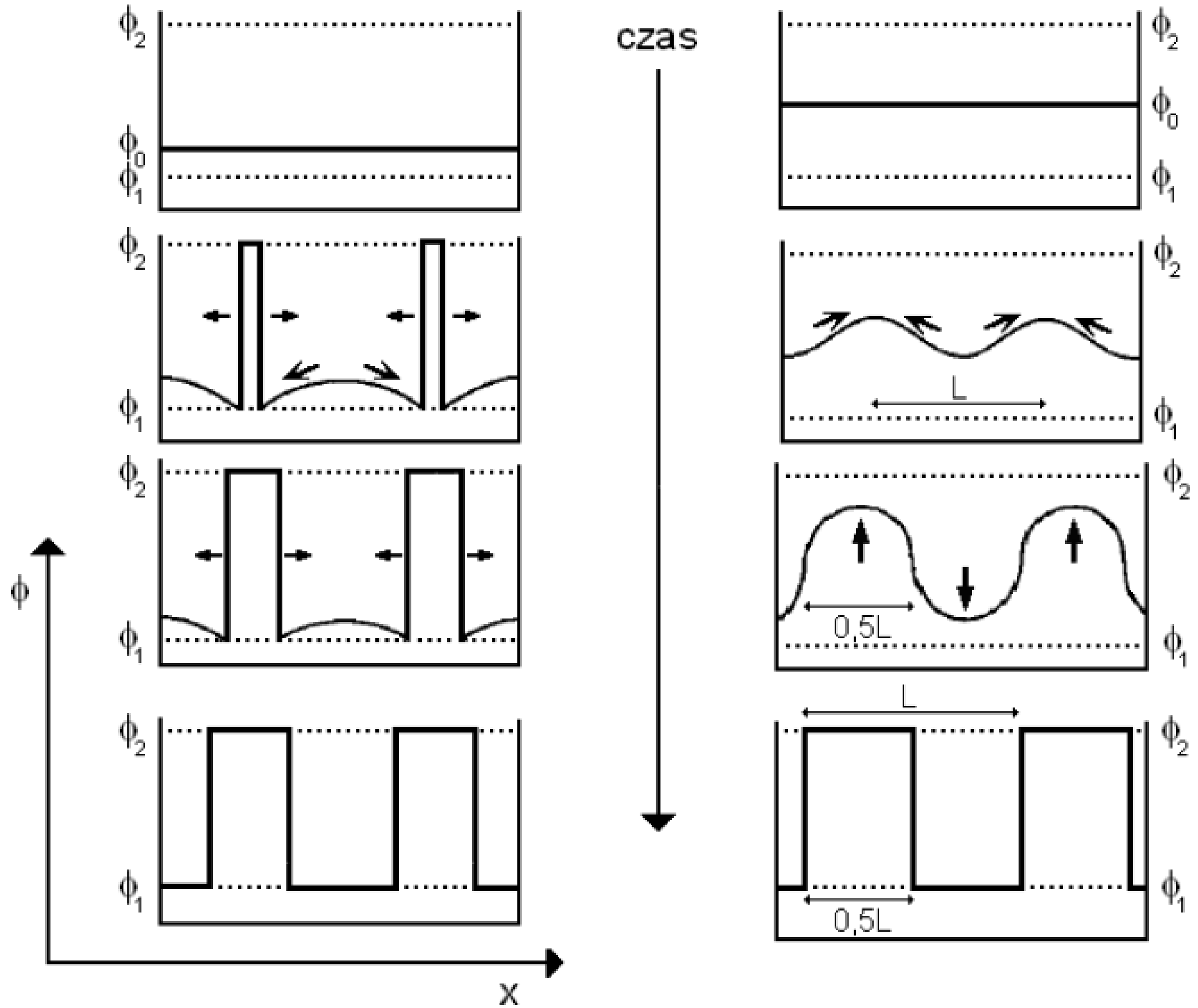
Regular solution model



Regular solution model



Spinodal decomposition vs nucleation & growth



Spinodal decomposition theory

$$f(\phi, \nabla \phi) = f_0(\phi) + K|\nabla \phi|^2$$

+ modified Fick's law

+ assumption: M is independent of local concentration

+ equation of continuity

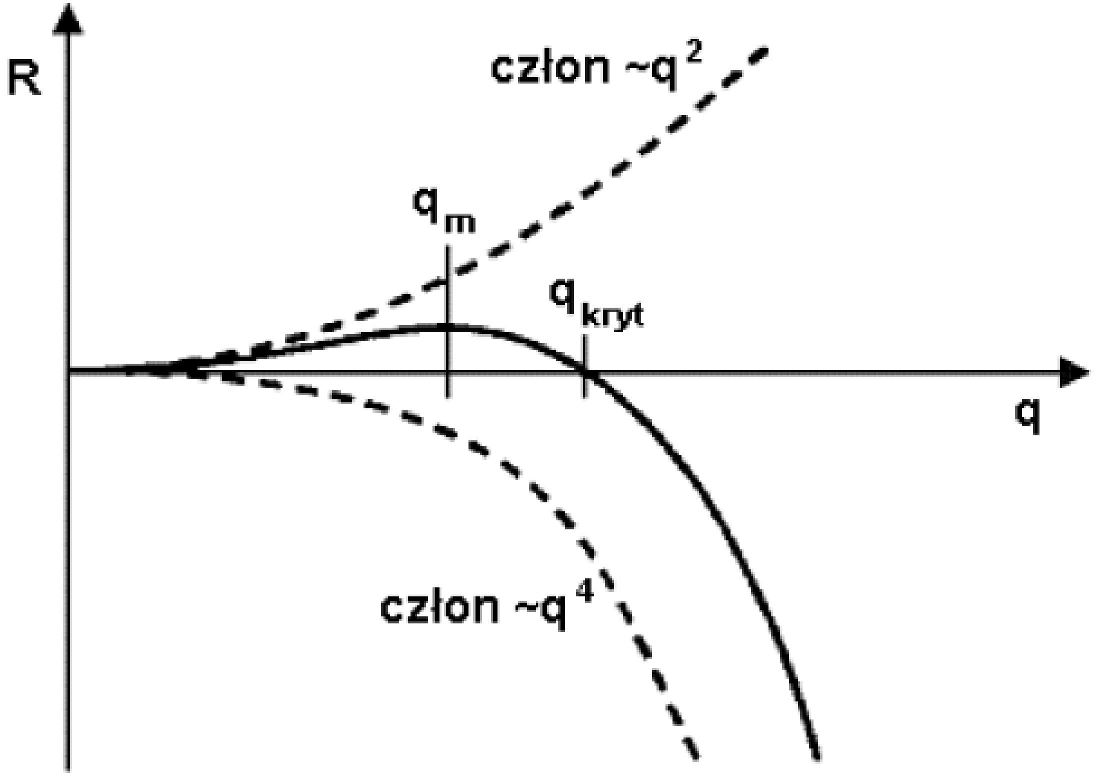
$$\rightarrow \quad \frac{\partial \phi}{\partial t} = M f_0'' \frac{\partial^2 \phi}{\partial x^2} + 2MK \frac{\partial^4 \phi}{\partial x^4}$$

$$\downarrow$$

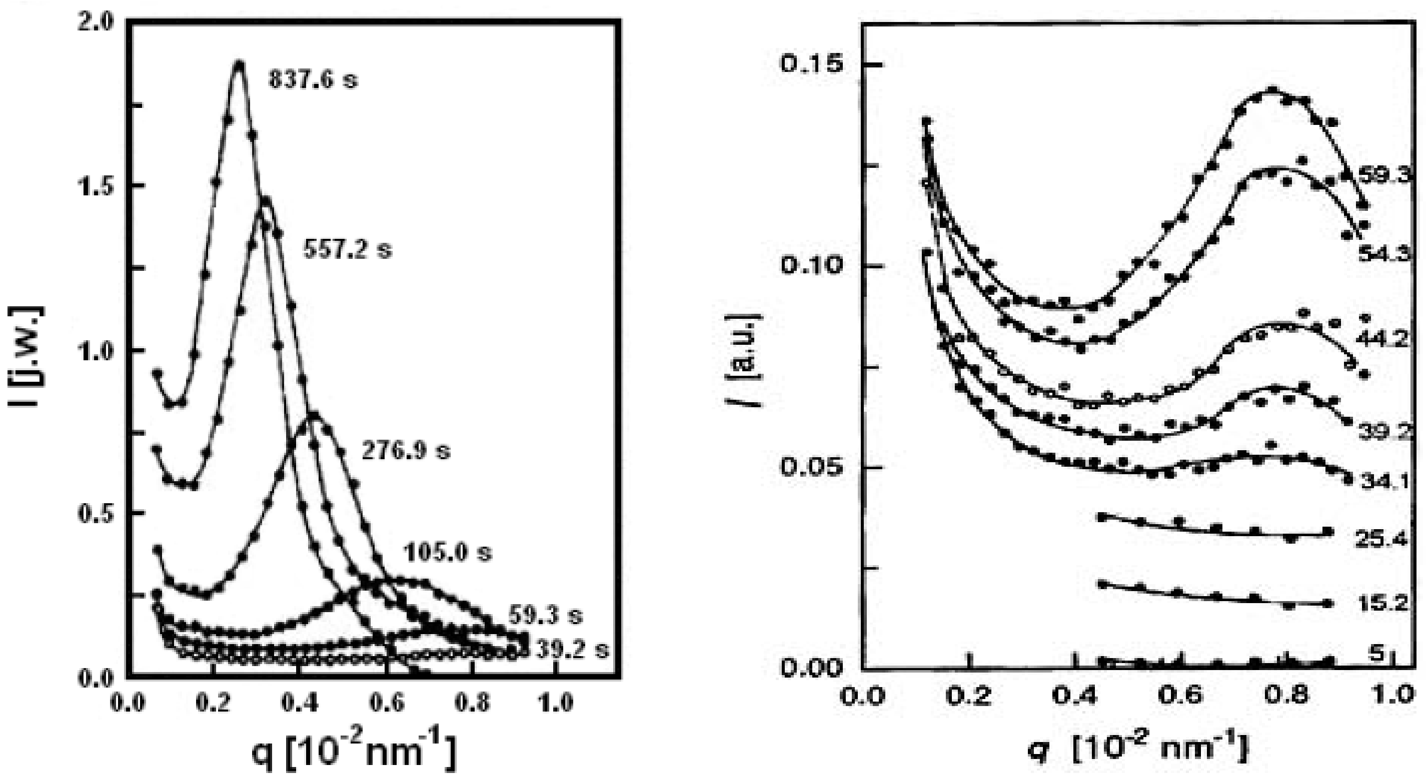
$$\phi(x,t) = \phi_0 + A \sin(qx) \exp(R(q)t)$$

$$R(q) = -Dq^2 \left(1 + \frac{2Kq^2}{f_0''} \right)$$

Amplification factor

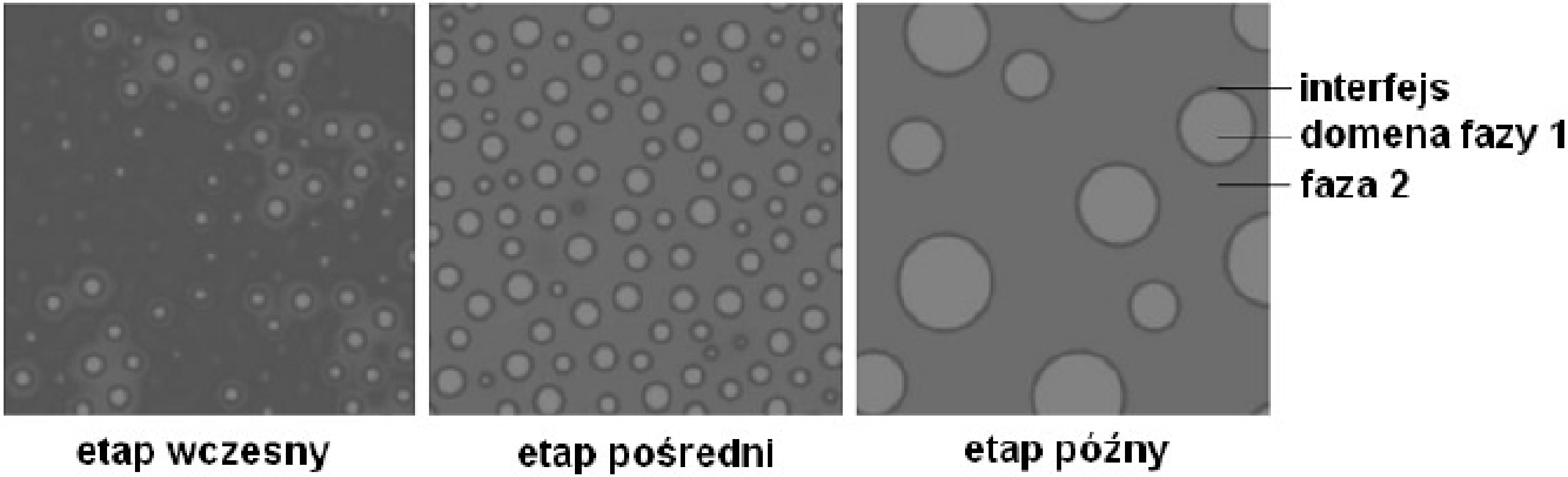


Example: polymer solution



[Hash83] Hashimoto T., Kumaki J., Kawai H., Macromolecules 16, 641 (1983)

