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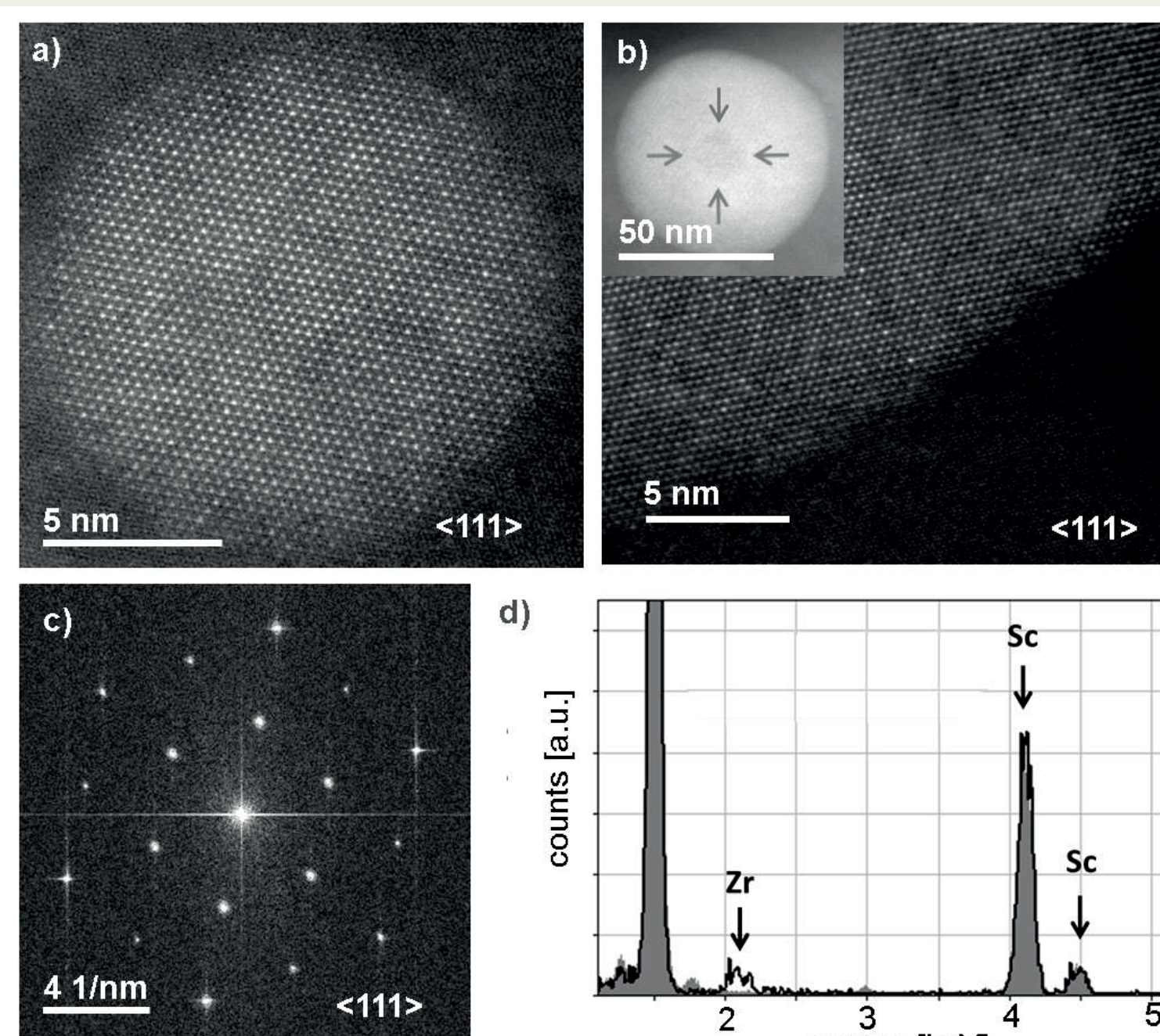
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Introduction

A detailed understanding of the entire precipitate forming process is necessary to ensure best applicability and use of precipitation hardened alloys. To approach the question of possible diffusion within a precipitate, atomic jump activation energies and Gibbs energy gradients with respect to chemical composition have to be considered. The order of the phase, which may vary locally and temporally, can influence the activation energy and the Gibbs energy. The system may undergo the formation of several phases during its kinetic evolution. For the technology relevant Al-Sc-Zr system it was previously shown that the ordered L₁₂ phase stabilizes the system in a non-equilibrium condition. Preliminary investigations of an industrially cast AlMgScZr alloy suggested that findings from previously performed investigations on lab-cast model systems^[1] are not sufficient to describe more complex systems.

