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In situ analysis of lattice parameter change during nanocrystalline iron nitriding

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Introduction

The nitriding of iron may lead to the formation of crystalline phases consisting of nitrogen dissolved in interstitial spaces of iron lattice, equilibrium phases (in certain conditions) or metastable phases [1].

It is well known, that nitrogen dissolves in α -Fe to some extent before the α -Fe to γ' -Fe₄N phase transition occurs [2, 3]. It was also shown before, that the lattice parameter shifts while creating interstitial compounds for coarse materials [4, 5], especially iron-based alloys [6]. This lattice parameter change was not, however, shown previously as a continuous shift for the whole range of nitriding potential in nanocrystalline iron.

The precise lattice parameter determination for the cubic α -Fe cell was performed using the standard addition method. Two calculation approaches were compared: a) a single reflection method and b) a whole-pattern analysis using Rietveld refinement. The first approach was also utilised to show the behaviour of the Fe-N system in further steps of the process.

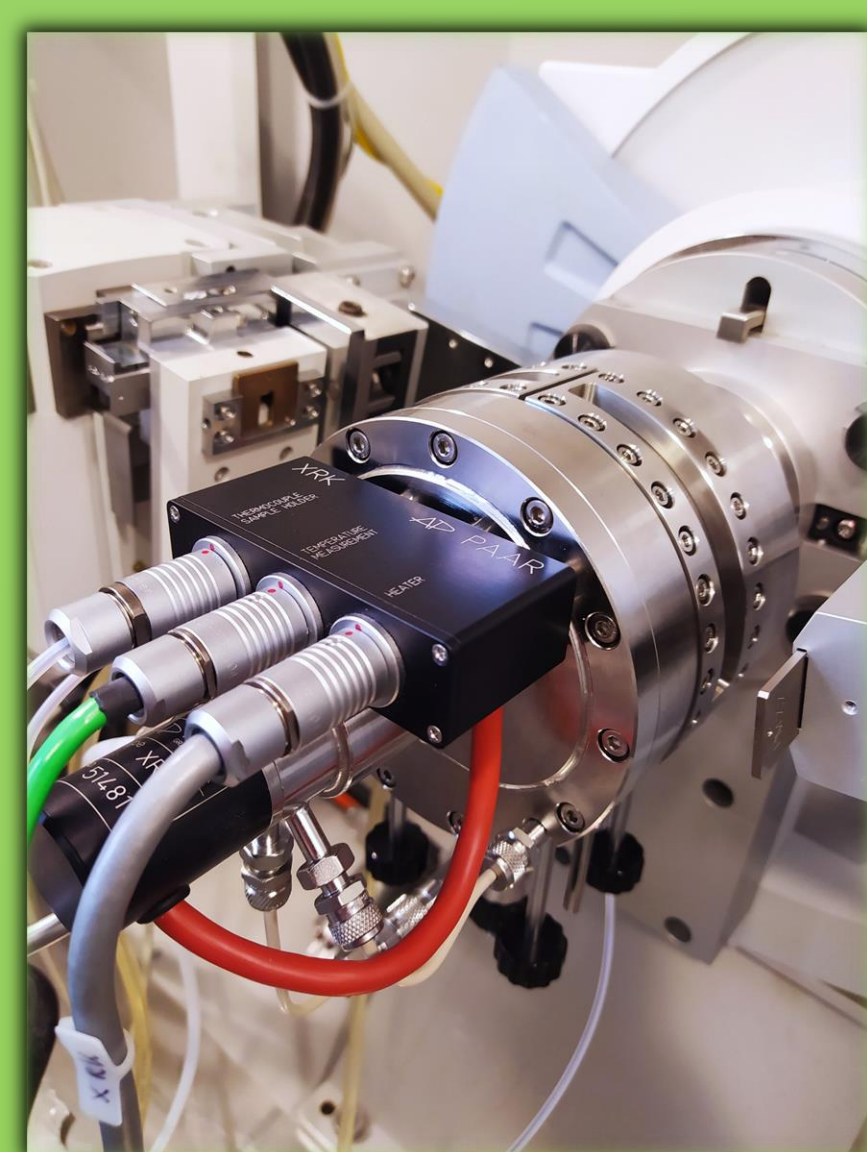


Diffractometer
- Philips X'Pert Pro MPD
- Co K α radiation
- PIXcel^{1D} detector
- 0.02 and 0.006°2 θ step



