

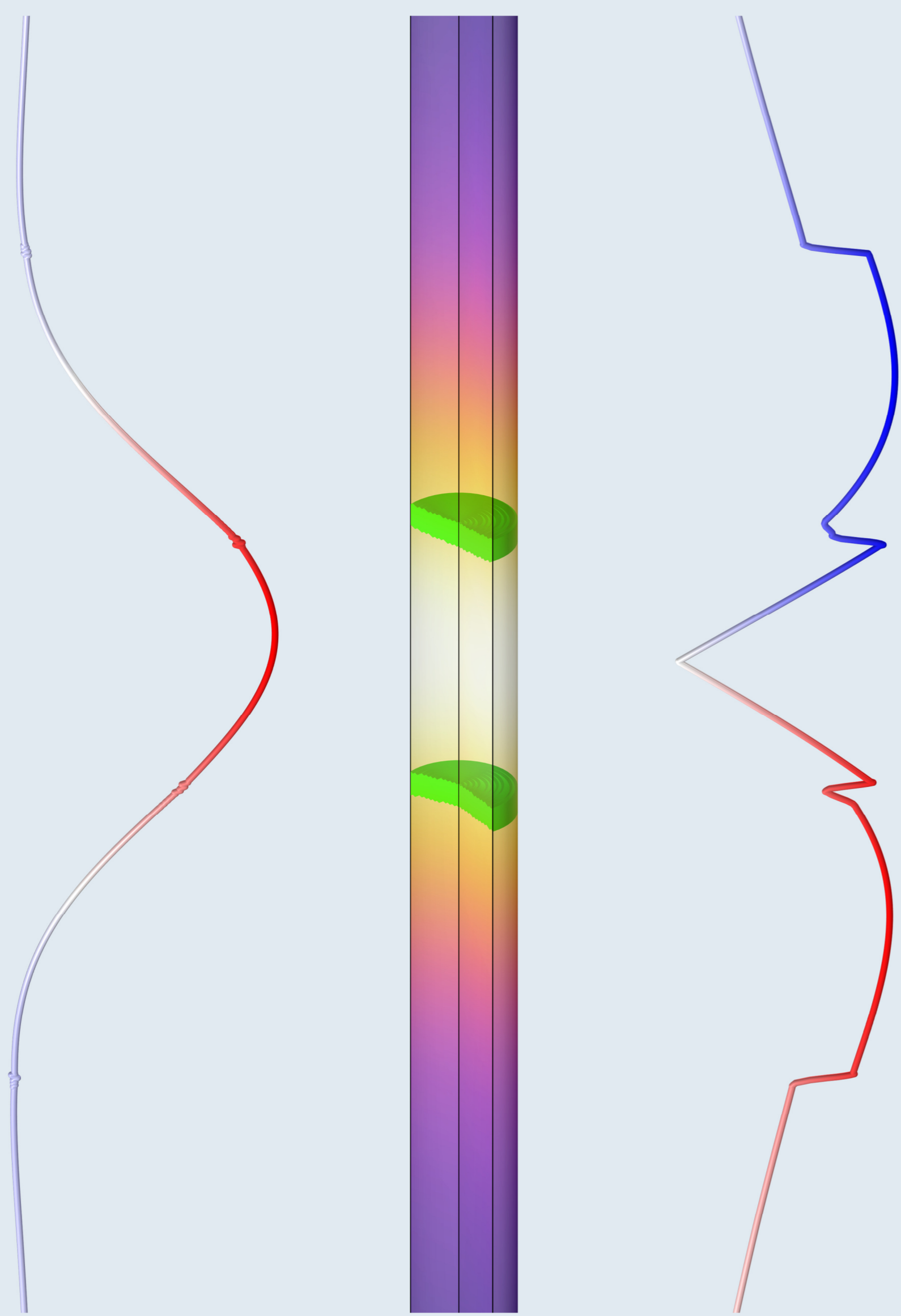
Modelling the Composition Gradient in Ni-Mn-Ga Single Crystal Grown by Floating Zone Method

The COMSOL Multiphysics® Heat Transfer Module is used to simulate the thermodynamics of the floating zone crystal growth process, and to calculate the macroscopic chemical segregation, and therefore composition variation in the resulting ternary Ni-Mn-Ga single crystals.