Nonlinear Cahn-Hillard equation



Lochte L. *et al.*, Acta. Mater. 48, 2969 (2000)

Scaling

$$L(t) \sim \; t^{s}$$

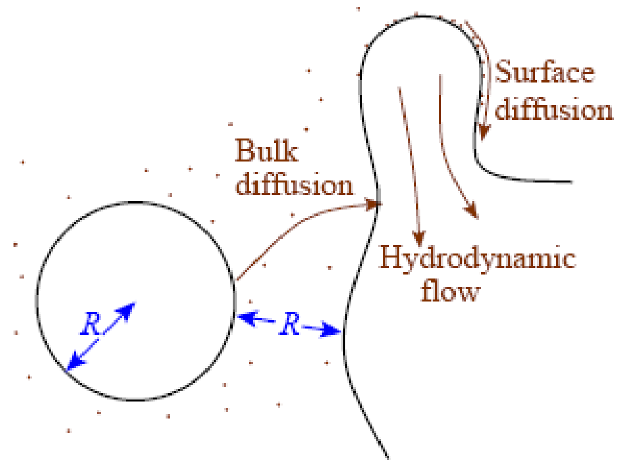
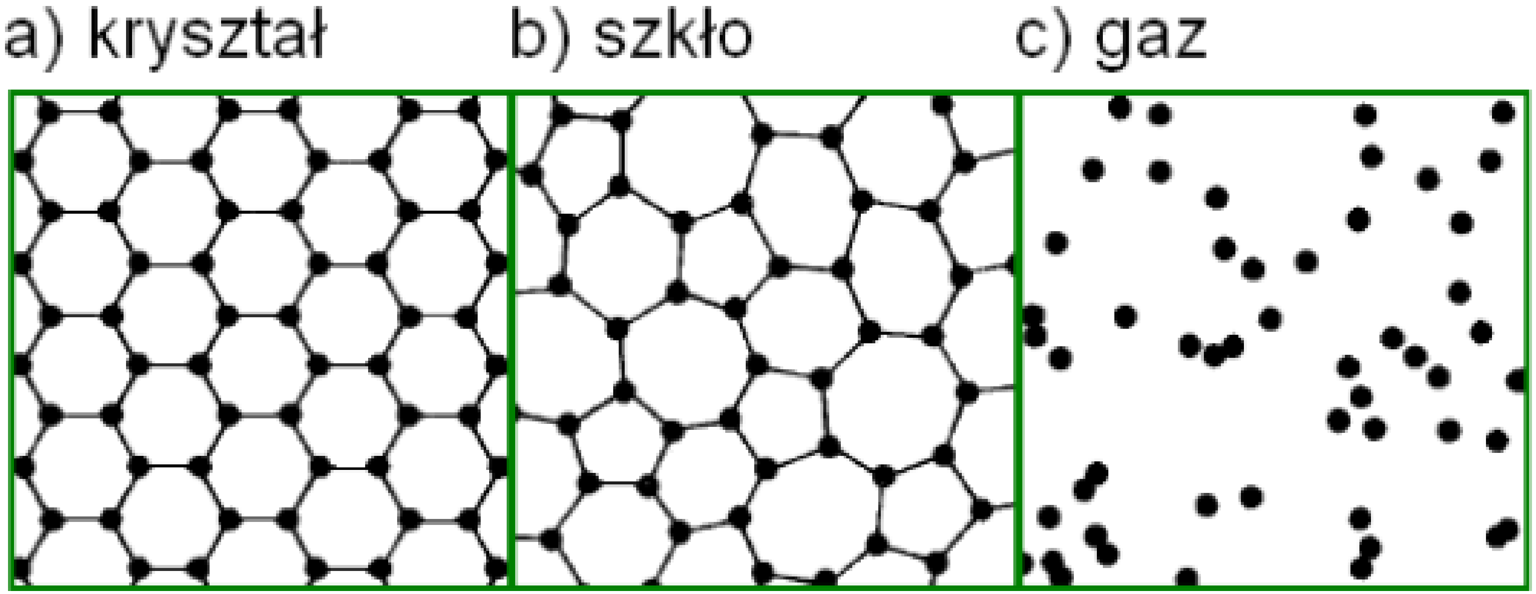
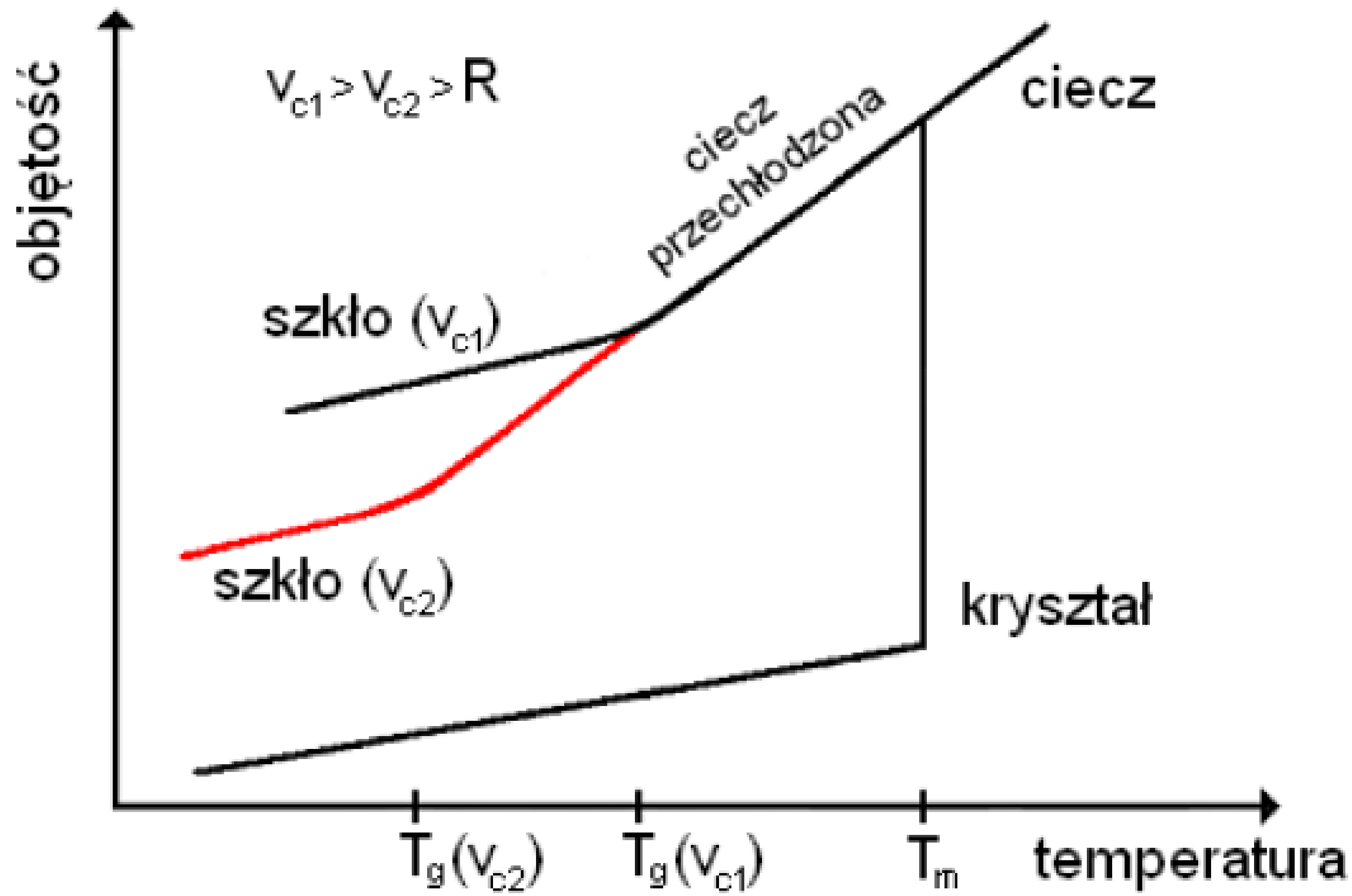


Fig. 11.9 Coarsening for conserved order parameter. Differences in local mean curvature drives the growth in the case of a conserved order parameter. Atoms will diffuse from regions of high positive curvature to regions of low or negative curvature. Bulk diffusion dominates on long length scales ($L(t) \sim t^{1/3}$); surface diffusion can be important when the scales are small ($L(t) \sim t^{1/4}$). For liquids, hydrodynamic flow makes things more complicated [134].

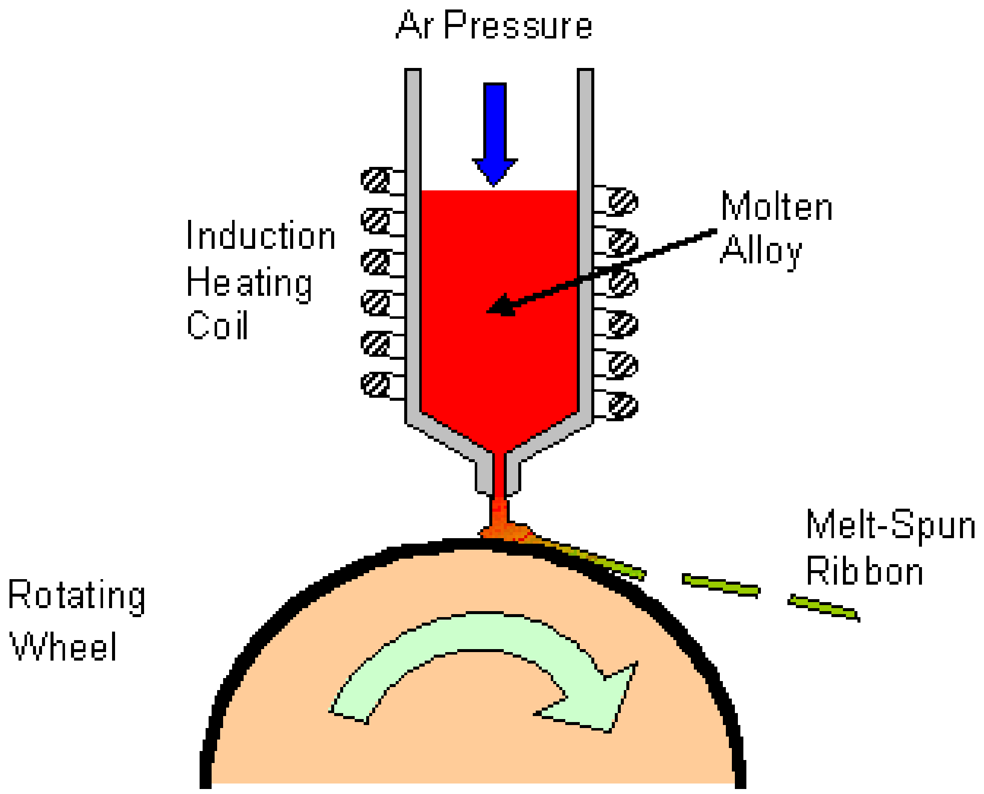
Amorphous phase - structure



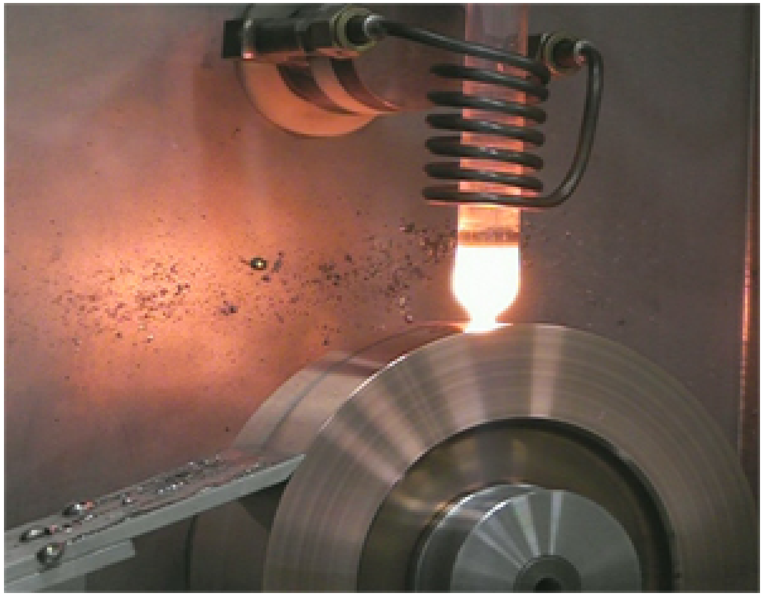
Amorphous phase - technology



Melt-spinning



cooling rate ~10^6 K/s



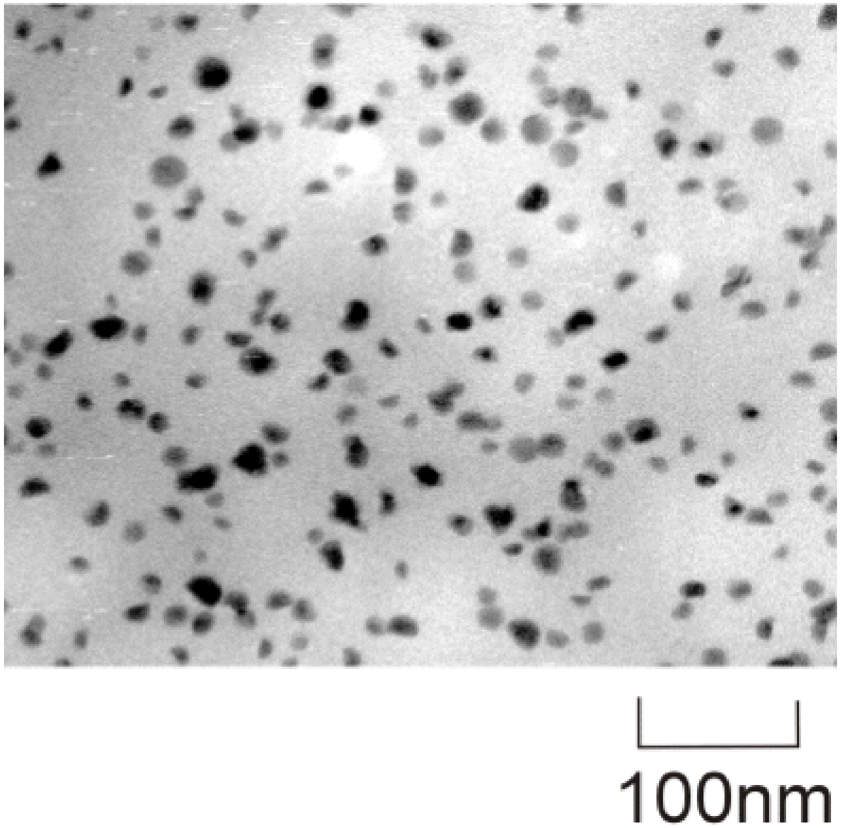
Amorphous aluminium alloys

- Al-RE, Al-TM-RE
  RE = Sm,Gd,Tb,Dy,Y...; TM = Fe,Ni,Co,...