Sample
- Commercial iron 99.8% (Sigma-Aldrich)
- 40-60 nm particle size,
- Standard: Silicon powder

Reaction chamber
Anton Paar XRK 900



Nitriding
(350°C)
1h/step

NH ₃	H ₂
[vol%]	
0	100
5	95
⋮	⋮
65	35
⋮	⋮
100	0

Results - α -Fe

The Fig. 1. presents the course of the isothermal process as a series of α -Fe (112) diffraction doublet intensities as a function of 2 θ angle (0.02°2 θ step). Dashed lines represent a shift of the observed diffraction angle due to cell expansion caused by incorporating nitrogen into iron lattice. It is worth noting, that no difference in the intensity is observed.

In the Fig. 2. change of observed diffraction angle for boundary cases of reflections collected during higher-resolution measurements process (with 0.006°2 θ step) throughout the process is shown.

The change of lattice parameter with rising ammonia concentration in the atmosphere is shown in Fig. 3. Each black point represents the result of a single measurement, where lattice parameter was calculated on the basis of diffractograms acquired with 0.02°2 θ step (41-126°2 θ) using Rietveld refinement method with silicon powder added as the peak position standard. The red dots show alike results calculated with the method basing on a single reflection for narrow-range, higher-resolution measurements (0.006°2 θ step). Uncertainties were estimated for both methods (error bars) and fitting of exponential function was performed (black and red lines).

The maximum N occupancy observed in the experiment, calculated on the basis of [4], is ca. 0.14 at. % of the nitrogen in iron lattice.