Preliminary Investigations



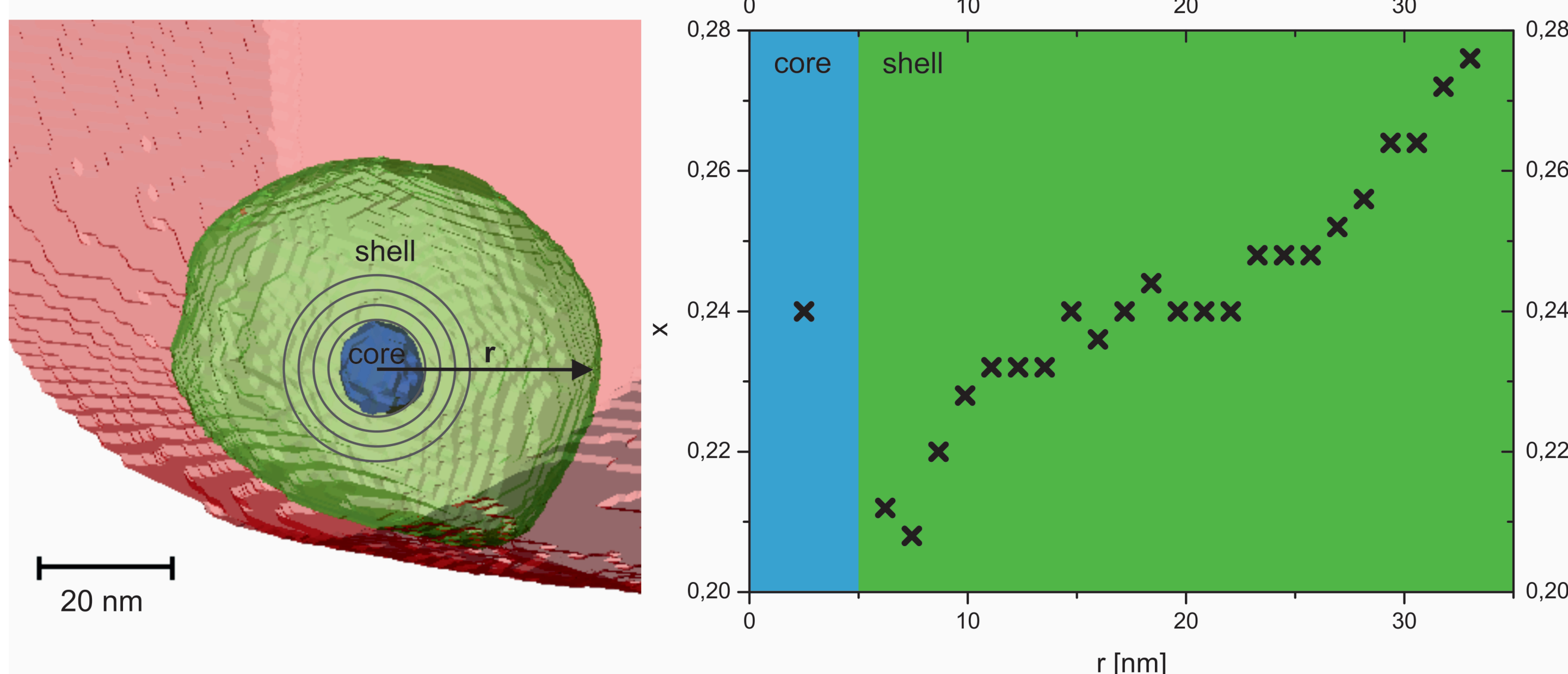
The material studied in this work^[2,3] is an alloy containing scandium and zirconium rich nanoprecipitates embedded in an aluminium-magnesium matrix. These nanoprecipitates increase the mechanical resistance of the material. Their sizes and chemical compositions can vary, depending on the aging process. Previous work reported that these particles exhibit a core-shell structure due to the difference in diffusivities of Sc and Zr in Al.^[1]

HR HAADF STEM investigations as depicted on the left (a and b) revealed the formation of spherical, coherently matching (as confirmed by FFT in c) Sc- and Zr- rich precipitates. A closer look at the long aged samples exposes surprisingly large shell regions with low contrast between core and shell.