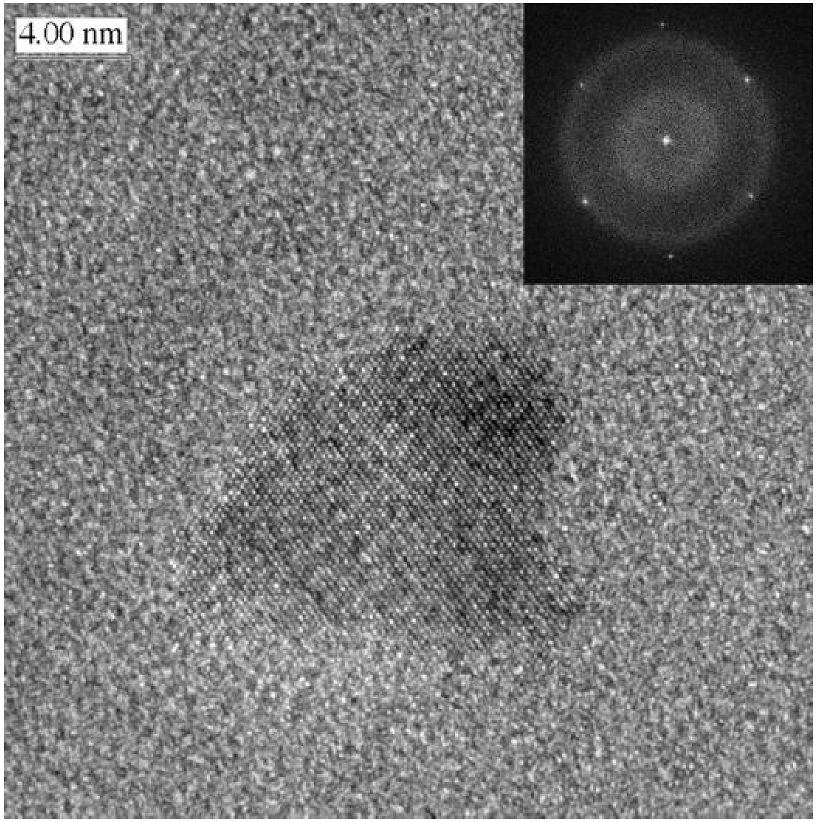
- High strength-to-weight ratio
- Good ductility

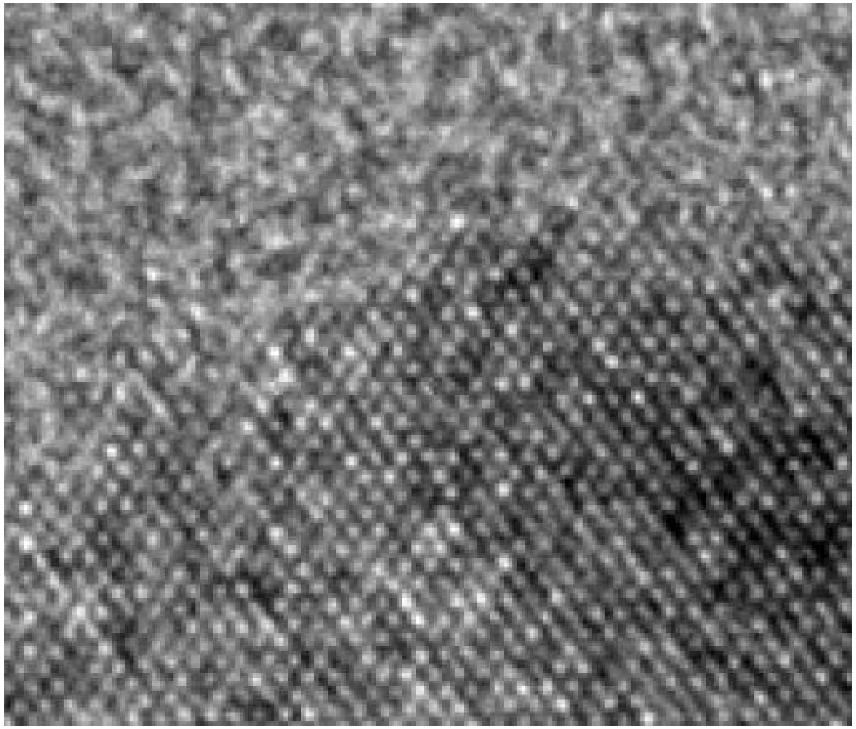
Nanocrystallization

Thermal annealing often leads to formation of a nanocrystalline microstructure consisting of about 10 nm fcc-Al grains embedded in an amorphous matrix.



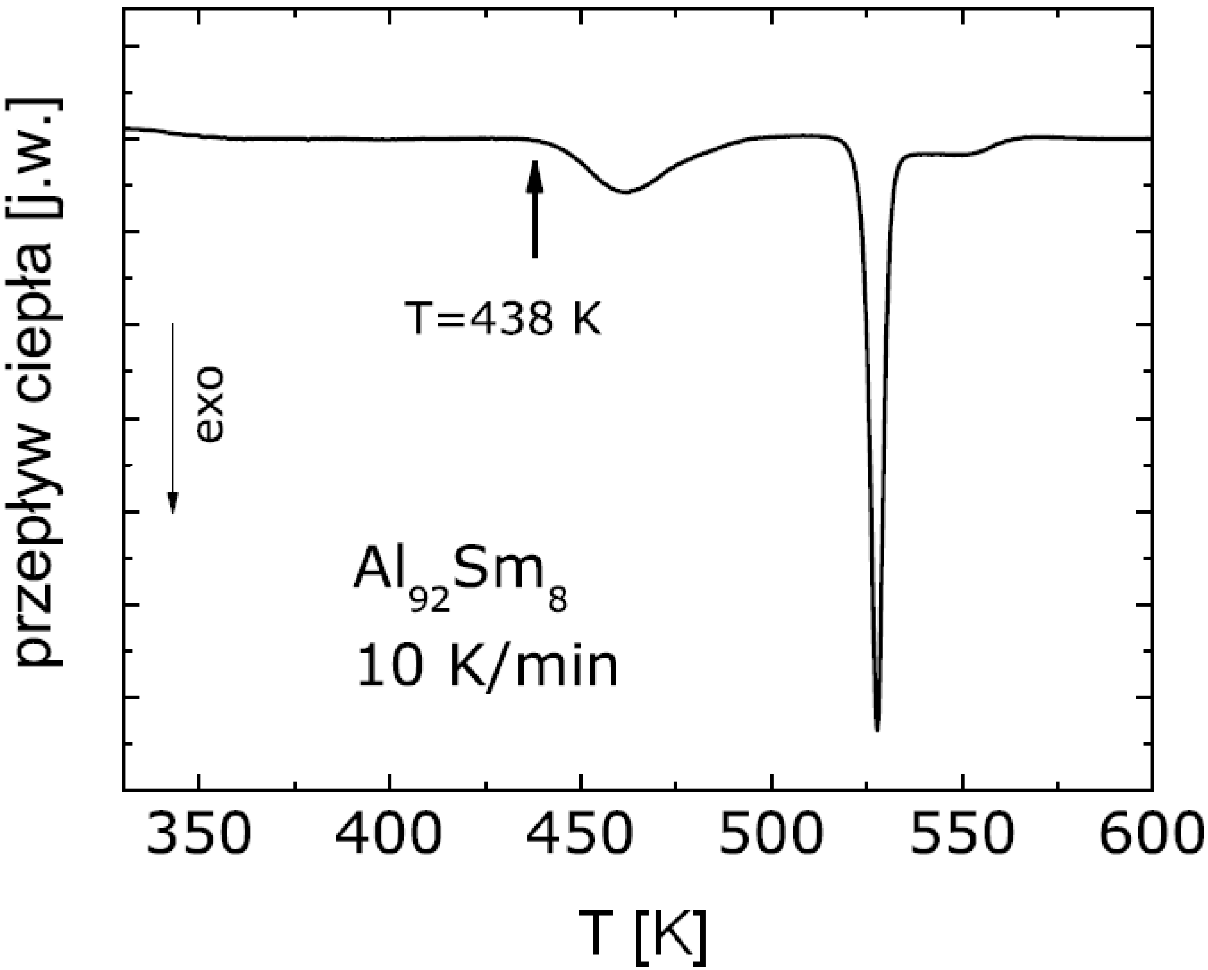
Microstructure





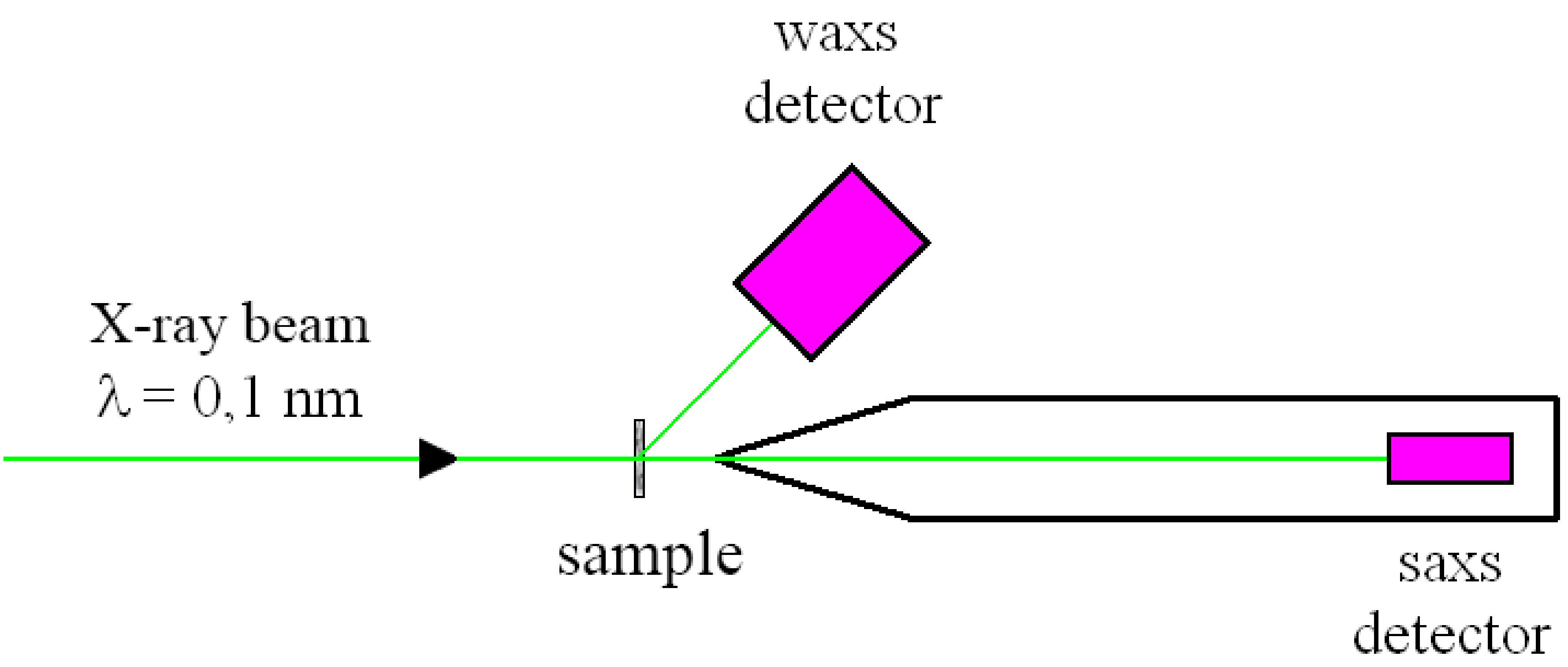
J. Antonowicz, E. Jezierska, **M. Kędzierski,**
A. R. Yavari, A. L.Greer, P. Panine, M. Sztucki
Early stages of phase separation and nanocrystallization in Al-rare earth metallic glasses studied using SAXS/WAXS and HRTEM methods. (in print)