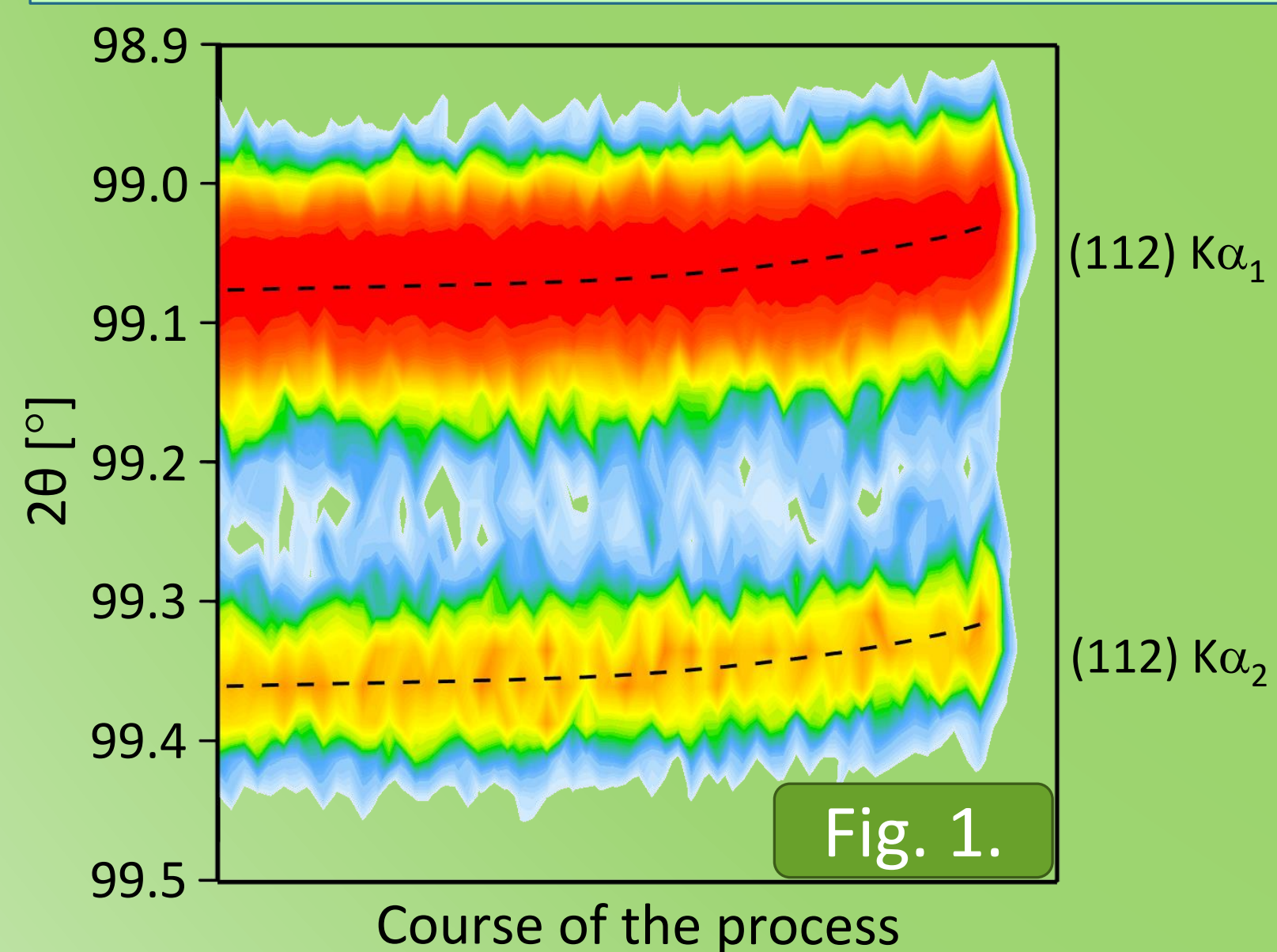


Fig. 1.