D. Musiienko¹, R. H. Colman²

¹Institute of Physics of the Czech Academy of Sciences, Prague, Czech Republic

²Faculty of Mathematics and Physics, Charles University, Prague, Czech Republic



Introduction

In contrast to the widely used Bridgman-Stockbarger method, the floating zone (FZ) crystal growth minimises the molten zone size during crystal growth, resulting in rapid melt saturation. After a certain growth length, the composition gradient approaches zero in a 'steady state' ingot region. However, re-crystallisation of Ni-Mn-Ga alloys in FZ optical furnace is a complex process depending on master alloy and seed crystal compositions, growth speed, and molten zone shape evolution during the crystal growth.

We present chemical composition calculations based on the Scheil-Gulliver equation, with liquification-solidification fractions obtained from the Heat transfer module's phase-change material node. Partition coefficients are derived from the X-ray fluorescence chemical composition data for as-grown crystal in the "quenched" region. Calculation results are then cross-referenced with the experimental composition analysis. This comparison enables better understanding of the physical processes affecting the molten zone shape change.

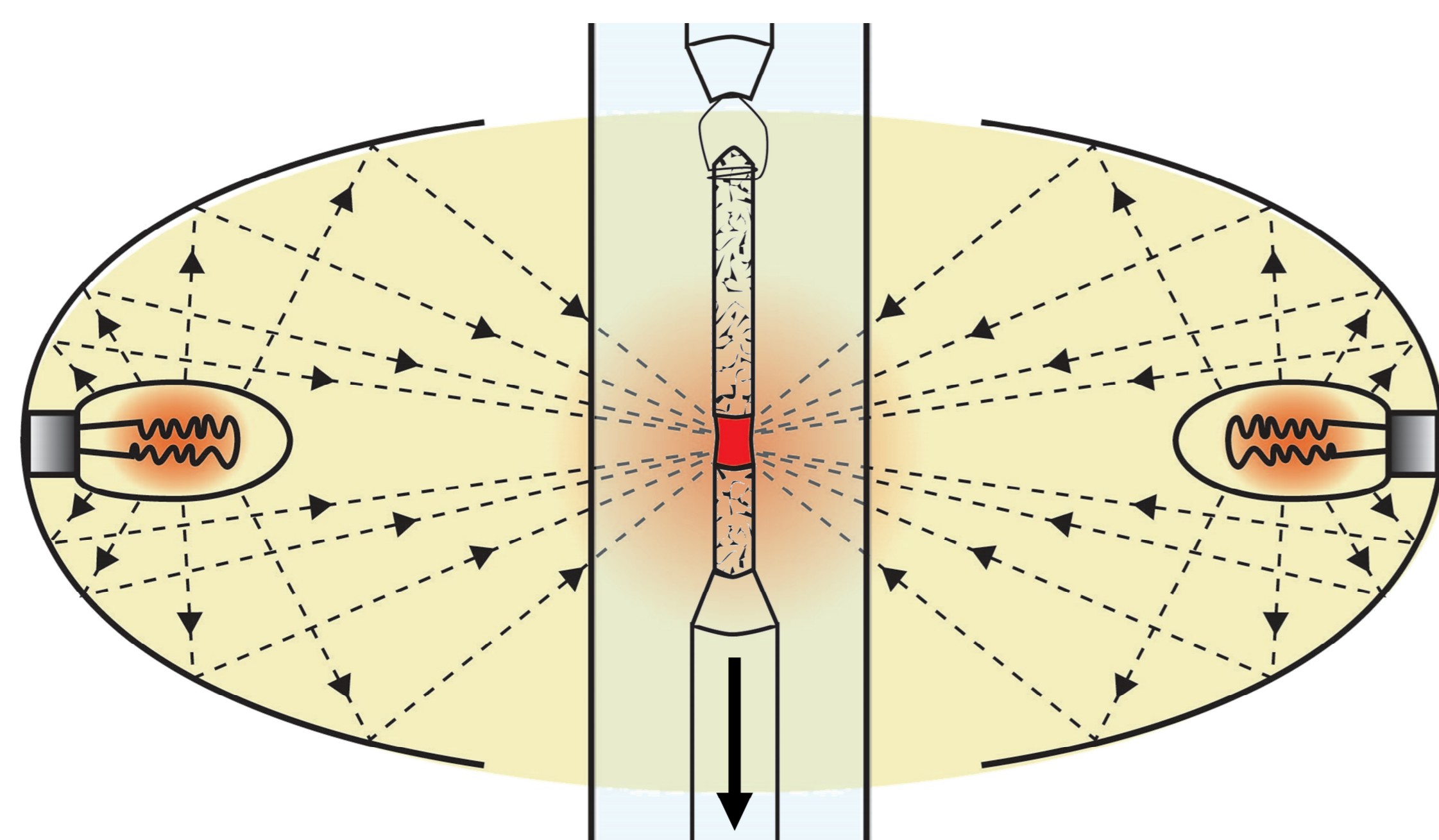


Figure 1. Schematic representation of re-solidification process inside floating zone optical furnace. Material is being heated by four focused halogen lamps assembly. Solid black arrow shows the direction of pulling.

Methods

A single crystalline Ni-Mn-Ga bar was grown in an optical floating zone furnace by re-crystallizing a master alloy rod enclosed in a sapphire crucible. The process began with melting the section of the polycrystalline rod in contact with the seed crystal. As a portion of the seed crystal melted and the molten zone (MZ) stabilised, the crystal holder descended, causing the MZ to ascend, re-crystallising the master rod into a single crystal with the seed crystal's structure and orientation. When the MZ reached the top of the master rod, the lamps were powered down, effectively quenching the upper part of the grown crystal.