This is in contradiction to previous findings, as first of all a small amount of Zr (0.12 wt%) would suggest a thin shell and, secondly, the higher atomic number of Zr would provide strong HAADF contrast. Furthermore observations of a non-perfect L₁₂ crystal structure, clarified that **explanations solely based on different diffusivities of Sc and Zr in the matrix are insufficient to understand the details of the composition and order of this system.** The short aged precipitates, forming the cores of the long aged core-shell type precipitates, are rich in Sc and contain no Zr, as visible by its EDX spectrum in d) (grey). By isolating the spectroscopic signal of the core region from shell and matrix effects via voxel spectroscopy^[4] in the long-aged sample, however, significant amounts of Zr become apparent, even though the precipitate was Zr-free after short ageing.

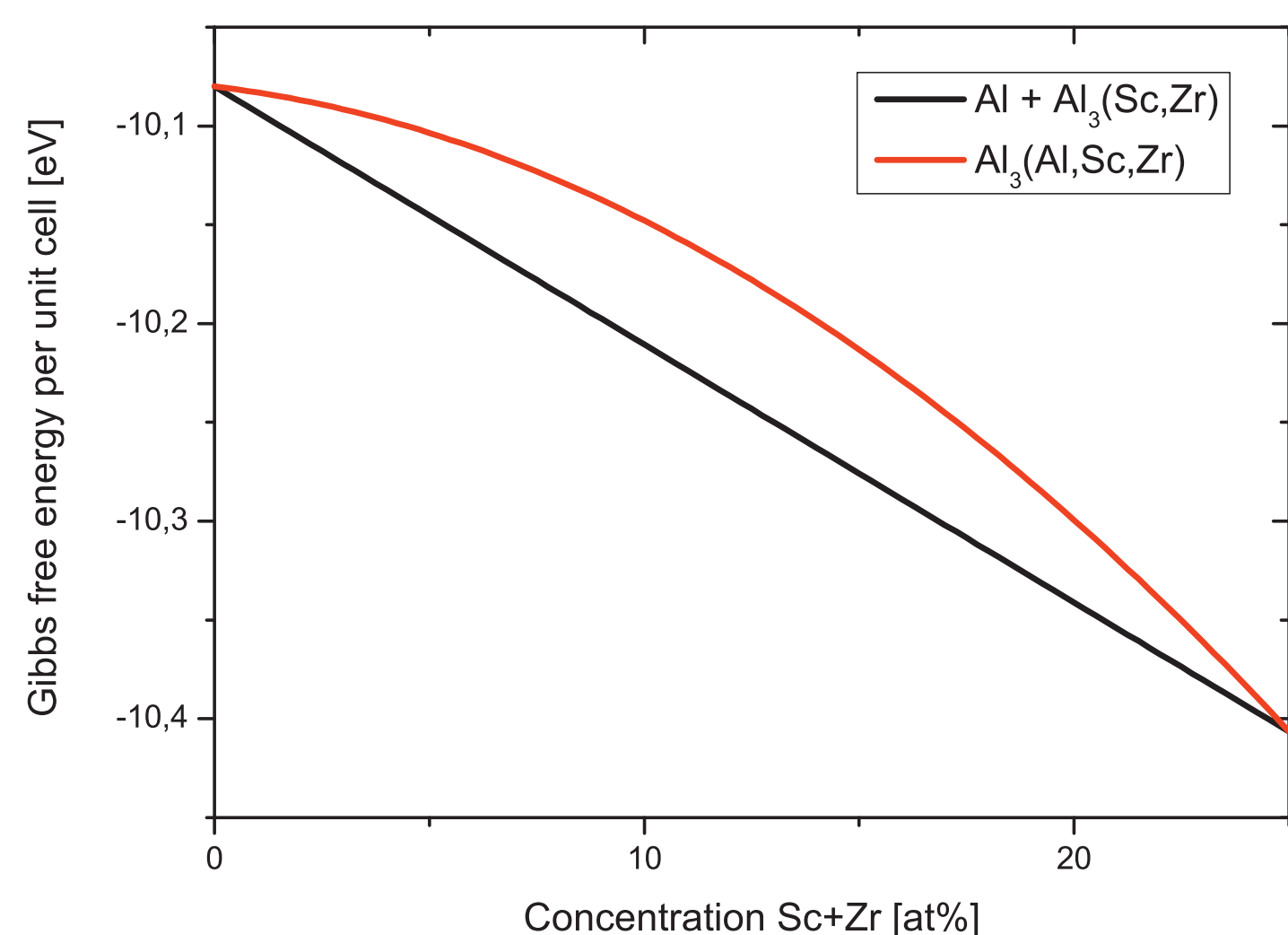