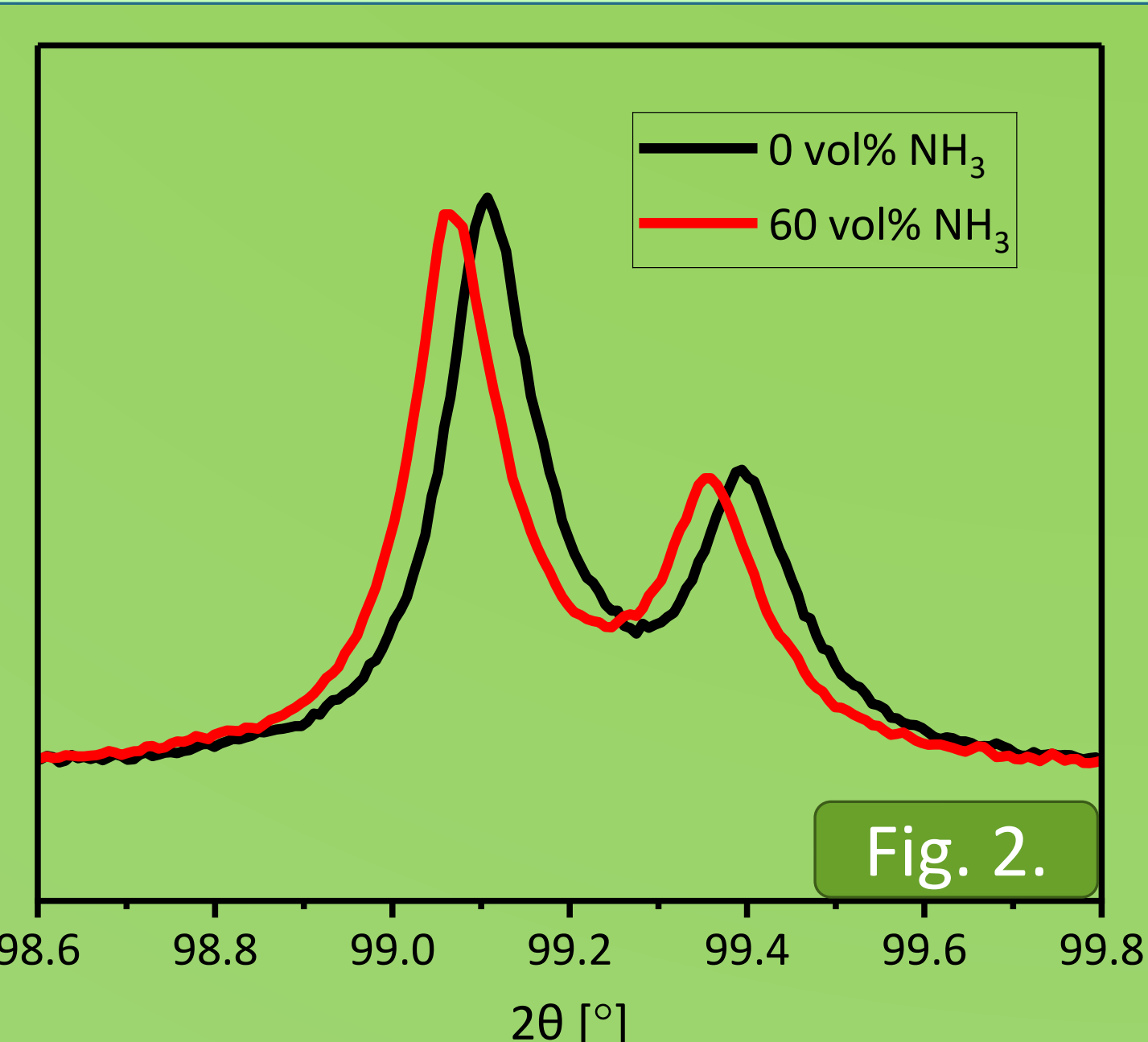


Fig. 2.

