ELSEVIER

Journal of Alloys and Compounds 281 (1998) 306–311

Journal of ALLOYS AND COMPOUNDS

Neutron and X-ray powder diffraction study on the compound $NdFe_{10.75}V_{1.25}N_y$

Ph. Oleinek[a,*], W. Kockelmann[b], K.-H. Müller[a], M. Loewenhaupt[c], L. Schultz[a]

[a] *Institut für Festkörper- und Werkstofforschung Dresden, D-01171 Dresden, Germany*
[b] *Mineralog.-Petrolog. Institute, Bonn University, Germany, c/o ISIS, Rutherford-Appleton-Laboratory, Chilton OX11 0QX, UK*
[c] *Institut für Angewandte Physik (IAPD), TU Dresden, D-01062 Dresden, Germany*

Received 17 July 1998

Abstract

The structural changes that occur in the compound $NdFe_{10.75}V_{1.25}$ due to nitrogenation have been investigated by neutron and X-ray powder diffraction. Nitrogen occupies less than 60% of the interstitial 2b site, even if the nominal nitrogen content in the structure is 2.4 N atoms/formula unit. The extra nitrogen is not believed to occupy other interstitial positions. V occupies preferentially the 8i site in the non-nitrided case. However, this occupancy decreases with increasing nitrogen content. The diffraction data show a strongly anisotropic behaviour of the profile parameters with nitrogen absorption due to the formation of anisotropic strain rather than stacking faults.

Keywords: Rare earth iron intermetallics; Gas–solid reaction; Nitrogenation; Amorphization; Neutron powder diffraction

---

1. Introduction

The magnetic properties of compounds of the type $R(Fe,M)_{12}$ (M=Ti, V, Cr, Mo, Si,...) change strongly upon interstitial modification with N or C [1]. These compounds crystallize in the body centered, tetragonal $ThMn_{12}$-type structure, space group *I4/mmm*. The rare earth (R) atoms are located at the 2a sites, the Fe and M atoms are distributed over the 8f, 8i and 8j sites. Some of these compounds, such as $Nd(Fe,V)_{12}N_y$ exhibit distinct intrinsic magnetic properties which are sufficient to make them interesting components for technological permanent magnet applications [1,2]. However, the feasibility of a controlled interstitial modification, and hence the intrinsic magnetic properties, depend on the stabilizing element M. Unfortunately, the structural stability of two of the compounds with the best magnetic properties decreases strongly on nitrogenation: $NdFe_{11}Ti$ transforms into an amorphous phase plus α-Fe if the applied temperature in the gas–solid reaction exceeds 500°C for 16 h [3]. Recently, we also found $R(Fe,V)_{12}$ with R=Nd or Sm to transform into a two phase mixture of amorphous phase and α-Fe(V) if the temperature of the nitrogenation treatment is above 530°C for at least 5 h [4].

By neutron diffraction experiments it was shown that N-atoms in $R(Fe,M)_{12}$ occupy the 2b site exclusively with varying occupancies depending on the stabilizing element M [2,5–8]. Some groups have reported compounds to absorb more nitrogen than the 2b site can accommodate [4,9,10]. One of them is $NdFe_{12-x}V_x$ ($1.25\leq x\leq 2$), which is able to absorb more than 3 N atoms/formula unit (f.u.), accompanied, however, by irreversible structural changes leading to a massive anisotropic peak broadening in the diffraction patterns [4].

The aim of this investigation was to determine the location of the nitrogen atoms and to study the structural changes due to nitrogenation of $NdFe_{10.75}V_{1.25}$. An appropriate method to obtain the positions of the N atoms, to determine the occupation numbers of Fe and V and to follow structural changes that occur with nitrogenation is neutron diffraction in combination with X-ray powder diffraction. The two diffraction methods are complementary to each other, allowing for the determination of the V occupation numbers. The coherent neutron scattering length of V is very small, which makes it difficult to distinguish V atoms from vacancies by using neutron data only. X-ray diffraction data can distinguish V atoms from vacancies, but cannot give an accurate value for the Fe/V

---

[*] Corresponding author. Tel.: +49-351-4659-669; fax: +49-351-4659-537; e-mail: oleinek@ifw-dresden.de

0925-8388/98/$ – see front matter
PII: S0925-8388(98)00782-8

ratio for a given crystallographic site because of the similar X-ray scattering cross sections of Fe and V. Combined neutron and X-ray diffraction can, however, reveal the total occupancy as well as the Fe/V ratio and thus the V occupancies, assuming that the difference in the occupation numbers originates from V atoms. The neutron scattering measurements also allow for the determination of the magnetic moments of Nd and Fe atoms. It is well known that $Nd(Fe,V)_{12}N_y$ orders ferromagnetically at room temperature (RT), with the moments of the Nd and Fe sublattices being parallel to the tetragonal *c*-axis [1].