DSC

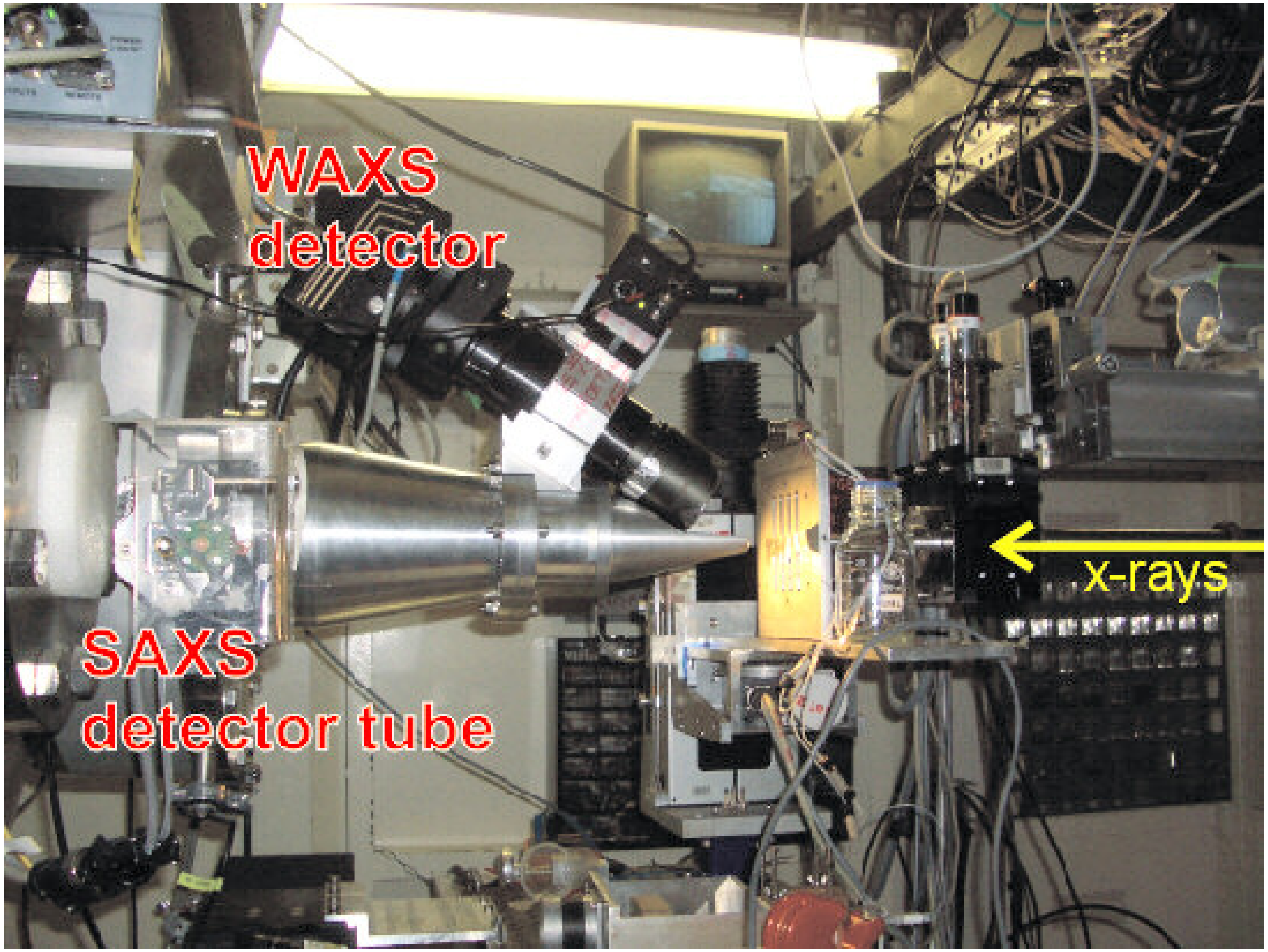


przepływ ciepła [j.w.]
T=438 K
exo
Al92Sm8
10 K/min
350
400
450
500
550
600
T [K]