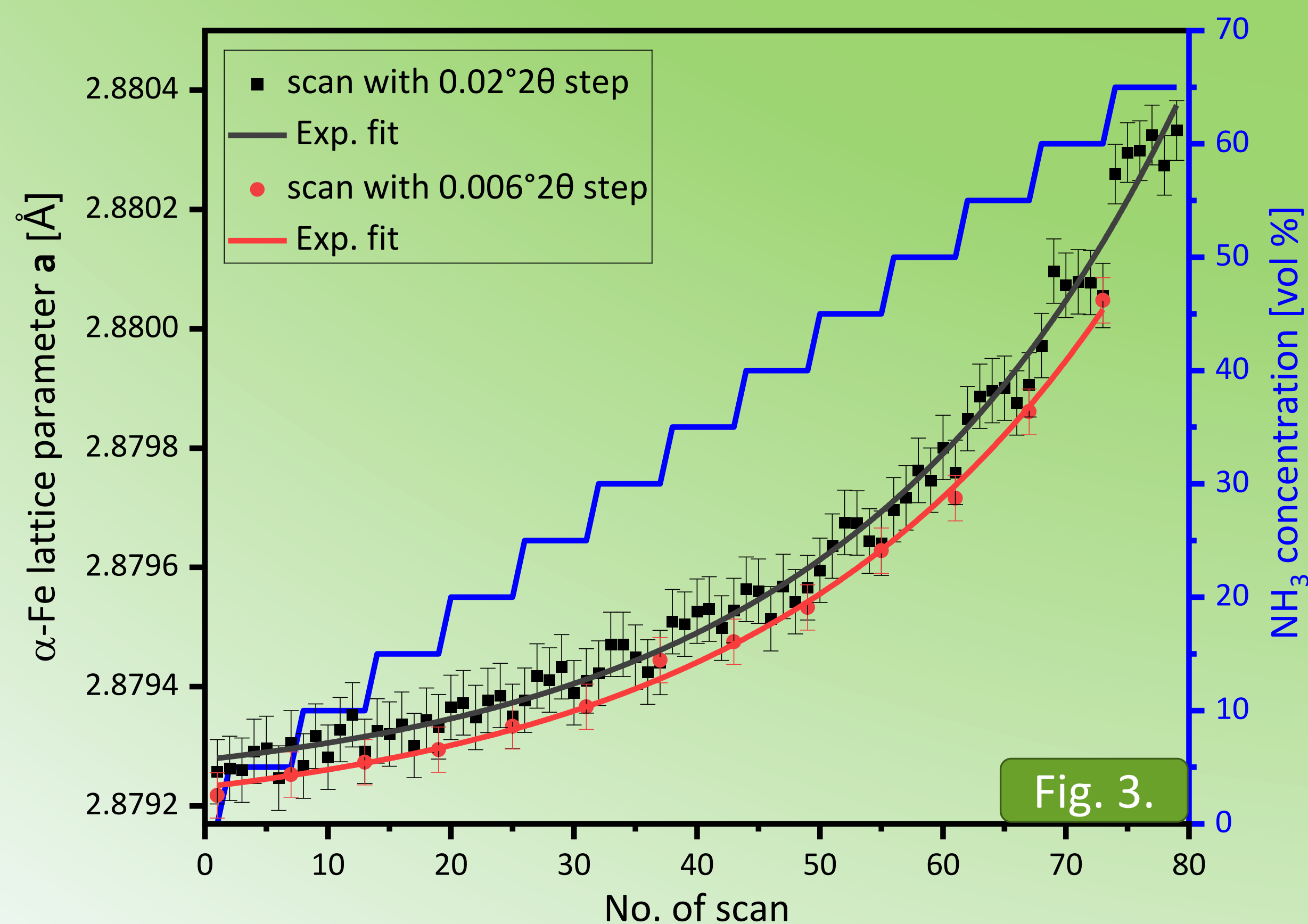


Fig. 3.

