

ARTICLE

Structural and Magnetic Characterization of Single-phase Sponge-like Bulk α'' -Fe₁₆N₂

Marc Widenmeyer,^[a,b] Larysa Shlyk,^[a] Anatoliy Senyshyn,^[c] Reiner Mönig,^[d] and Rainer Niewa^{*[a]}

Dedicated to Professor Hans-Jörg Deiseroth on the Occasion of His 70th Birthday

Keywords: Nitrides; Iron; Neutron diffraction; Magnetic properties; Microstructure

Abstract. Improvements of the two-step reaction sequence starting from γ -Fe₂O₃ enabled us to synthesize α'' -Fe₁₆N₂ in single phase according to the applied diffraction methods. Simultaneous Rietveld refinements were carried out on powder X-ray and neutron diffraction data. Scanning electron microscopy images of the in situ formed α -Fe and α'' -Fe₁₆N₂ indicate the formation of pores during reduction and ammonolysis reaction, respectively, resulting in a sponge-like morphology of the α'' -Fe₁₆N₂ particles and simultaneously a large surface area facilitating a complete reaction at comparably low temperatures

Introduction

Since a noticeable enhanced magnetic moment and saturation magnetization were observed by *Kim* and *Takahashi* in 1972 on thin films of α'' -Fe₁₆N₂,^[1] exceeding those of elemental iron and iron-cobalt alloys,^[2] large efforts to produce single phase samples of α'' -Fe₁₆N₂ in form of thin films, nanoscale particles as well as bulk material were put forward by the scientific community. A survey on the different approaches was given previously in literature.^[3,4] The experimental work was supported by various theoretical methods, because generally excepted theoretical models fail to explain the reported large saturation magnetization.^[5] Related to the fact that single

Prof. Dr. R. Niewa Fax: +49-711-685-64241 E-Mail: rainer.niewa@iac.uni-stuttgart.de [a] Institute of Inorganic Chemistry University of Stuttgart, Pfaffenwaldring 55 70569 Stuttgart, Germany [b] Institute of Materials Science University of Stuttgart Heisenbergstr. 3 70569 Stuttgart, Germany [c] Heinz Meier-Leibnitz Zentrum, MLZ Technische Universität München Lichtenbergstr. 1 85747 Garching, Germany [d] Institute of Advanced Materials

- KIT Karlsruhe Institute of Technology Hermann-von-Helmholtz-Platz 1 76344 Eggenstein-Leopoldshafen, Germany
- Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/zaac.201500013 or from the author.

of 125 °C. The large surface area is susceptible to the sorption of impurities and indeed chemical analysis reveals significant oxygen and hydrogen contamination of the sample. From EDX measurements in combination with the results of chemical analysis a sorption of humidity to the surface seems to be more likely to explain this contamination than an incorporation of oxygen into the bulk of the sample. Magnetization measurements on the bulk sample of α'' -Fe₁₆N₂ did not reveal any indication for the presence of a proposed giant magnetic effect.

phase samples of α'' -Fe₁₆N₂ are difficult to obtain due to its metastability,^[6] the magnetic properties of α'' -Fe₁₆N₂ still remain unclear. The best samples of bulk α'' -Fe₁₆N₂ reported so far contained 90.7 wt%^[7] and 93(2) wt%^[4] of α'' -Fe₁₆N₂, respectively, next to elemental iron. Additionally, the production of single phase nanoparticles of α'' -Fe₁₆N₂ according to Mößbauer spectroscopy measurements was presented.^[8]

The crystal structure of α'' -Fe₁₆N₂ was reported for the first time by Jack in 1951.^[9] Typically, the crystal structure is described as a tetragonal distorted $2 \times 2 \times 2$ superstructure of elemental α -Fe (bcc) in the space group I4/mmm with lattice parameters a = 572 pm and c = 629 pm. The tetragonal distortion is induced by the occupation of interstitial sites with nitrogen resulting in three crystallographic different iron sites: Fe(1) at 4e, Fe(2) at 4d and Fe(3) at 8h, while nitrogen is situated at the 2b site (cf. Figure 1). Occupation of all such voids by nitrogen in a disordered manner leads to the crystal structure of α' -Fe₈N (nitrogen martensite) lacking the crystallographic superstructure with respect to elemental iron. In previous in situ powder neutron diffraction experiments on α'' -Fe₁₆N₂ with increasing temperature a decomposition of α'' -Fe₁₆N₂ into α' -Fe₈N, γ' -Fe₄N, and iron was observed. The formation of α' -Fe₈N was detected above 236 °C by a significant change in the *c/a* ratio of α'' -Fe₁₆N₂.^[4]