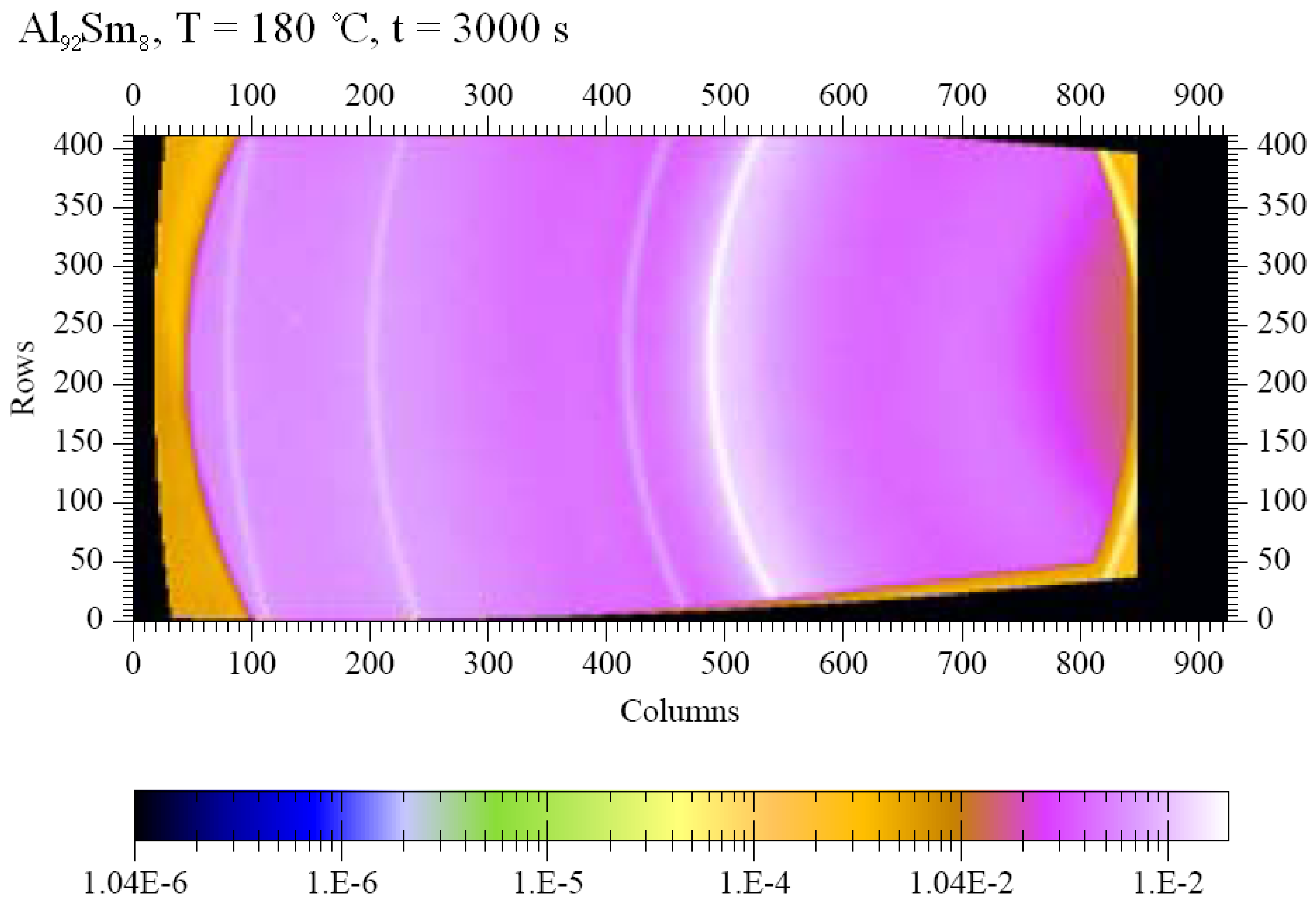
SAXS/WAXS – experimental setup



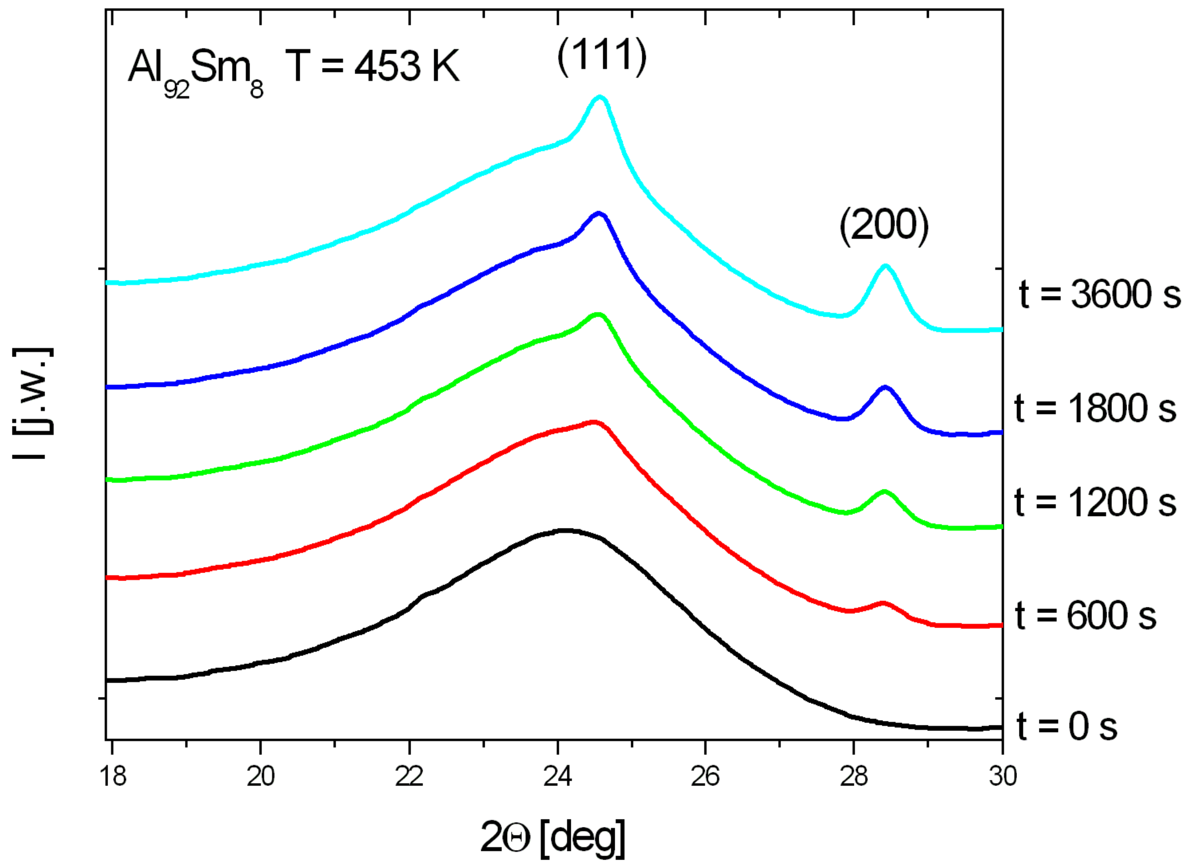
SAXS/WAXS – experimental setup



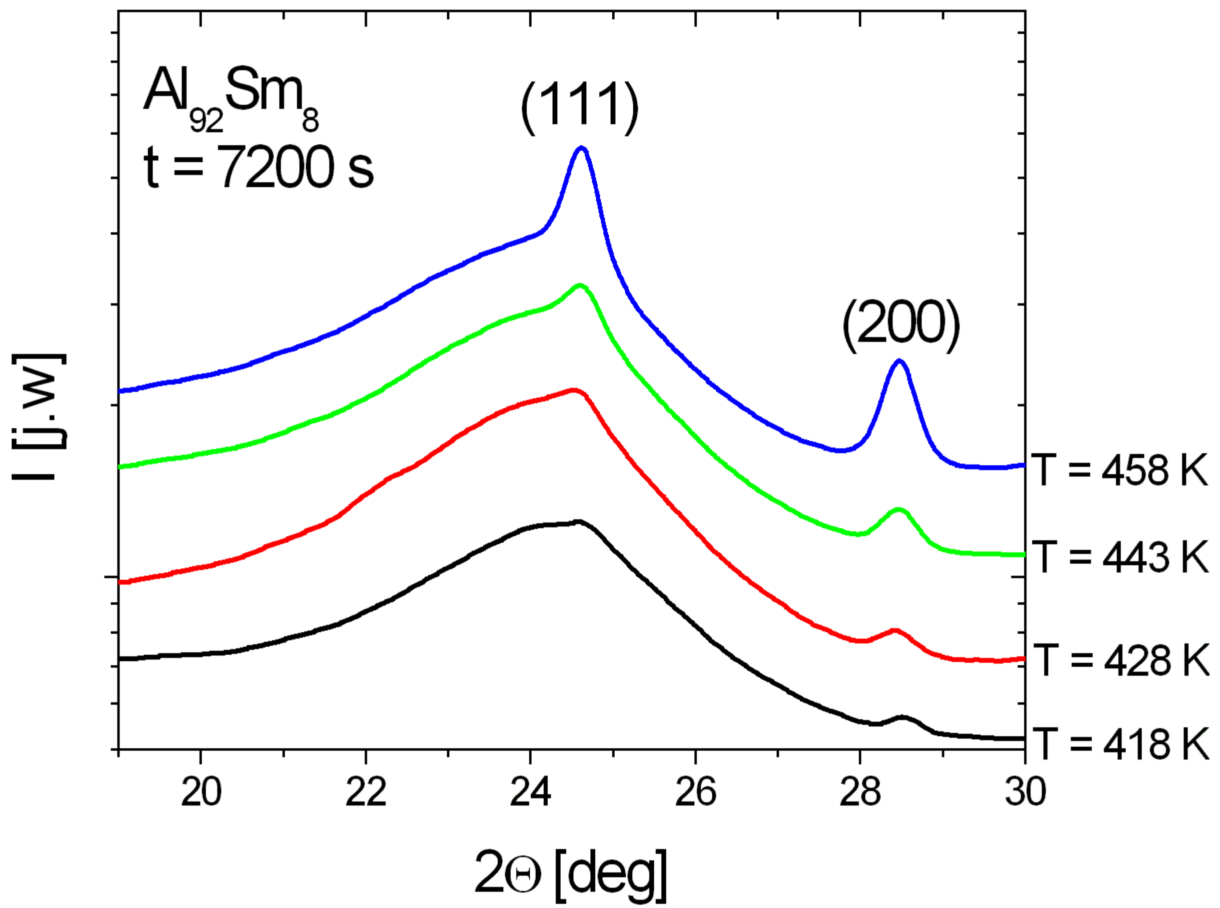
WAXS – 2D spectra



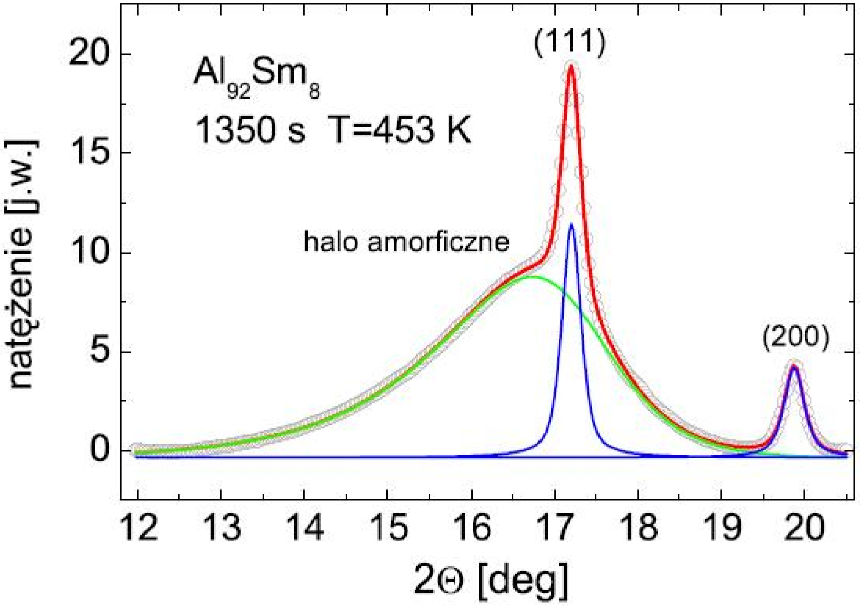
WAXS – 1D spectra

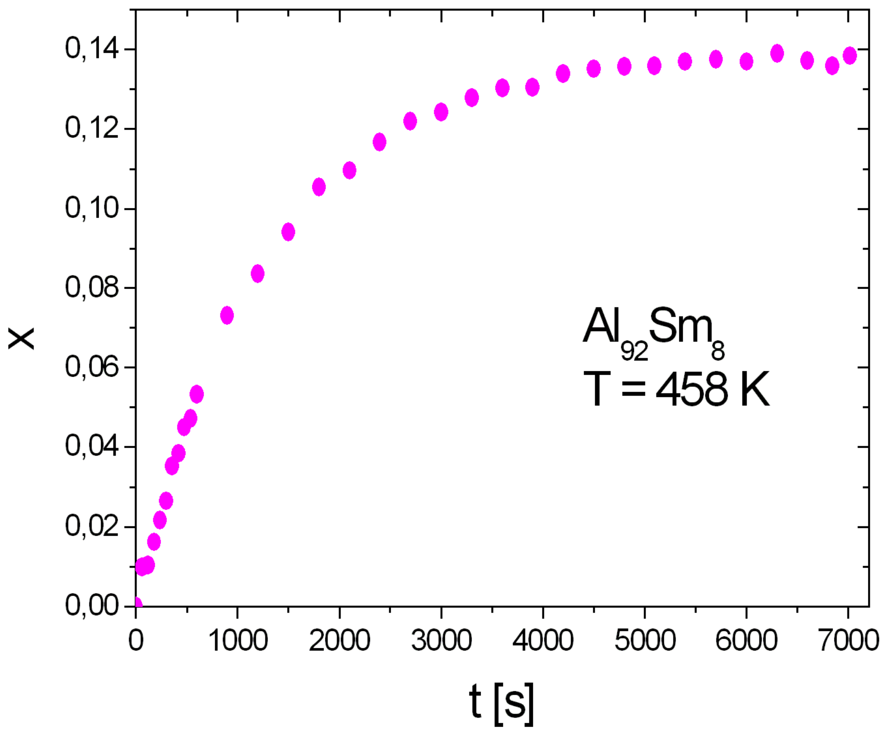


WAXS – 1D spectra



Crystalline volume fraction

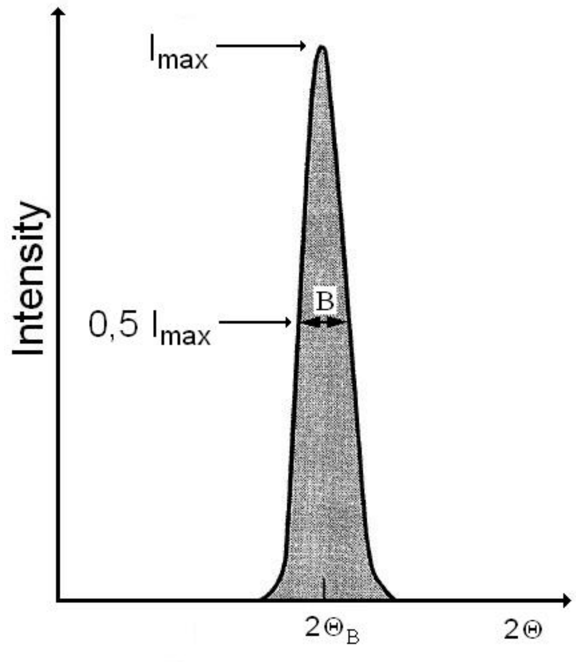


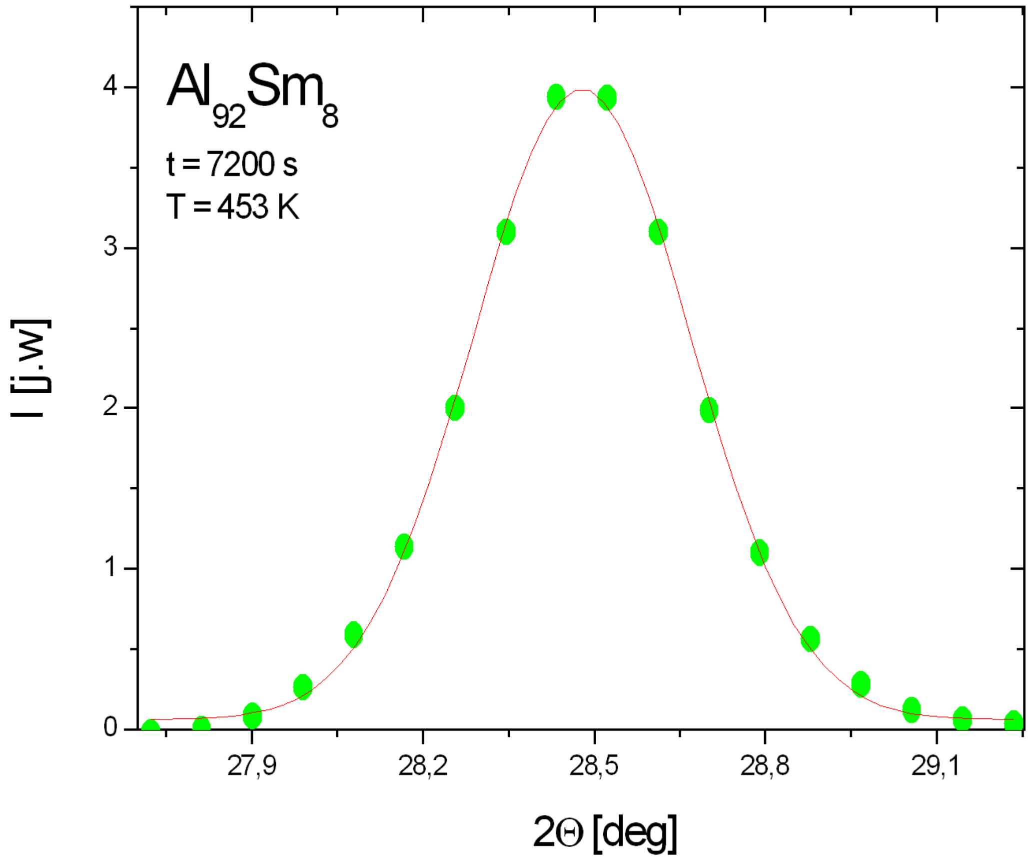


Mean nanocrystal size

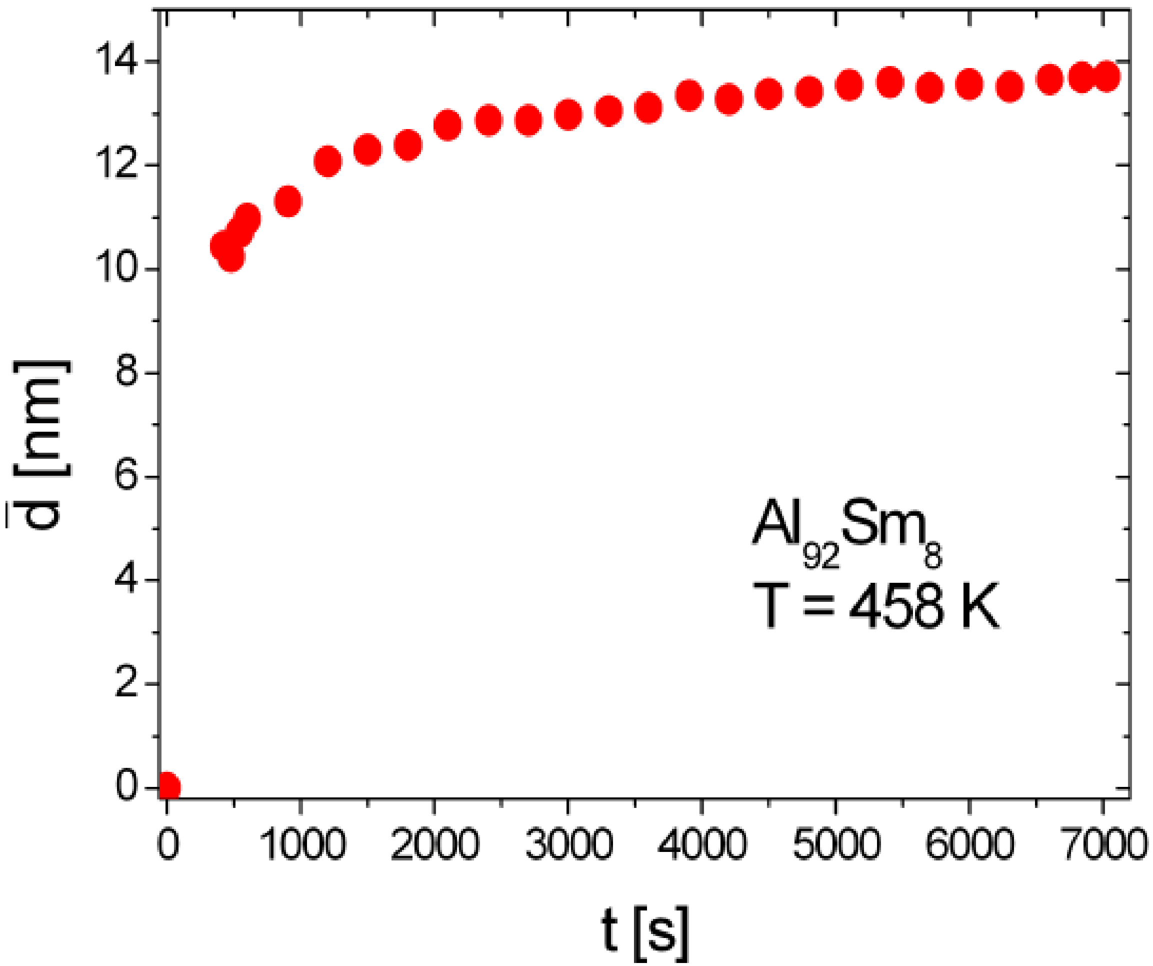
Scherrer formula

$$\bar{d} = \frac{0{,}9\lambda}{B\cos\Theta_B}$$