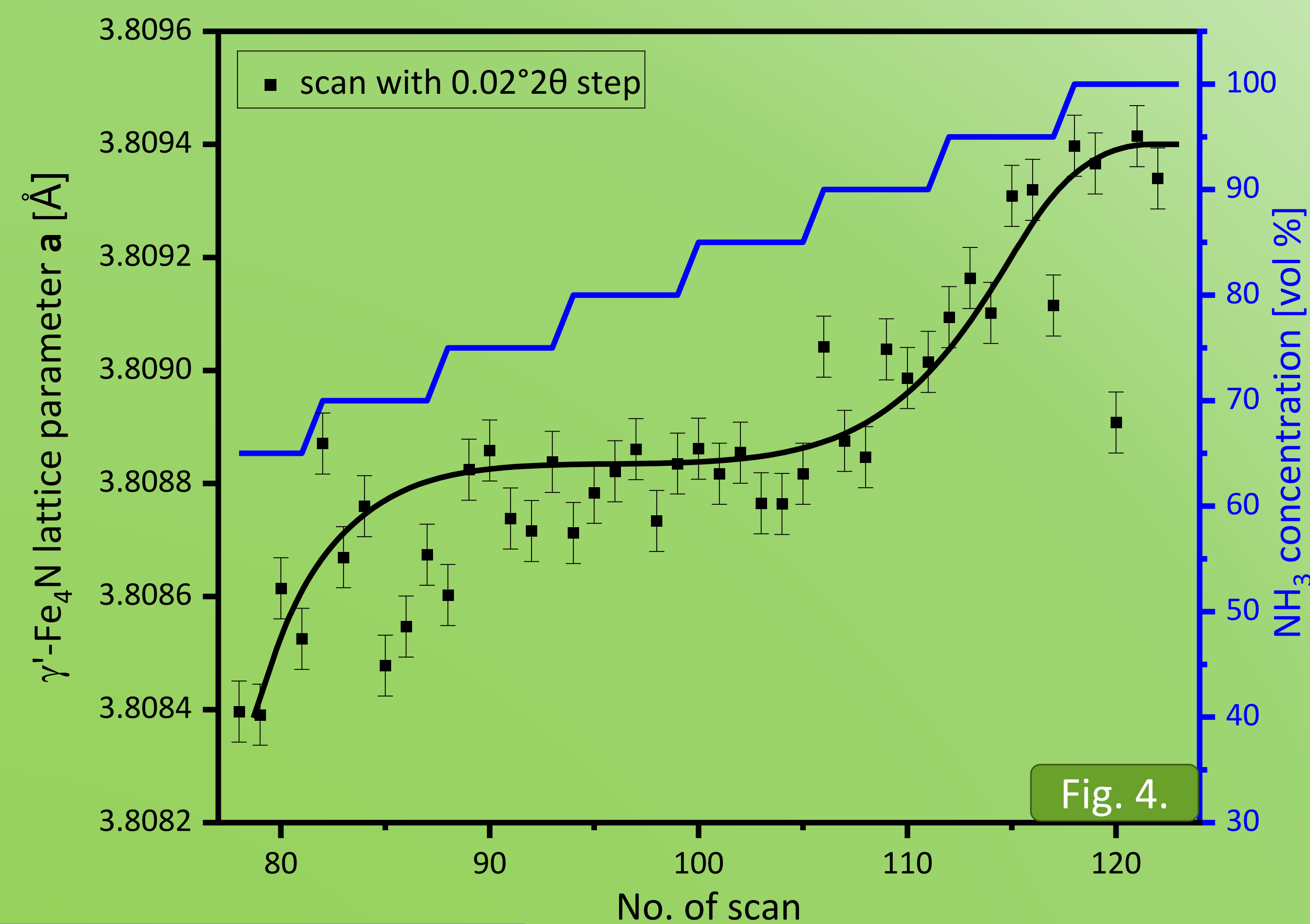


Fig. 4.

Results - γ' -Fe₄N and ϵ -Fe₃₋₂N

The Fig. 4. presents preliminary data showing the changes in the observed lattice parameter of cubic γ' -Fe₄N phase that appears in the system when ammonia concentration exceeds 65 vol%. Each point corresponds to a value calculated using Rietveld refinement on the basis of a measurement with 0.02°2 θ step (41-126°2 θ). The fit line was hand-drawn to highlight the phenomenon. The lattice parameter grows to a certain level (between 65 and 75 vol% of NH₃), then stabilizes (until 85 vol%), to finally grow again just before phase transition to ϵ -Fe₃₋₂N occurs.

The Fig. 5. shows analogous results for hexagonal ϵ -Fe₃₋₂N phase that appears just before the end of the process. The lattice parameter a was chosen, as it exhibits the shifts more substantially. The ϵ phase is characteristic for its wide homogeneity range, due to incorporation of N atoms, that goes along significant changes in lattice parameters. The shift of ca. 0.06 Å for 5 vol% of NH₃ is notable, though expected value.