In this study, we report the single phase synthesis of bulk α'' -Fe₁₆N₂ according to powder X-ray diffraction (PXRD) and neutron diffraction (ND) data. The magnetic properties and the morphology of the sample were investigated using measurements of the magnetization at different temperatures and scanning electron microscopy (SEM), respectively.



Figure 1. Section of the crystal structure of α'' -Fe₁₆N₂. The gray lines indicate the relation to the *bcc* substructure of elemental iron. The black lines represent the size of the tetragonal unit cell of α'' -Fe₁₆N₂.

Results and Discussion

Synthesis

Via optimization of our previously reported synthesis route based on the reduction of γ -Fe₂O₃ in flowing hydrogen followed by nitridation with ammonia to form bulk α'' -Fe₁₆N₂ the phase content of α'' -Fe₁₆N₂ was increased from 93(2) wt %^[4] to single phase (see below). In 2010 Yamanaka et al. correlated the achieved amounts of α'' -Fe₁₆N₂ to residual humidity in the reaction zone.^[10] Based on this finding, we have optimized the reaction conditions attributing a reduction of humidity in the reaction zone. This was achieved by a prolonged heating segment of 12 h at 125 °C in flowing hydrogen, which is well above the boiling point of water. Additionally, hydrogen can act as reduction agent and therefore remove eventually formed iron oxides at the surface of the iron particles. Sorption of water vapor resulting from the reduction process of the initial iron(III) oxide during cooling could cause an oxygen containing surface layer and, thus, hamper an effective nitridation of in situ formed iron powder by ammonia due to the low reaction temperature (T = 125 °C) applied. However, in the previously described reaction programs either no or only a short purging step was used.^[4,10]

Evaluation of Diffraction Data

According to the collected PXRD and ND data the achieved sample of α'' -Fe₁₆N₂ is single phase with all reflections completely described by the applied structure model (Figure 2). It should be noted that a broad particle size distribution (see below) together with a complex microstructure in terms of shape and strain is reflected in the reflection profiles resulting in a significantly structured background at higher diffraction angles



Figure 2. Rietveld refinements of the crystal structure of α'' -Fe₁₆N₂. The observed (black circles), calculated (light gray line) and difference (gray line, observed–calculated) ND data ($\lambda = 153.78(8)$ pm) (a) and PXRD data ($\lambda = 70.93$ pm) (b). The Bragg positions of α'' -Fe₁₆N₂ are indicated by the vertical black bars. Unknown scattering contribution is marked with *.