Analytical Tomography

The 3D radial composition profile of the precipitate yields a **minimum deviation from the stoichiometric L₁₂ (x=0) composition at the interface between core and shell.** It shall be noted, that this deviation corresponds to a mean, 3D-azimuthally averaged, value for a given radius, with the implication that the local deviation could be even lower or higher, even reach zero. Over a wide region of the shell, the deviation from the L₁₂ composition is fairly constant and similar to that of the shell. Approaching the interface between core and matrix, the deviation rises.



Gibbs Energy

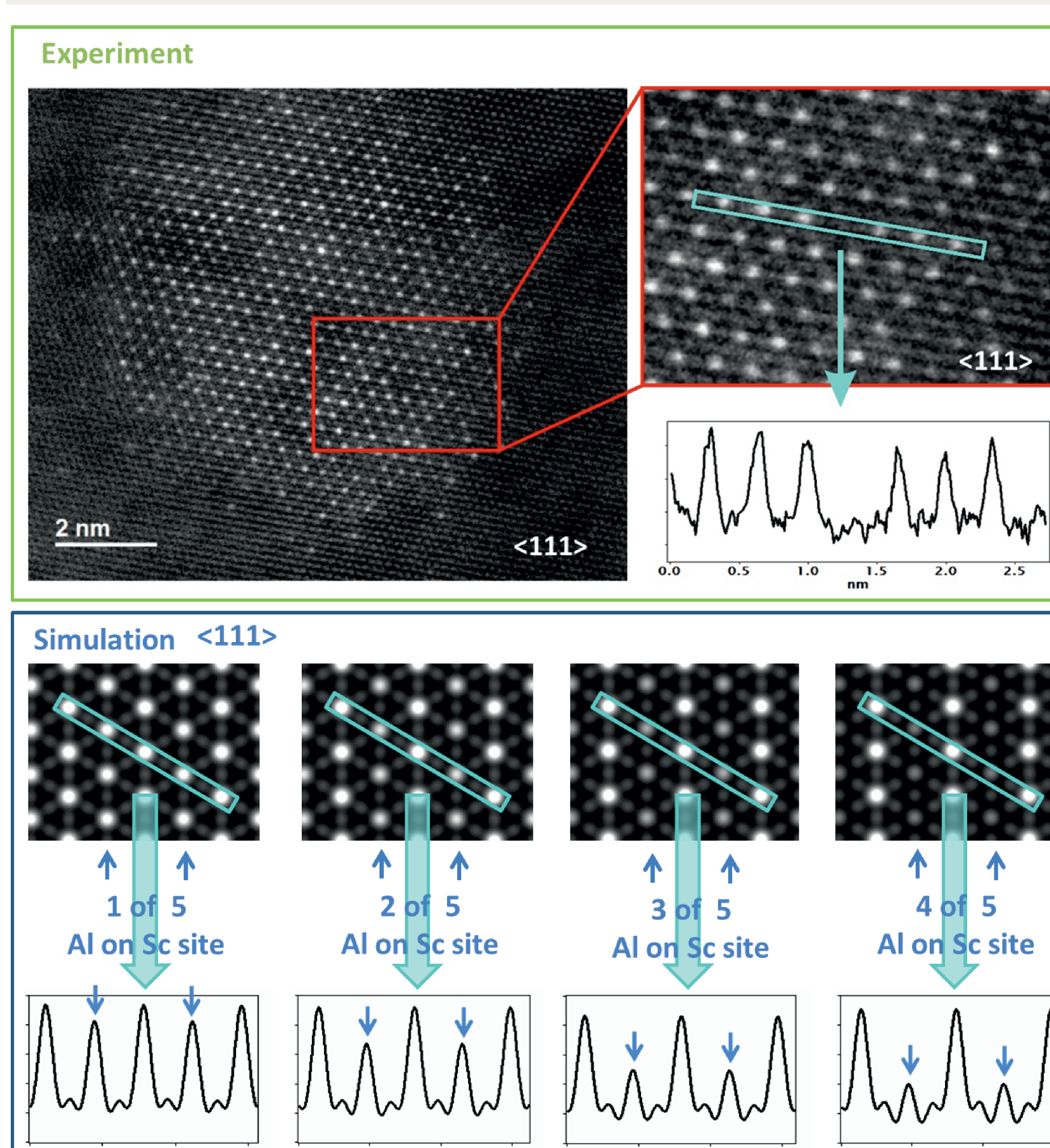
The figure below indicates the result of a Gibbs energy calculation computed assuming a regular solution model consisting of an enthalpy and an entropy part (red curve) reaching from a pure Al-matrix (left side of the diagram) to an ordered stoichiometric Al₃(Sc,Zr) compound.