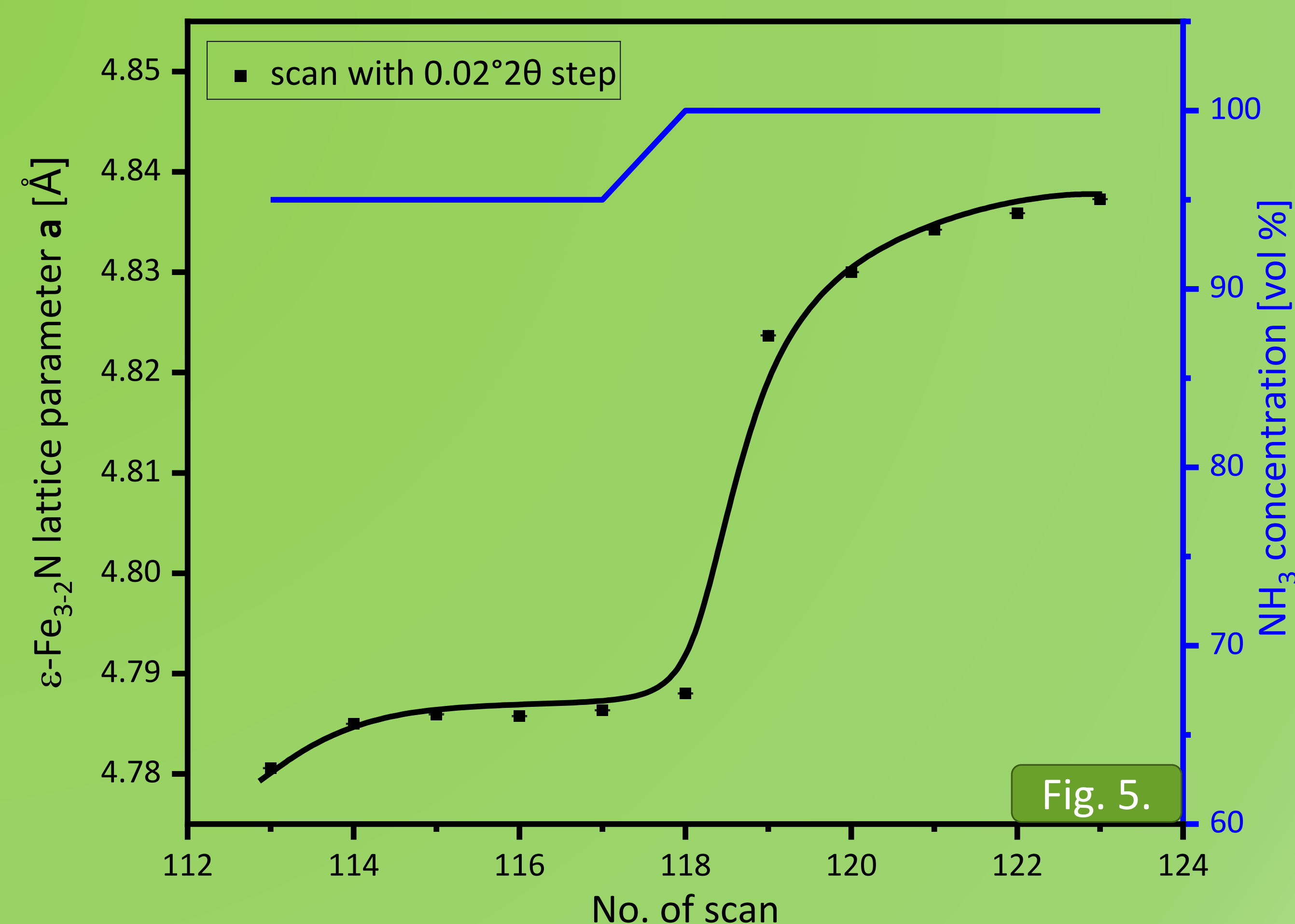


Fig. 5.

Conclusions

Obtained results prove expansion of α -Fe crystalline phase lattice with raising nitriding potential until transforming to γ' -Fe₄N phase at around 65 vol% of ammonia in the H₂:NH₃ atmosphere.

Fitted exponential regression lines expose that plots obtained with different methods have the same character, but absolute values slightly vary.

The change of α -Fe a lattice parameter depicted as a dependence of ammonia concentration is of exponential character. However, usually, studies of nitriding show the logarithm of nitriding potential as the domain. The presented plot would be of linear character then.

The lattice parameter values calculated for γ' -Fe₄N phase show noteworthy changes that need to be confirmed with data of higher resolution.

The results for the ϵ -Fe₃₋₂N affirm, that the phase exhibits widest homogeneity range and the shift in lattice parameter a may exceed 0.06 Å for data collected with narrower changes of NH₃ concentration.

Bibliography

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Acknowledgements

Aleksander Albrecht thanks the Polish Ministry of Education and Science for support through the project "Diamantowy Grant" no. DI2018003348 funded in years 2019-2022.