and unexpected scattering contributions particularly in ND data. The crystallographic details achieved by simultaneous Rietveld refinements of ND and PXRD data are summarized in Table 1. Furthermore the ND data were described sufficiently solely by a nuclear structure model excluding any kind of magnetic contribution. This fact may surprise in the view of the large magnetic moments located on the three different iron atoms calculated by DFT method (VASP): 2.21(1) μ_B on Fe(1), 2.87(1) μ_B on Fe(2) and 2.43(3) μ_B on Fe(3)^{[7]} (Figure 1) with ferromagnetic ordering (see below) and an extrapolated Curie temperature of 813 K.^[11] In a very recent study a sample of α'' -Fe₁₆N₂ nanoparticles (approx. 100 nm in size) containing minor impurities of elemental iron, γ' -Fe₄N and iron(III) oxide was examined with polarized neutron diffraction at 170 K in an external magnetic field of 5 T. By using the difference in intensity applying a parallel or antiparallel orientation of the polarized neutrons towards the external magnetic field the nuclear scattering contribution is eliminated and only the ferromagnetic fraction is retained. A significant magnetic scattering was only observed for the (202) and (220) reflections. The obtained magnetic moments are drastically reduced compared the values resulting from the above mentioned calculations [1.4(2) μ_B on Fe(1), 2.6(3) μ_B on Fe(2) and 1.8(2) µ_B on Fe(3)].^[12] Refinements of our ND data including a ferromagnetic structure model with all moments aligned to the c axis resulted in insignificant improvements of the residual parameters. In accordance to the polarized neutron diffraction data discussed above, a noticeable contribution of magnetic scattering was observed only for the (202) and (220) reflections. Due to the small magnetic contribution to the pattern the resulting magnetic moments are highly erroneous (see Figure S1, Supporting Information). A close inspection of the observed isotropic displacement parameters (Table 1) also indicates a strong influence of the ferromagnetic contribution for the iron atoms: (i) Compared to the displacement parameter of nitrogen these are markedly enlarged $[B_{iso}(N) =$ $0.19(9) \times 10^4 \text{ pm}^2 \text{ vs. } B_{iso}(\text{Fe}) = 1.1(1) - 1.5(1) \times 10^4 \text{ pm}^2$]. (ii) The Fe(2) atoms with the highest magnetic moment exhibit the highest B_{iso} values. In the above described polarized neutron diffraction study remarkably large B_{iso} values for the iron atoms were observed as well.^[12] According to theoretical and experimental studies^[7,12] the magnetic moment of Fe(2) is remarkably increased compared to elemental iron, due to an expansion of the distorted bcc iron subcell in combination with the exclusive coordination of this site by solely further iron atoms. Therefore, the observed results are in full agreement with the proposed magnetic structure of α'' -Fe₁₆N₂.

Table 1. Results of simultaneous Rietveld refinements of the crystal structure of α'' -Fe₁₆N₂ from ND [λ = 153.78(8) pm] and PXRD (λ = 70.93 pm) data measured at ambient temperature.

Parameter	ND		PXRD
a /pm		567.7(3)	
c /pm		625.3(3)	
$V/10^{6} \text{ pm}^{3}$		201.5(2)	
x[Fe(1)]		0.2109(7)	
$B_{iso}[Fe(1)] / 10^4 \text{ pm}^2$		1.14(9)	
$B_{iso}[Fe(2)] / 10^4 \text{ pm}^2$		1.5(1)	
$B_{iso}[Fe(3)] / 10^4 \text{ pm}^2$		1.11(6)	
$B_{iso}(N) / 10^4 \text{ pm}^2$		0.19(9)	
$R_n / \%$	6.41		9.06
R'_{wp} /%	8.01		11.6
$R_{\rm Bragg}$ /%	18.8		24.2

Composition Analysis

urnal of Inorganic and General Chemistry

Zeitschrift für anorganische

und alloemeine Chemi

Chemical analysis on the nitrogen and oxygen content of α'' -Fe₁₆N₂ resulted in $w(N) = 3.07 \pm 0.01$ wt% and $w(O) = 1.2 \pm 0.5$ wt%. Additionally, a hydrogen content of $w(H) = 0.027 \pm 0.002$ wt% was detected. For a composition of α'' -Fe₁₆N₂ a nitrogen content of 3.04 wt% is expected, which is in excellent agreement with the experimentally observed amount. The large variance of the measured oxygen content indicates an inhomogeneous distribution of oxygen over the sample. This is more likely for a surface contamination/oxidation of α'' -Fe₁₆N₂ rather than an incorporation of oxygen into the bulk of α'' -Fe₁₆N₂. Taking into account the measured





Figure 3. SEM image of an α'' -Fe₁₆N₂ particle (a) and EDX measurements (b). The first measurement (gray) was taken at the edge of the particle (region 1) and the second one (black) in the middle of the particle (region 2).