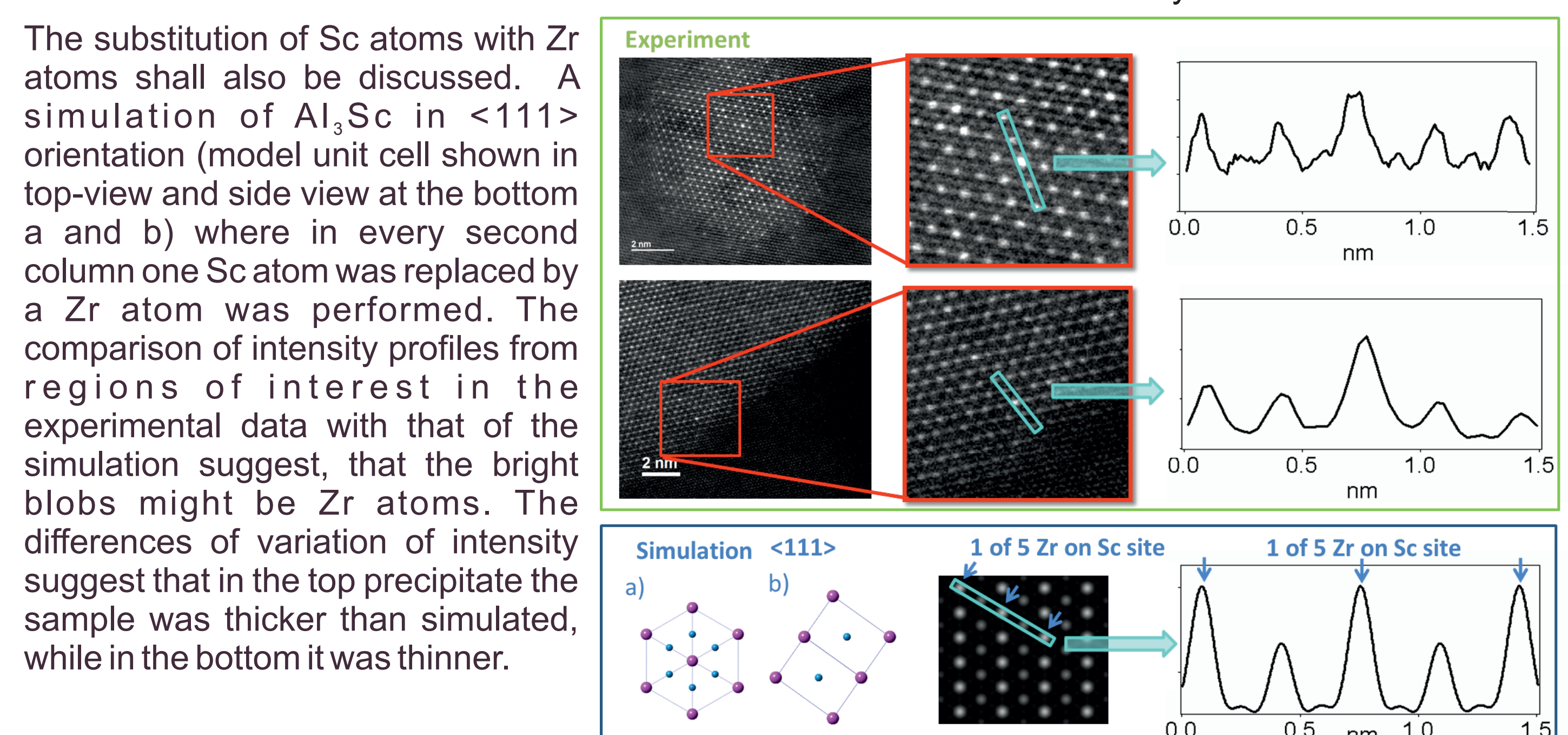
- **A negative curvature of the Gibbs free energy occurs in the whole composition range, suggesting a decomposition of the system.** This is supported by comparing to the free Gibbs energy curve of the 2-phase system matrix (pure Al) plus precipitate (stoichiometric composition), indicated as black curve.