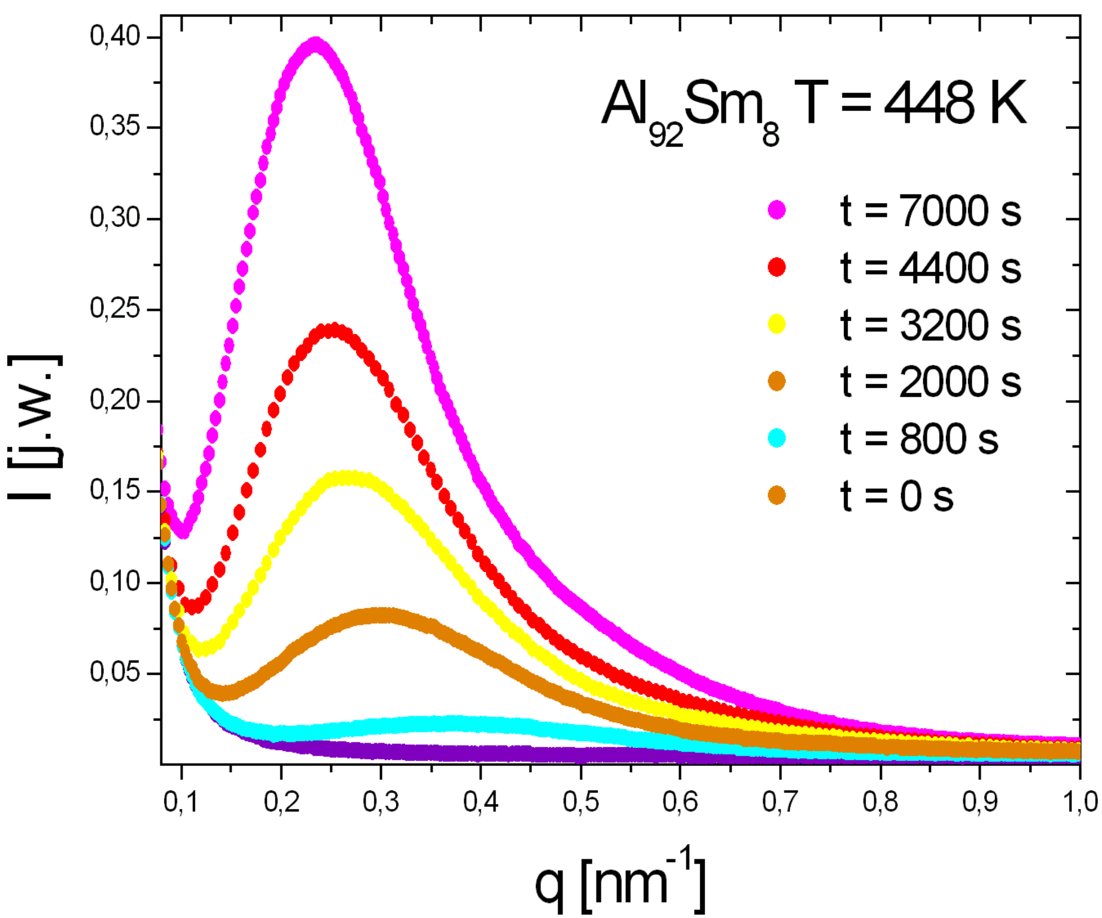




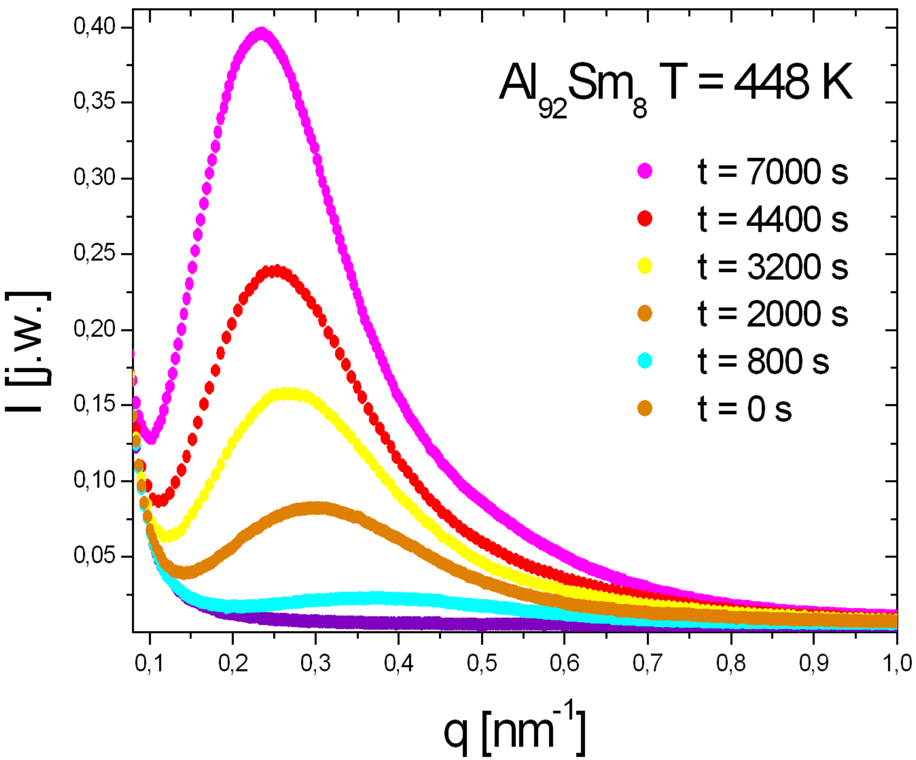
Mean nanocrystal size



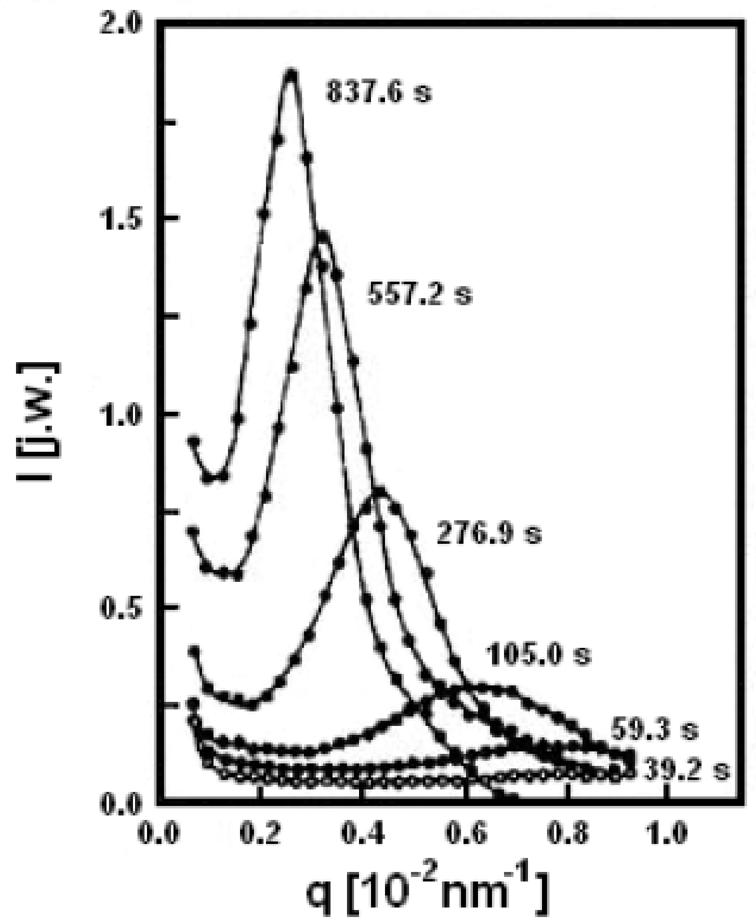
SAXS – 1D spectra



Comparison

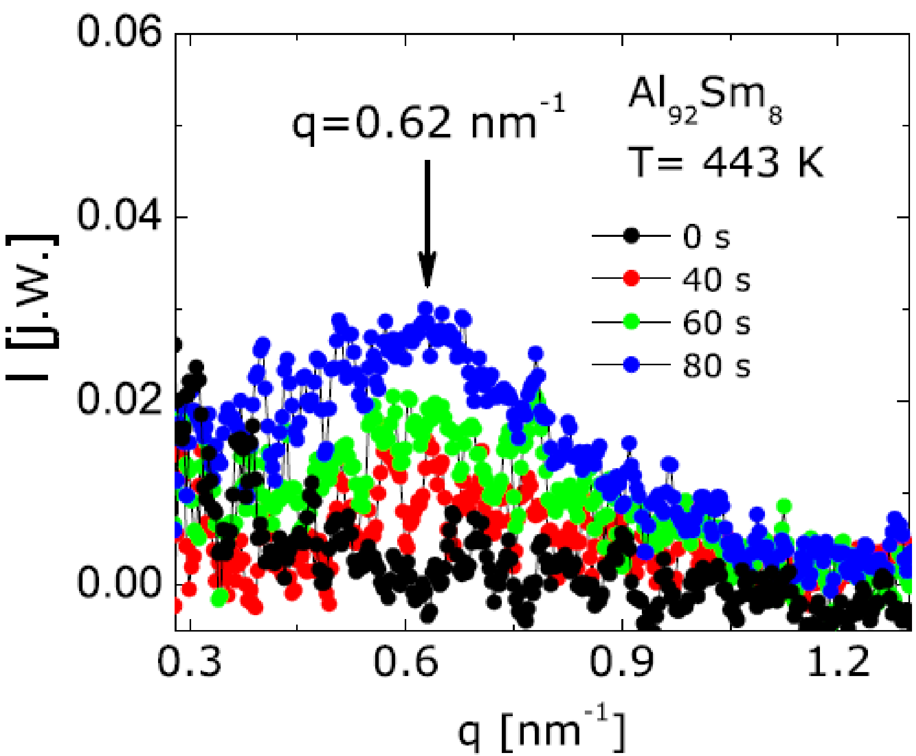


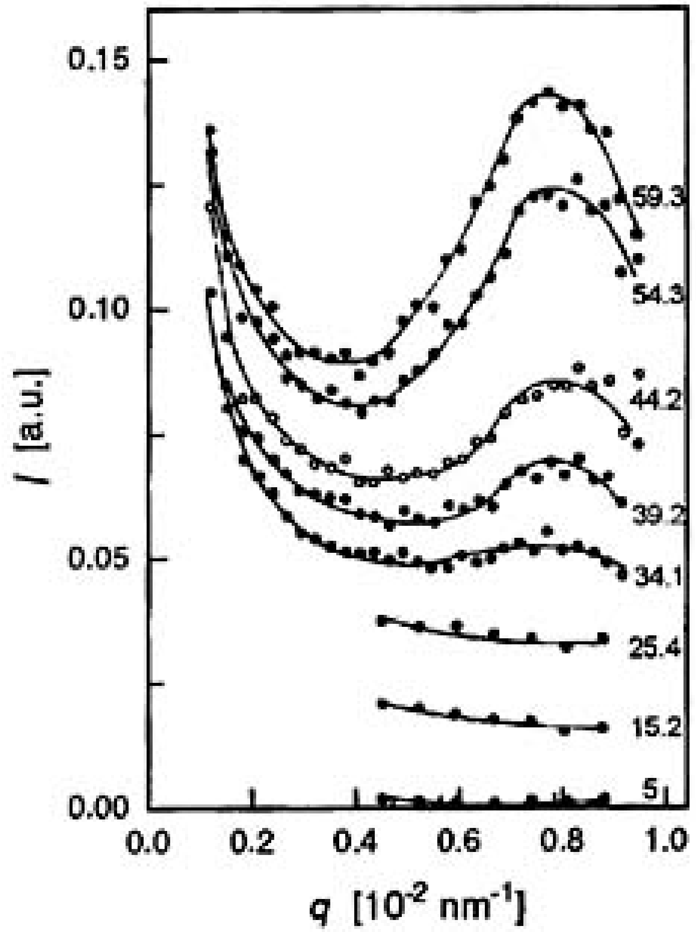
$Al_{92}Sm_8$ T = 448 K
t = 7000 s
t = 4400 s
t = 3200 s
t = 2000 s
t = 800 s
t = 0 s
I [j.w.]
q [nm^{-1}]
0,40
0,35
0,30
0,25
0,20
0,15
0,10
0,05
0,1
0,2
0,3
0,4
0,5
0,6
0,7
0,8
0,9
1,0



837.6 s
557.2 s
276.9 s
105.0 s
59.3 s
39.2 s
I [j.w.]
q [10^{-2}nm^{-1}]
2.0
1.5
1.0
0.5
0.0
0.0
0.2
0.4
0.6
0.8
1.0