hydrogen content of the sample, more than 30% of the detected oxygen impurity can be attributed to a sorption of humidity to the surface. Further support for this hypothesis was gathered by energy dispersive X-ray analysis (EDX). Two measurements were carried out on the same particle (Figure 3): (i) One measurement only on the edge region (region 1) of the particle resulting in a large contribution of the surface and (ii) one measurement concentrated on the middle (region 2) of the particle aiming at a large fraction of the bulk to the collected spectrum. Both spectra show carbon peaks due to used carbon grid. As it can be seen from the SEM image in region 1 a large area is only showing the carbon grid, while in region 2 only a small area was not covered by the α'' -Fe₁₆N₂ particle. Consequently, in the EDX spectra for region 1 a high intensity peak of carbon K_{α} transition was observed, which was much smaller for region 2. Further peaks were found for iron $(K_{\alpha}, K_{\beta}$ and L_{I-III}) as well as for oxygen (K_{α}) and nitrogen (K_{α}) . For nitrogen a detection is known to be difficult in general^[13] and actually in both measurements only very small signals for nitrogen were detected. However, a clear enhancement of the signal intensity of nitrogen was observed for the bulk part of the particle, while coincidently the signal intensity of oxygen was markedly reduced. The achieved results make a surface contamination of α'' -Fe₁₆N₂ with oxygen more likely than an accumulation in the bulk sample.

Particle Morphology

Journal of Inorganic and General Chemistry

Zeitschrift für anorganische und allgemeine Chemi-

The morphology of the α'' -Fe₁₆N₂ particles additionally supports the presence of an oxygen containing surface layer, because the particles exhibit a sponge-like morphology (Figure 4) providing a large surface area susceptible for surface contamination. Formation of pores was to the best of our knowledge not reported for α'' -Fe₁₆N₂ so far, however, it is well known for various ammonolysis reactions, for example during the reaction of compact iron with ammonia at elevated temperatures yielding ε -Fe₃N_{1±x} and γ' -Fe₄N^[14–16] as well as for the synthesis of oxide nitrides from their parent oxides.^[17] Nevertheless, a massive influence of existing porosity in dense steel working parts was observed during the industrial gas nitridation process to achieve steel hardening:^[18] A high density (< 10 % porosity) typically leads to the formation of γ' -Fe₄N and ε -Fe₃N_{1±x} on the surface of the corresponding work piece.^[19,20] A higher porosity allows the precipitation of α'' -Fe₁₆N₂ after quenching and aging of a supersaturated ferrite, synthesized at elevated temperatures in a low ammonia containing nitrogen atmosphere.^[18] Therefore, we conclude the high porosity observed in our SEM images of α'' -Fe₁₆N₂ is necessary to achieve a larger reaction surface which allows full conversion to α'' -Fe₁₆N₂ at the applied low reaction temperatures. In a SEM image of the in situ formed iron powder indications of the formation of pores during the reduction of γ -Fe₂O₃ were observed, likely due to the evaporation of produced water. Additionally, the particles of α'' -Fe₁₆N₂ exhibit a broad size distribution ranging from about 5 µm to 250 µm (Figure 5).

Magnetic Properties

In measurements of the magnetization between 50 K and 300 K in accordance to results of PXRD and ND data no magnetic impurities such as elemental iron (ferromagnetic $T_{\rm C}$ = 1044 K^[21]) or iron oxides (ferrimagnetic Fe₃O₄ T_N = 850 K,^[22] antiferromagnetic Fe₂O₃ $T_{\rm N}$ = 940 K,^[23] antiferromagnetic $Fe_{1-x}O T_N = 185 K^{[24]}$ were detected. At 50 K a saturation magnetization of $M_{\rm S}$ = 183 emu·g⁻¹ resulted for α'' -Fe₁₆N₂ (Figure 6), which was decreased to 165 $emu \cdot g^{-1}$ at 300 K resulting in an extrapolated saturation magnetization of $M_{\rm S}$ = 213.7 $emu \cdot g^{-1}$ at 0 K. This value is slightly lower than the value of α -Fe at 0 K (221.7 emu·g⁻¹).^[25] The magnetic data extracted from the hysteresis curves are summarized in Table 2. No indication for the earlier reported giant magnetic effect was observed in the bulk sample. This observation might be related to two different origins: (i) A giant magnetic effect was typically detected for nanoparticles and thin films of α'' - $Fe_{16}N_2$ (226 emu·g⁻¹ $\leq M_S \leq$ 240 emu·g⁻¹),^[3,8] whereas for the presented bulk sample a much larger particle size is ob-



Figure 4. SEM images of an α'' -Fe₁₆N₂ particle in two different magnifications.