The chemical compositions were measured by X-ray fluorescence method. In Figure 2, squares depict experimental data for the elemental composition of the single crystalline bar. Concentration values below the 18 mm mark represented the seed composition at the contact point with the master rod, while a concentration jump around the 106 mm mark marked the lower boundary of the "quenched" zone. Average concentrations above this mark and those immediately below the "quenched" zone defined partition coefficients for the Scheil-Gulliver re-crystallisation model:

$$k = C_{Solid} / C_{Liquid}$$

Typically, Scheil-Gulliver equations are solved under assumptions of a decreasing MZ length for the Bridgman method or a constant MZ length for the FZ method, enabling analytical solutions [1,2]. However, simulations using the COMSOL Multiphysics® Heat Transfer Module revealed significant MZ length variations (up to 2 times!) during the FZ re-crystallisation process for finite-sized crystals. Here we calculate composition changes at each time step $\Delta t(t)$ and assume that concentration variation in the melt, caused by diffusion, stabilises rapidly, and the immediate partition coefficient, $k^* = k$, remains constant after an initial acceleration of the solidification interface.

Results and Discussion

Figure 2 presents the results: it shows measured elemental concentrations along the grown crystal as coloured squares, overlaid with calculated radially averaged values as coloured lines. The black line represents the evolution of the radially averaged molten zone length in relation to the position of the centre of the solidification mushy zone.

To account for the initial jump in concentrations near the 19 mm mark, we introduced a smoothed reversed step function f_{step} , to approximate the immediate partition coefficient:

$$k^* = F f_{step}(t-t_0) \cdot k,$$

where t_0 is the time when the crystal holder began to descend, and F represents the factor by which the partition coefficient changes during the initial acceleration of the solidification interface.

The resulting calculated composition variation aligns with the experimental data within the margin of instrumental error. This alignment, along with adjustments to the simulation model, has enhanced our understanding of the re-crystallisation process in our material. We intend to further refine the model and apply it to optimise our material fabrication processes.