Early stages evolution





Amplification factor

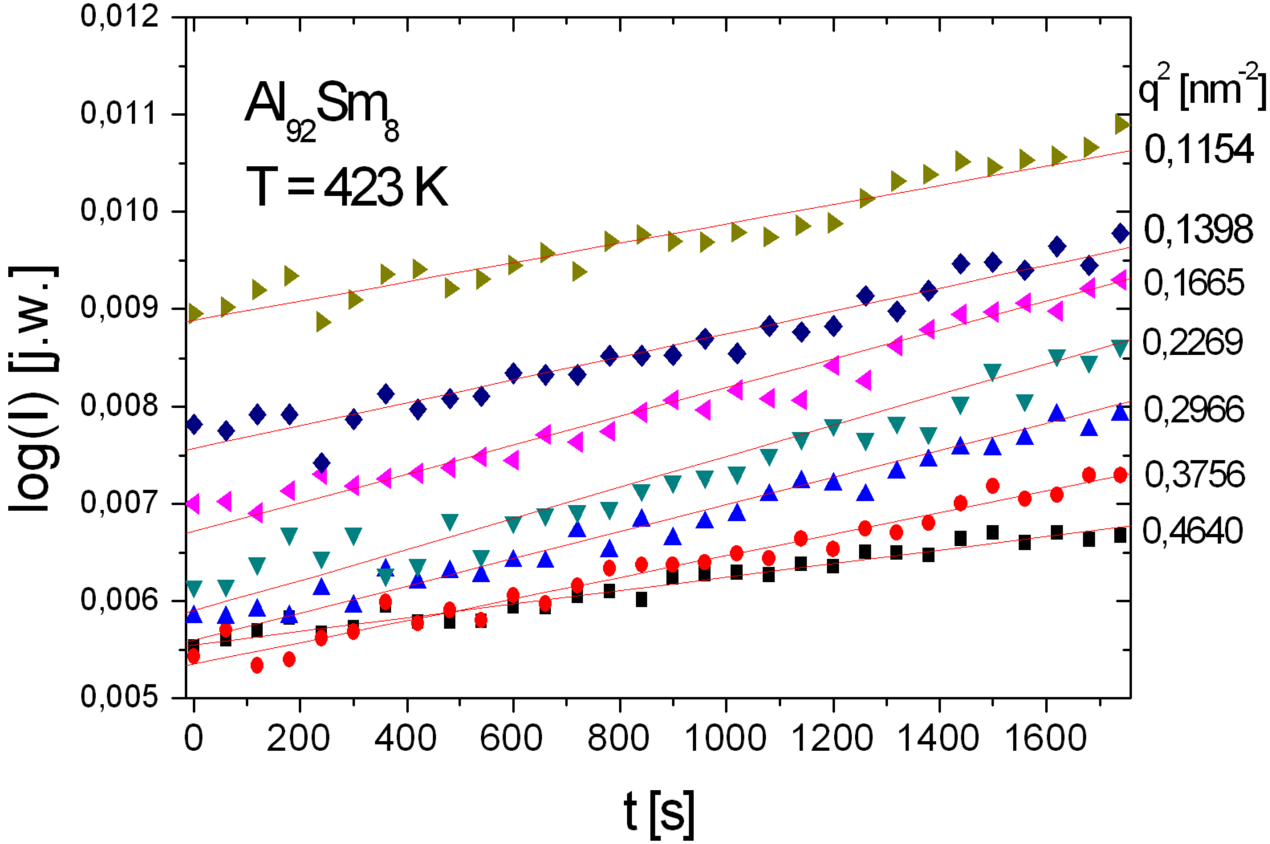
$$\rho(\vec{r},t) \propto \phi(\vec{r},t) \cdot f_{Al} + (1-\phi(\vec{r},t)) f_{Sm}$$

$$\eta(\vec{r}) = \rho(\vec{r}) - \langle \rho \rangle$$

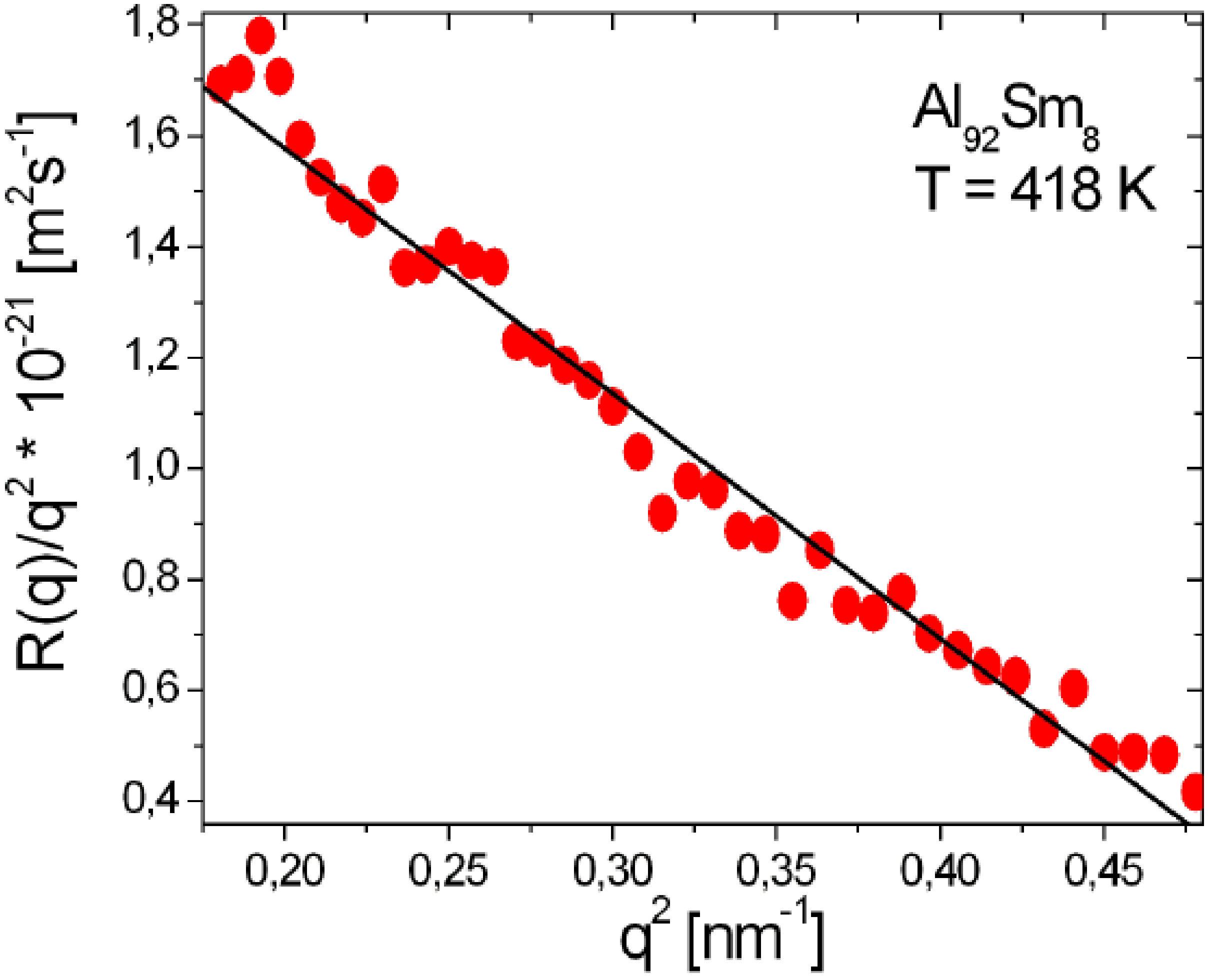
$$\eta(\vec{r},t) \propto [\phi(\vec{r},t) - \phi(\vec{r},0)](f_{Al} - f_{Sm})$$

$$I \propto \langle \eta^2 \rangle \propto \langle |\phi - \phi_0|^2 \rangle \propto \exp(2R(t) \cdot t)$$