Figure 5. SEM image of in situ formed iron (a). Representative SEM image of the α'' -Fe₁₆N₂ sample showing a broad size distribution of the synthesized particles (b).



inic and General Chemistr

allgemeine Chemi

Zeitschrift für anorganische

Figure 6. Magnetization *M* vs. field of α'' -Fe₁₆N₂ at 50 K (a) and 300 K (b); Temperature dependence of the coercive fields H_C (c). The magnetization curves of α'' -Fe₁₆N₂ at 77 K, 200 K, and 250 K can be found in Figure S2 (Supporting Information).

served ranging from approximately 5 μ m to 250 μ m (Figure 5) compared to 100 nm in maximum for the nanoparticles. In a recent study using polarized neutron reflectometry a strong influence of epitaxial stress on the presence of a giant magnetic effect was observed for 40 nm thin films of α'' -Fe₁₆N₂. An increased magnetic induction was only observed in vicinity of

the sample substrate interface up to 20 nm distance.^[26] (ii) The oxygen containing surface layer. In a recent study it was observed for core-shell nanoparticles consisting of an α'' -Fe₁₆N₂ core covered with a surface layer of up to 20 wt% amorphous Al₂O₃ and an average particle size of 43 nm the saturation magnetization was only 190 emu•g⁻¹ at 300 K.^[27]

Table 2. Summarized temperature dependent magnetic properties of $\alpha^{\prime\prime}\mbox{-}Fe_{16}N_2.$

<i>T /</i> K	$M_{\rm S}$ /emu·g ⁻¹ (saturation)	$M_{\rm R}$ /emu•g ⁻¹ (residual)	H_C /T (coercive field)
50	183	55	0.107
77	176	56	0.106
200	170	54	0.102
250	168	54	0.101
300	165	54	0.100

Only a very small variation of the observed coercive fields $H_{\rm C}$ with increasing temperature was determined. At 50 K a coercive field of $H_{\rm C} = 0.107$ T was detected, which decreases to $H_{\rm C} = 0.1$ T at 300 K (Figure 6). Typically, for nanoparticles (44–100 nm) of α'' -Fe₁₆N₂ coercive fields ranging from 0.088 T to 0.135 T were observed.^[7,28] For significantly smaller nanoparticles of α'' -Fe₁₆N₂ (22 nm) a strong increase in the coercive field up to 0.4 T was reported earlier.^[8,29] The obtained residual magnetization $M_{\rm R}$ is nearly temperature independent and the observed values are in the vicinity of 55 emu•g⁻¹.

Conclusions

The introduction of an additional purging step with flowing hydrogen into the previously described synthesis route prior the actual nitridation process of in situ formed iron particles provides a single phase sample of bulk α'' -Fe₁₆N₂ according to Rietveld refinements of PXRD and ND data. The existence of a giant magnetic effect was not confirmed by temperature dependent measurements of the magnetization, while no magnetic impurities such as α -Fe, Fe_{1-x}O, Fe₂O₃, and Fe₃O₄ were present. However, chemical analysis revealed a significant contamination of the sample with oxygen and hydrogen. From SEM images a sponge-like morphology of the α'' -Fe₁₆N₂ particles was observed, indicating that most of the observed oxygen contamination is related to sorption of humidity to the large surface area. EDX measurements reveal an accumulation of oxygen at the surface region of the particles supporting this assumption. A large surface is highly desirable to allow nitridation of in situ formed iron powders at rather low reaction temperatures. The absence of a giant magnetic effect might be related either to the dramatically increased particle size of the bulk sample compared to earlier reported thin films and nanosized samples in combination with the formation of a small oxygen containing surface layer on the sponge-like and porous particles of α'' -Fe₁₆N₂.

Experimental Section

Journal of Inorganic and General Chemistry

Zeitschrift für anorganische und allgemeine Chemie

Synthesis of α'' -Fe₁₆N₂: Due to the pyrophoric nature of the obtained α'' -Fe₁₆N₂ powder all sample manipulations were performed in an argon filled glove box [$p(O_2) < 0.1$ ppm, MBraun] to avoid oxygen and water contamination.