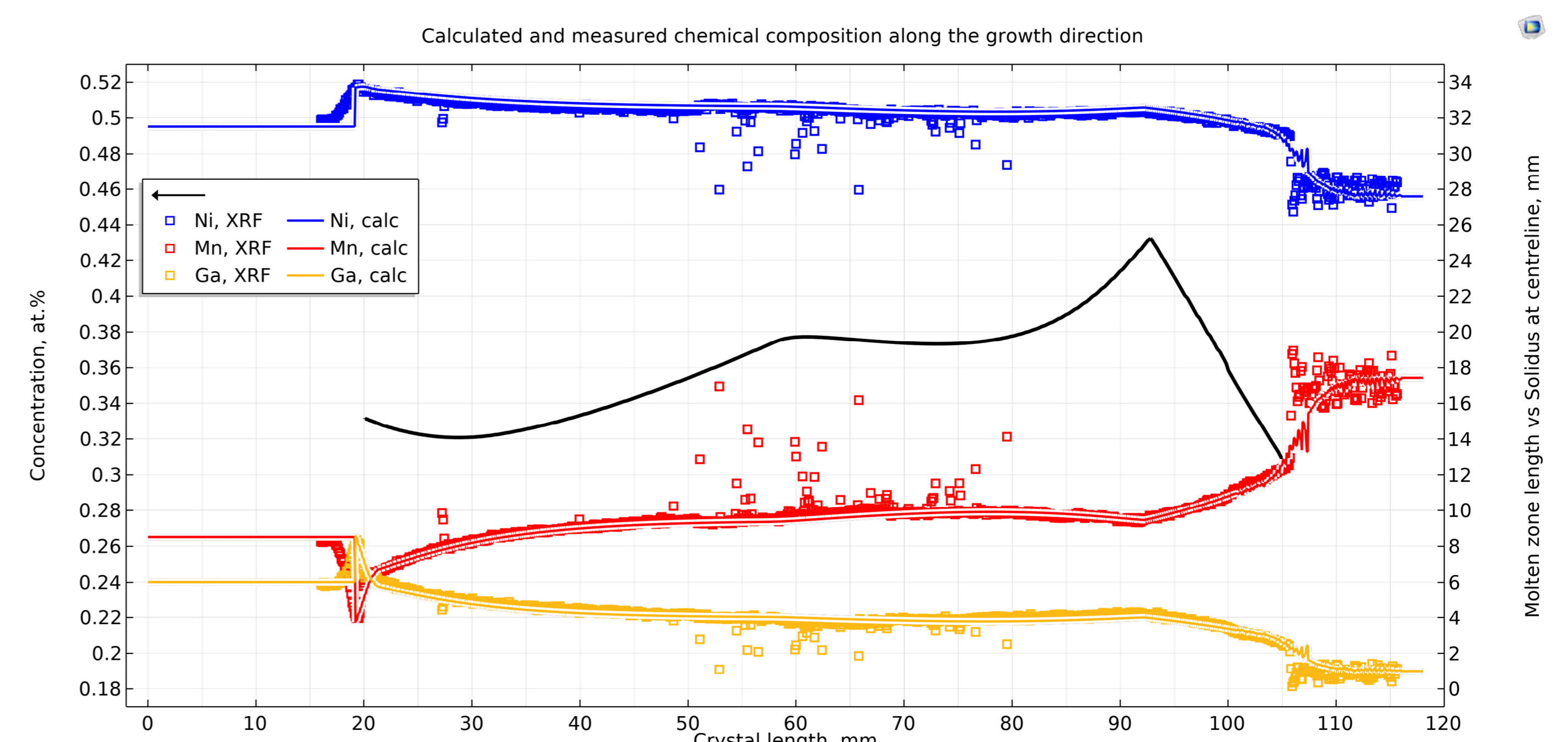
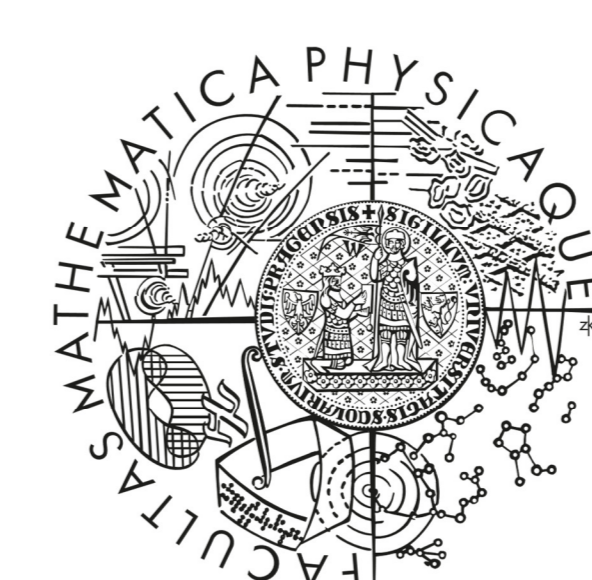


Figure 2. Comparison of the measured composition variation along the grown single crystal (empty squares) and calculated (solid lines). Black solid line shows radially averaged length of the molten zone at the given position of the solidification interface.

REFERENCES

1. Pamplin, Brian R., ed. Crystal Growth: International Series on the Science of the Solid State, 2nd edition. Elsevier, 1980.
2. Marin-Alvarado, Tanai. "Modelling Scheil Cooling of a Metal Alloy—Thermodynamic and Multiphysics Solidification." In COMSOL Conference. 2016.



FACULTY
OF MATHEMATICS
AND PHYSICS
Charles University