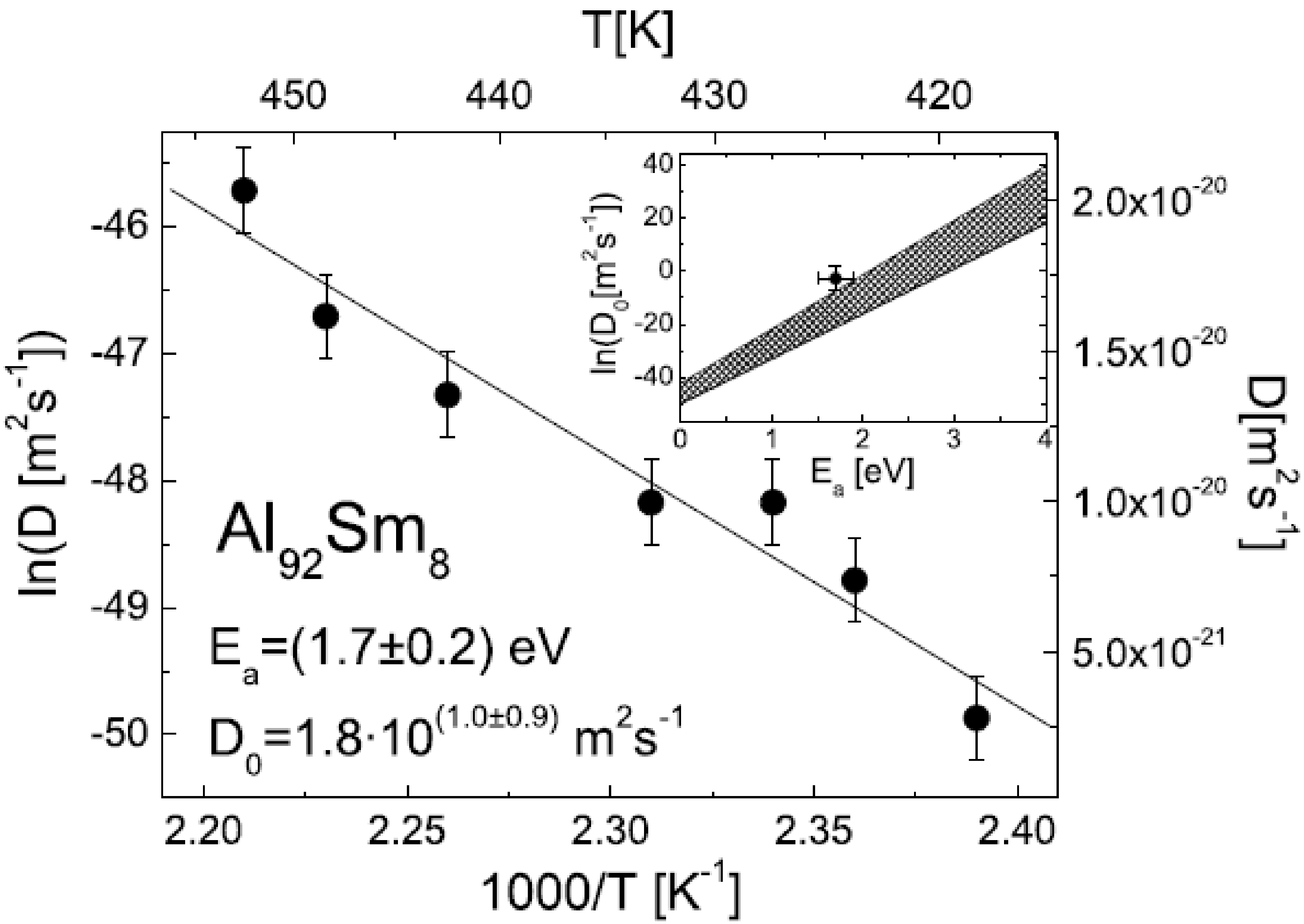
Amplification factor



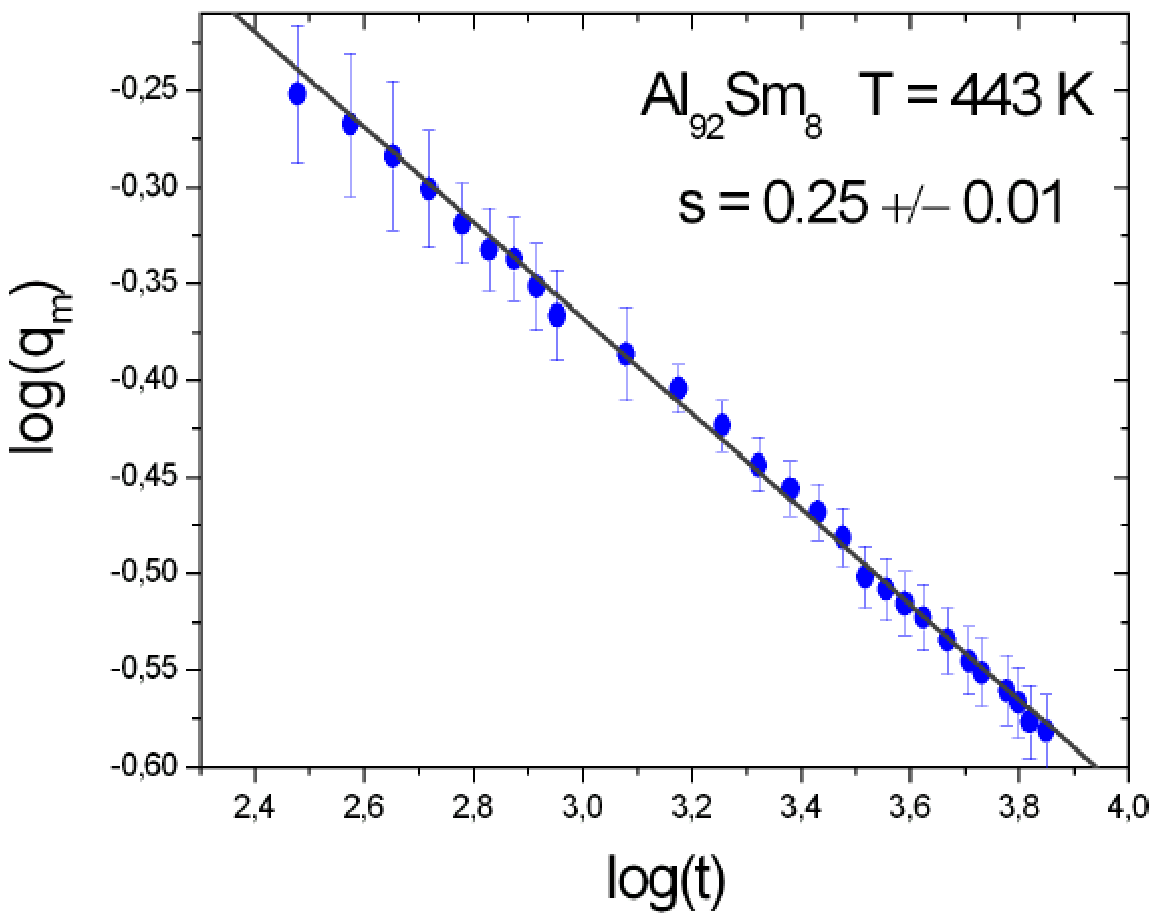
Diffusion coefficient



Activation energy



Scaling



$$L(t) \sim t^{s}$$

$$q_m(t) \sim t^{-s}$$

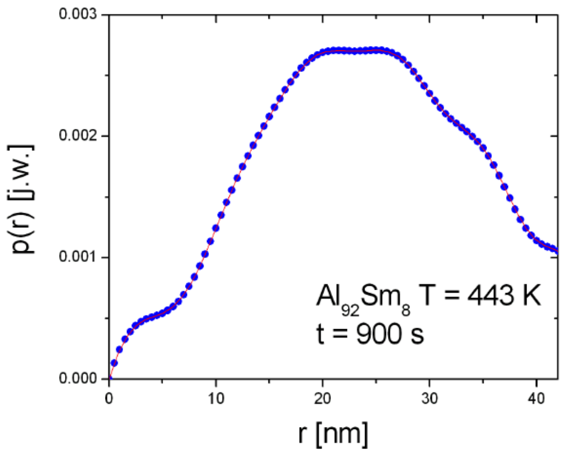
Pair distribution function

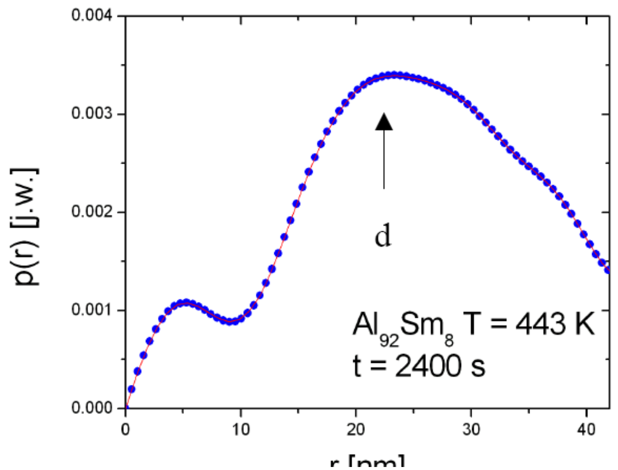
$$I(q) = \langle \eta^2 \rangle \int p(r) \cdot \frac{\sin(qr)}{qr} dr$$

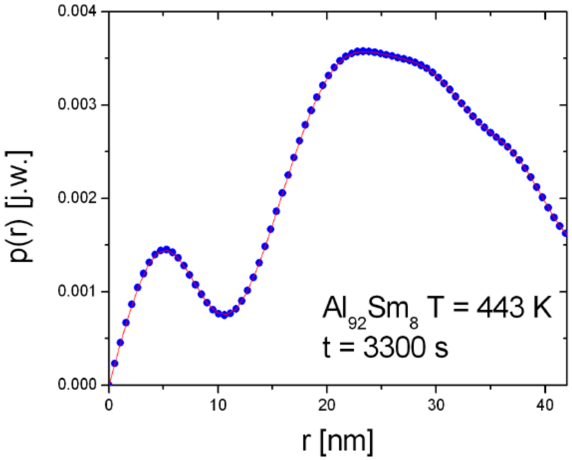
ATSAS

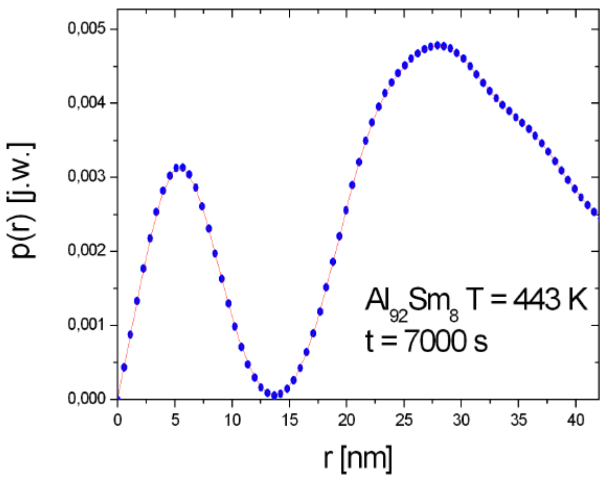
package

PDF

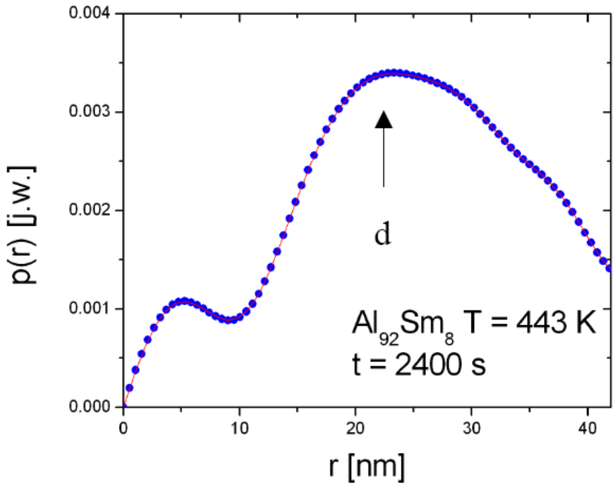

0.003
0.002
0.001
0.000
0
10
20
30
40
p(r) [j.w.]
r [nm]
$Al_{92}Sm_8$ T = 443 K
t = 900 s

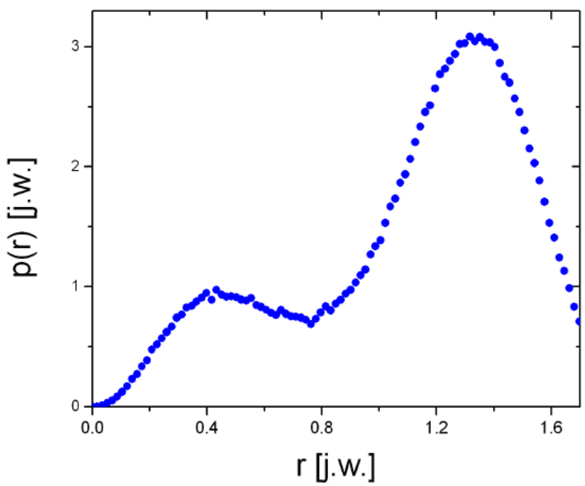

0.004
0.003
0.002
0.001
0.000
0
10
20
30
40
p(r) [j.w.]
d
$Al_{92}Sm_8$ T = 443 K
t = 2400 s

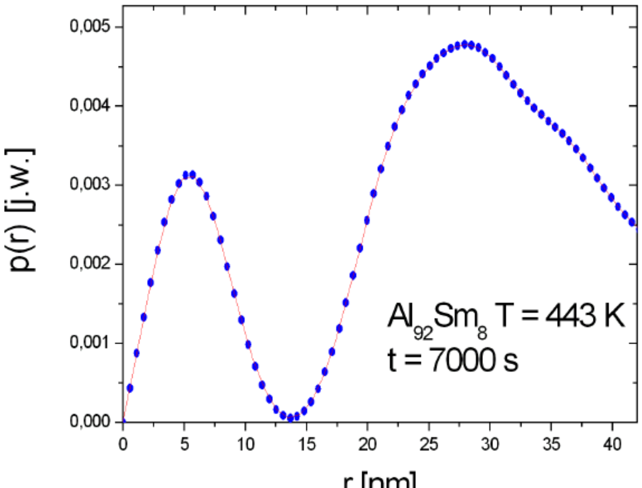

0.004
0.003
0.002
0.001
0.000
0
10
20
30
40
p(r) [j.w.]
r [nm]
$Al_{92}Sm_8$ T = 443 K
t = 3300 s

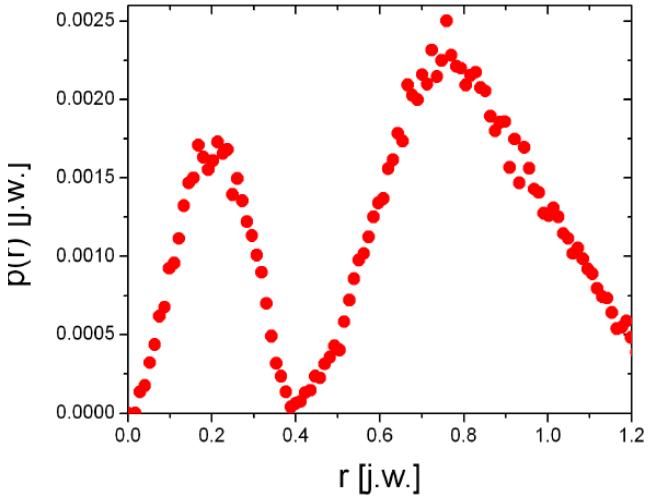

0,005
0,004
0,003
0,002
0,001
0,000
0
5
10
15
20
25
30
35
40
p(r) [j.w.]
r [nm]
$Al_{92}Sm_8$ T = 443 K
t = 7000 s

PDF – MC results

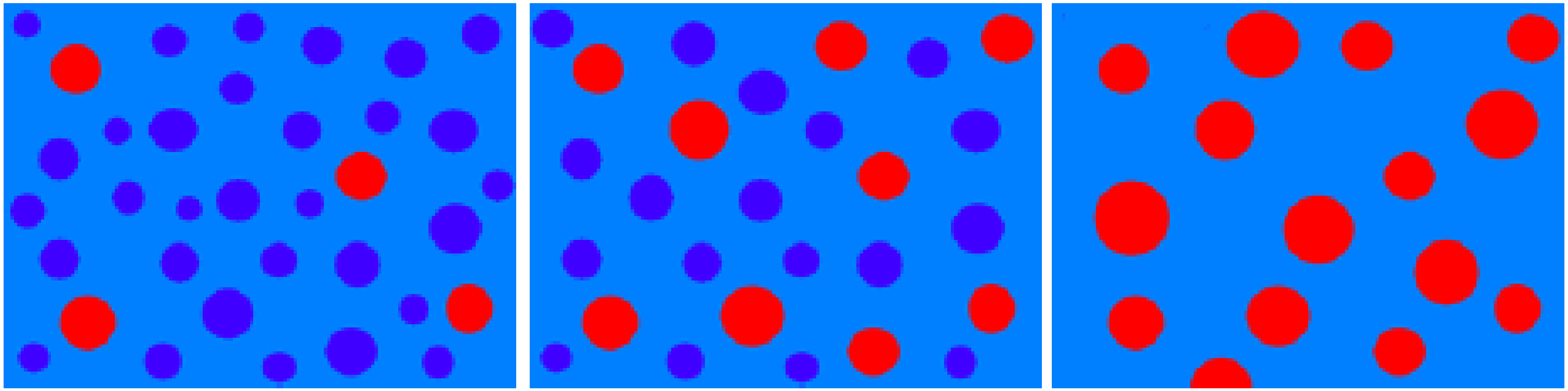








Conclusion – the model



1. Glassy phase initially decomposes into Al-rich and RE-rich amorphous regions
2. Nanocrystals nucleate preferentially inside the Al-rich amorphous regions and their growth is constrained by the region size

References

1. Antonowicz J., Jezierska E., **Kędzierski M.**, Yavari A.R., Greer L., Panine P., Sztucki M.,

   Early stages of phase separation and nanocrystallization in Al-rare earth metallic glasses studied using SAXS/WAXS and HRTEM methods.

   J. Alloys Comp. (in print)

2. Antonowicz J., **Kędzierski M.**, Jezierska E., Yavari A.R., Greer L., Panine P., Sztucki M.,

   Small-angle X-ray scattering from phase-separating amorphous metallic alloys undergoing nanocrystallization

   J. Alloys Comp. (submitted)

The End