The single phase synthesis route of α'' -Fe₁₆N₂ was based on results previously described.^[4] Single phase samples were achieved through optimization of the steps in the temperature program. In a first reaction step nano-sized γ -Fe₂O₃ (25 nm, >99.9%, Alfa Aesar) was reduced to elemental iron at 390 °C within 3 h in flowing hydrogen (100 ml·min⁻¹, 99.999%, AirLiquide), followed by decreasing the reaction temperature to 125 °C within 3 h and an additional annealing step at 125 °C for 12 h in hydrogen. Afterwards the gas atmosphere was changed to flowing ammonia (40 ml·min⁻¹, 99.999%, Linde). Single phase α'' -Fe₁₆N₂ was achieved via nitridation within 100 h at 125 °C.

Powder X-ray Diffraction: Powder X-ray diffraction data were collected with a STOE STADI P equipped with a Mythen1K micro-strip detector in Debye-Scherrer set-up using Mo- K_{a1} radiation ($\lambda = 70.93$ pm). Samples of α'' -Fe₁₆N₂ were measured in sealed thin-walled glass capillaries.

Powder Neutron Diffraction: Powder neutron diffraction patterns were recorded at the two-axis neutron powder diffractometer SPODI (FRM-II, Garching) in the range of $1^{\circ} \le 2\Theta \le 150^{\circ}$ with an angular resolution of $\Delta(2\Theta) = 0.05^{\circ}$. The exposure time was 30 min per scan, resulting in a total exposure time of 7.5 h. A high take-off angle of 155° from the (551) atomic plane of the vertically focused Ge-monochromator was chosen resulting in a good resolution $\Delta d/d$, a neutron flux at the sample of approximately 2×10^6 neutrons s⁻¹ cm⁻² and a nominal wavelength of 154.9 pm.[30] The exact determination of the wavelength was achieved using a silicon standard (NIST 640b) with corrected unit cell parameters^[31] in a thin wall vanadium cylinder (6 mm outer diameter). By using the variable detector height routine for integration of the reflection intensities from the Debye-Scherrerrings^[30] a wavelength of $\lambda = 154.832(2)$ pm was determined by Rietveld refinements of the collected data. The observed neutron diffraction data and reflection intensities of α'' -Fe₁₆N₂ were described entirely by the applied nuclear structure model. In principle an influence of ferromagnetic ordered α'' -Fe₁₆N₂ on the reflection intensities is expected.^[32,33] However, through the position in 2Θ of the first significant influenced reflections by the ferromagnetic ordering the effect of the present magnetic moments is massively reduced, due to its strong angular dependency.^[34] Additionally, the evaluation of the magnetic influence is complicated by the complex microstructure of the sample.

Rietveld Refinements: Simultaneous Rietveld refinements^[35,36] on the crystal structure of α'' -Fe₁₆N₂ on powder X-ray and neutron diffraction data were carried out with the *FULLPROF2.k*^[37] program. The following parameters were initially allowed to vary: Scale factor, the zero point of the 2Θ scale, three reflection widths (Caglioti formula U, V and W), one mixing (η), two asymmetry parameters, the lattice parameters a and c as well as the isotropic thermal displacement parameters (B_{iso}). As function to describe the reflection profiles a pseudo-Voigt function was chosen and an angle dispersive correction of the mixing parameter (χ) was applied. The background was either described by polynomial of fourth order (X-ray) or by interpolation between chosen background points with refineable heights (neutron).

Magnetization Measurements: For measurements of the magnetization the sample of α'' -Fe₁₆N₂ was sealed in an argon atmosphere into

a polycarbonate capsule, which was glued into a small polyvinylchloride tube. Magnetization measurements were performed using a SQUID magnetometer (Quantum Design) in the temperature range of 50– 300 K and magnetic fields up to 5 T.