For every potential system composition, a splitting into the two phases, matrix and stoichiometric precipitate is energetically more favourable compared to a one-phase system.

HR STEM & Frozen Phonon Multislice Simulations



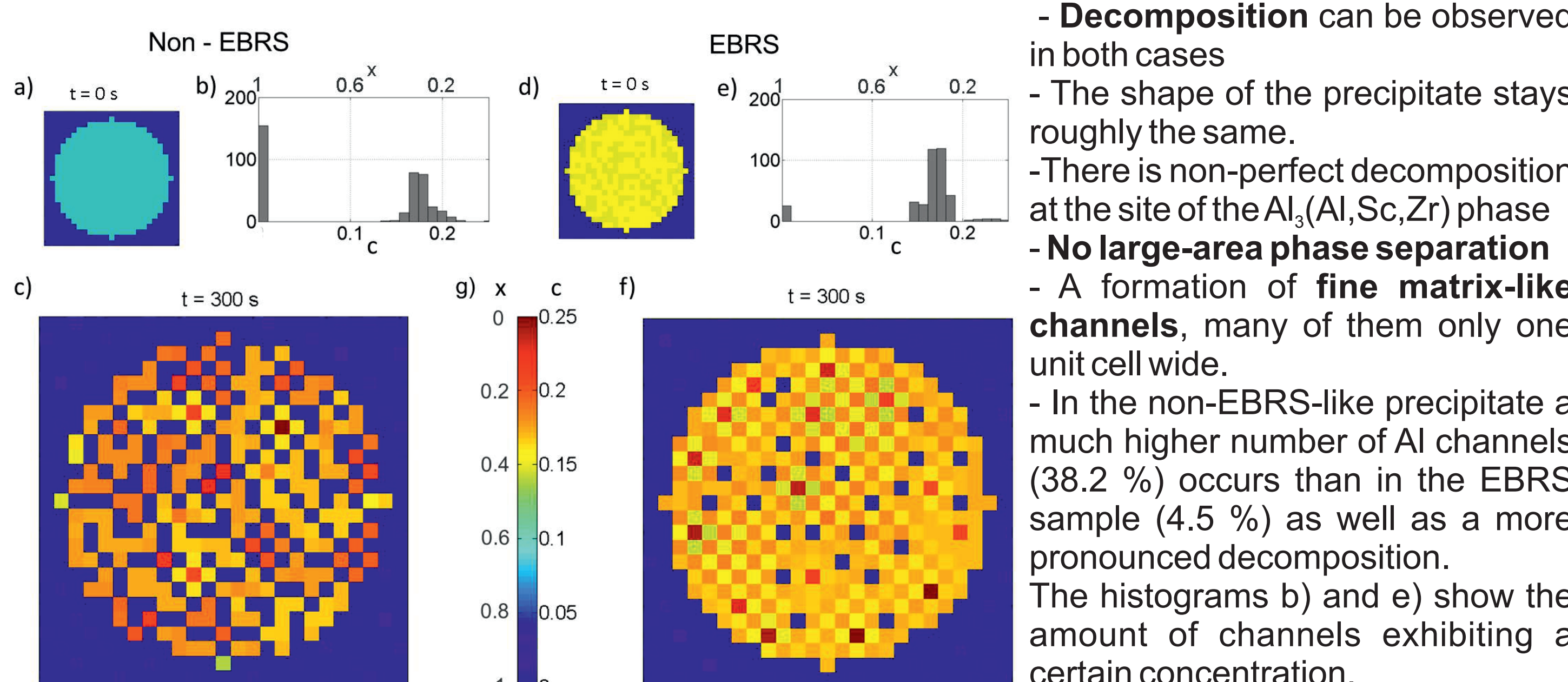
HAADF imaging at atomic resolution revealed the inhomogeneous distribution of Al defects within the Al₃(Al,Sc,Zr) phase, and a collection of matrix-like channels, with widths down to one single-atomic-column on the Sc/Zr sublattice, as can be seen in the figure on the left (top). In the enlarged area a column of same HAADF intensity as in the matrix can be seen within the precipitate, which suggests a **matrix-like channel with the width of only one atomic column on the Sc/Zr sublattice, which is orientated exactly in beam direction.** In other regions of the precipitate columns are found, which have a higher intensity level, than matrix columns, but lower intensity than full Sc/Zr column, implying not all the Sc/Zr sites are occupied by Sc/Zr. Frozen phonon multi-slice simulations confirm, that only channels running through the crystal in very similar directions as the beam can be seen with the naked eye.