Electron Microscopy: For electron microscopy images a Zeiss Merlin scanning electron microscope additionally equipped with an Oxford Instruments X-Max80 energy dispersive X-ray analysator was used. Absorption edges of iron (K_a , $\bar{E} = 6.398$ keV; K_β , $\bar{E} = 7.083$ keV, L_{I-III} , $\bar{E} = 0.759$ keV),^[38] nitrogen (K_a , E = 0.392 keV), oxygen (K_a , E = 0.525 keV) and carbon (K_a , E = 0.277 keV) were detected.^[39]

Chemical Analysis: Quantitative analysis of the oxygen, nitrogen, and hydrogen content of α'' -Fe₁₆N₂ was carried out by the hot gas extraction method on a LECO ONH826 with oxygen containing steel standards (w(O) = 0.0028 wt% and 0.0364(5) wt%) as well as WO₃ [w(O) = 20.7 wt%] for oxygen and nitrogen containing steel standards [w(N) = 0.0023(2) wt% and 0.535(9) wt%] as well as Si₃N₄ (w(N) = 38.1 wt%) for nitrogen. For the hydrogen content calibration a hydrogen containing steel standard [$w(H) = 5.4(6) \times 10^{-4} \text{ wt\%}$] was used for calibration.

Supporting Information (see footnote on the first page of this article): Results of Rietveld refinements respecting the complex microstructure and the magnetic contribution are given in Figure S1. The magnetic hysteresis loops at 77, 200 and 250 K are shown in Figure S2.

Acknowledgements

This work was promoted by the Deutsche Forschungsgemeinschaft within the priority program 1415 (SPP1415). Additionally, the authors gratefully acknowledge the financial support provided by FRM II to perform the neutron scattering measurements at the Heinz Maier-Leibnitz Zentrum (MLZ), Garching, Germany. *Felicitas Predel* and Prof. *Dr. Peter van Aken* (Max Plank Institute for Intelligent Systems – StEM, Stuttgart) are sincerely thanked for the collection of different SEM images.

References

- [1] T. K. Kim, M. Takahashi, Appl. Phys. Lett. 1972, 20, 492–495.
- [2] R. C. O'Handley, *Modern Magnetic Materials Principles and Applications*, New York: Wiley, **2000**.
- [3] M. Takahashi, H. Shoji, J. Magn. Magn. Mater. 2000, 208, 145– 147.
- [4] M. Widenmeyer, T. C. Hansen, R. Niewa, Z. Anorg. Allg. Chem. 2013, 639, 2851–2859.
- [5] J.-P. Wang, N. Ji, X. Liu, Y. Xu, C. Sánchez-Hanke, Y. Wu, F. M. F. de Groot, L. F. Allard, E. Lara-Cuzio, *IEEE Trans. Magn.* 2012, 48, 1710–1717.
- [6] F. Tessier, A. Navrotsky, R. Niewa, A. Leineweber, H. Jacobs, S. Kikkawa, M. Takahashi, F. Kanamaru, F. J. DiSalvo, *Solid State Sci.* 2000, 2, 457–462.
- [7] S. Yamashita, Y. Masubuchi, Y. Nakazawa, T. Okayama, M. Tsuchiya, S. Kikkawa, J. Solid State Chem. 2012, 194, 76–79.
- [8] T. Ogawa, Y. Ogata, R. Gallage, N. Kobayashi, N. Hayashi, Y. Kusano, S. Yamamoto, K. Kohara, M. Doi, M. Takano, M. Takahashi, *Appl. Phys. Express* **2013**, *6*, 073007.
- [9] K. H. Jack, Proc. R. Soc. London A 1951, 208, 200-224.
- [10] K. Yamanaka, Y. Onuma, S. Yamashita, Y. Masubuchi, T. Takeda, S. Kikkawa, J. Solid State Chem. 2010, 183, 2236–2241.
- [11] Y. Sugita, K. Mitsuoka, M. Komura, H. Hoyashi, Y. Kozono, M. Hanazono, J. Appl. Phys. 1991, 70, 5977–5982.
- [12] H. Hiraka, K. Ohoyama, Y. Ogata, T. Ogawa, R. Gallage, N. Kobayashi, M. Takahashi, B. Gillon, A. Gukasov, K. Yamada, *Phys. Rev. B* 2014, 90, 134427.

- [13] M. F. Gazulla, M. Rodrigo, E. Blasco, M. Orduna, X-ray Spectrom. 2013, 42, 394–401.
- [14] B. Prenosil, Härterei-Technol. Mitt. 1973, 28, 157–164.
- [15] H. Jacobs, D. Rechenbach, U. Zachwieja, *Härterei-Technol. Mitt.* 1995, 50, 205–213.
- [16] K. Vogelsang, W. Schröter, R. Hoffmann, H. Jacobs, Härterei-Technol. Mitt. 2002, 57, 42–48.
- [17] Y.-I. Kim, Ceram. Int. 2014, 40, 5275-5281.

Journal of Inorganic and General Chemistry

Zeitschrift für anorganische und allgemeine Chemie

- [18] A. Salak, E. Rudnayova, M. Selecka, *Powder Metall.* **1999**, *42*, 45–50.
- [19] A. Salak, E. Rudnayova, M. Selecka, Pokroky Práškové Metalurgie VUPM 1997, 3, 42.
- [20] M. R. Pinasco, G. Palombarini, M. G. Ienco, G. F. Bocchini, J. Alloys Compd. 1995, 220, 217–224.
- [21] T. Oguchi, K. Terakura, N. Hamada, J. Phys. F 1983, 13, 145– 160.
- [22] G. A. Samara, A. A. Giardini, Phys. Rev. 1969, 186, 577-580.
- [23] Z. Sun, H. Yuan, Z. Liu, B. Han, X. Zhang, Adv. Mater. 2005, 17, 2993–2997.
- [24] W. H. Meiklejohn, J. Appl. Phys. 1958, 29, 454-455.
- [25] H. Danan, A. Herr, A. J. P. Meyer, J. Appl. Phys. **1968**, 39, 669–670.
- [26] N. Ji, V. Lauter, X. Zhang, H. Ambaye, J.-P. Wang, *Appl. Phys. Lett.* 2013, 102, 072411.
- [27] R. Zulhijah, K. Yoshimi, A. B. D. Nandiyanto, T. Ogi, T. Iwaki, K. Nakamura, K. Okuyama, *Adv. Powder Technol.* 2014, 25, 582– 590.

- [28] S. Kikkawa, A. Yamada, Y. Masubuchi, T. Takeda, *Mater. Res. Bull.* **2008**, *43*, 3352–3357.
- [29] E. Kita, K. Shibata, H. Yanagihara, Y. Sasaki, M. Kishimoto, J. Magn. Magn. Mater. 2007, 310, 2411–2413.
- [30] M. Hoelzel, A. Senyshyn, N. Juenke, H. Boysen, W. Schmahl, H. Fuess, Nucl. Instrum. Methods Phys. Res. Sect A 2012, 667, 32– 37.
- [31] D. Yoder-Short, J. Appl. Crystallogr. 1993, 26, 272-276.
- [32] L. Van Hove, Phys. Rev. 1954, 95, 1374-1384.
- [33] M. K. Wilkinson, C. G. Shull, Phys. Rev. 1956, 103, 516-524.
- [34] A. Leineweber, H. Jacobs, F. Hüning, H. Lueken, H. Schilder, W. Kockelmann, J. Alloys Compd. 1999, 288, 79–87.
- [35] H. M. Rietveld, Acta Crystallogr. 1967, 22, 151-152.
- [36] H. M. Rietveld, J. Appl. Crystallogr. 1969, 2, 65-71.
- [37] J. Rodriguez-Carvajal, *FULLPROF2.k*, Version 5.3, Mar2012-ILL-JRC, **2012**.
- [38] R. D. Deslattes, E. G. J. Kessler, P. Indelicato, E. Lindroth, *Inter-national Tables of Crystallography, Mathematical, Physical and Chemical Tables*, vol. C (Ed.: E. Prince), Dordrecht, Kluwer Academic Press, 2003.
- [39] E. Browne, R. B. Firestone, *Table of Radioactive Isotopes*, New York, John Wiley and Sons, **1986**.

Received: January 9, 2015 Published Online: February 3, 2015