The substitution of Sc atoms with Zr atoms shall also be discussed. A simulation of Al₃Sc in <111> orientation (model unit cell shown in top-view and side view at the bottom a and b) where in every second column one Sc atom was replaced by a Zr atom was performed. The comparison of intensity profiles from regions of interest in the experimental data with that of the simulation suggest, that the bright blobs might be Zr atoms. The differences of variation of intensity suggest that in the top precipitate the sample was thicker than simulated, while in the bottom it was thinner.

2D Diffusion Simulations

A two dimensional spatially resolved diffusion simulation based on chemical potentials derived from free Gibbs energies and diffusion coefficients was performed. Initially (a, d) an Al₃(Al,Sc,Zr) phase was introduced in an Al phase with higher (left - a, b and c) and lower (right - d, e and f) deviation from the ideal composition of an L₁₂ crystal structure, corresponding to the measured compositions of a non-electron beam resolidified (non-EBRS) and an EBRS sample. The cell size was chosen to equal the Al₃Sc unit cell size in <100> orientation.



- **Decomposition** can be observed in both cases
 - The shape of the precipitate stays roughly the same.
 - There is non-perfect decomposition at the site of the Al₃(Al,Sc,Zr) phase
 - **No large-area phase separation**
 - A formation of **fine matrix-like channels**, many of them only one unit cell wide.
 - In the non-EBRS-like precipitate a much higher number of Al channels (38.2 %) occurs than in the EBRS sample (4.5 %) as well as a more pronounced decomposition. The histograms b) and e) show the amount of channels exhibiting a certain concentration.

Conclusion

It follows, that the resulting core-shell structure is not simply a result of the faster diffusion of Sc in the matrix compared to Zr, but that a **secondary self-limiting diffusion process is responsible for the final composition** of the different regions of the precipitate. The imperfections in the L₁₂ structure (Al atoms on Sc/Zr sites) arising during the primary precipitate forming diffusion process are responsible for the formation of matrix-like channels via spinodal decomposition, where Sc and Zr can diffuse. Locally this diffusion takes place until the random encounter and immobilisation of diffusing atoms leads to the formation of further L₁₂ structure and thus to a narrowing and subsequently a blockade of the diffusion channel. Globally the core is sealed off from the shell as soon as a gapless closed surface of L₁₂ structure has formed. The less perfect the precipitate forms originally, the more matrix-like channel material is left, where Sc and Zr can diffuse, the less defined the core-shell structure of the final precipitate.

References

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