2. Experimental details

The alloy was prepared by arc melting the elements in Ar atmosphere, followed by annealing at 900°C for 1 week, wrapped in Ta foil and sealed in an Ar filled quartz tube. The sample was checked by X-ray diffraction which revealed single phase $ThMn_{12}$-type structure with a small amount of α-Fe impurity. The ingots were then milled to a powder with a particle size between 1 and 15 μm. Nitrogenation was performed in a closed container filled with pure N_2 gas. Three samples with absorbed nitrogen contents corresponding to $y=0$, 1.4 and 2.4 N atoms/f.u. were prepared. For the sample containing 1.4 N atoms/f.u. the nitrogenation time and temperature was 3 h and 400°C, respectively, whereas for the sample with 2.4 N atoms/f.u. nitrogenation was performed at a temperature of 450°C for 5 h. The amount of absorbed nitrogen was calculated from the mass difference before and after nitrogenation and by hot extraction. The homogeneity of nitrogenation was estimated by thermomagnetic analysis. The material with the higher nitrogen content ($y=2.4$) consists of only one ferromagnetic phase additionally to α-Fe. The sample with lower nitrogen content, however, has several ferromagnetic phases originating from incomplete nitrogenation, all of them having a clearly recognizable higher T_c than the non-nitrided material.

The neutron diffraction experiments were carried out at RT on the ROTAX time-of-flight diffractometer at the ISIS facility, Rutherford Appleton Laboratory, UK. Two detector banks were used, one in backscattering and one in forward scattering position, covering an angular range of 10° to 46° and 133° to 164°, respectively. They provide data in a *d*-spacing interval ranging from 0.3 Å to 10 Å using an incident wavelength band of 0.4 to 5.0 Å. Refinement of the diffraction patterns was done in a *d*-spacing range from 0.5 Å to 2.6 Å and from 0.8 Å to 7 Å for the forward and backscattering bank, respectively. For the coherent neutron scattering length we used 7.69 fm for Nd, 9.45 fm for Fe, −0.038 fm for V and 9.30 fm for N. Magnetic form factor values of Nd and Fe were taken from [11]. X-ray diffraction experiments were carried out at RT on the identical samples on a Philips PW1820 diffractometer using Co K_α radiation.

Neutron and X-ray data were analysed simultaneously by the Rietveld refinement method [12] using the GSAS program package [13]. In order to ensure that neutron and X-ray data sets were equally weighted in the refined parameter sets, we took care to have approximately the same quality of fit of the neutron and X-ray diagrams. The overall agreement between observed and calculated intensities, including magnetic and nuclear neutron diffraction data as well as XRD data, is expressed by weighted reliability profile values R(wp).

Additionally, transmission electron microscopy (TEM) specimens were prepared from the annealed ingots. After thinning, the TEM specimens were nitrogenated. The nitrogenation process, holding at a temperature of 450°C for 5 h, was the same as for the powder samples. This characterisation method was used because the thickness of the electron transparent region of the specimen is of the order of or smaller than the particle diameter of the powder described earlier. The TEM specimens should therefore absorb an amount of nitrogen comparable to that of the powder samples used for the diffraction experiments. The TEM specimens were examined in the TEM before and after the nitrogenation process, which enables a direct observation of the microstructural changes due to nitrogenation. A preparation of TEM specimens from the powder samples was not successful.

3. Experimental results

Neutron and X-ray diffraction patterns of $NdFe_{10.75}V_{1.25}$ and $NdFe_{10.75}V_{1.25}N_{2.4}$ are shown in Fig. 1. The structure refinements confirm the tetragonal $ThMn_{12}$-type structure for all three specimen with Nd on the 2a sites and Fe and V atoms distributed over mixed sites 8f, 8i and 8j. In addition the magnetic moments of Nd and of Fe at the three different sites were refined independently.

A significant occupation of Nd on sites 8f, 8i and 8j could not be observed for the non-nitrided material. In order to find the relative occupation numbers of the various crystallographic sites, the Nd fraction on the 2a site was therefore fixed to one whereas the relative fractions of Fe and V on positions 8f, 8i and 8j were refined. This refinement procedure was performed with and without the constraint of a total occupancy of 1 on the three Fe sites.

V occupies all the Fe sites in the non-nitrided case, with a preference for the 8i site, which was already found by Helmholdt et al. [14]. When the total occupancy on the Nd and Fe sites was fixed to one, the V fraction on the preferred site 8i strongly decreased with increasing nitrogen absorption (Fig. 2). For the highest nitrogen content, it was found to be smaller than the V fraction on site 8j. When Fe and V fractions were refined without the constraint of total occupancy, the 8f and 8j sites were over-occupied in total by about 3% in the non-nitrided sample (Fig. 3). However, only the occupancy of the 8f site

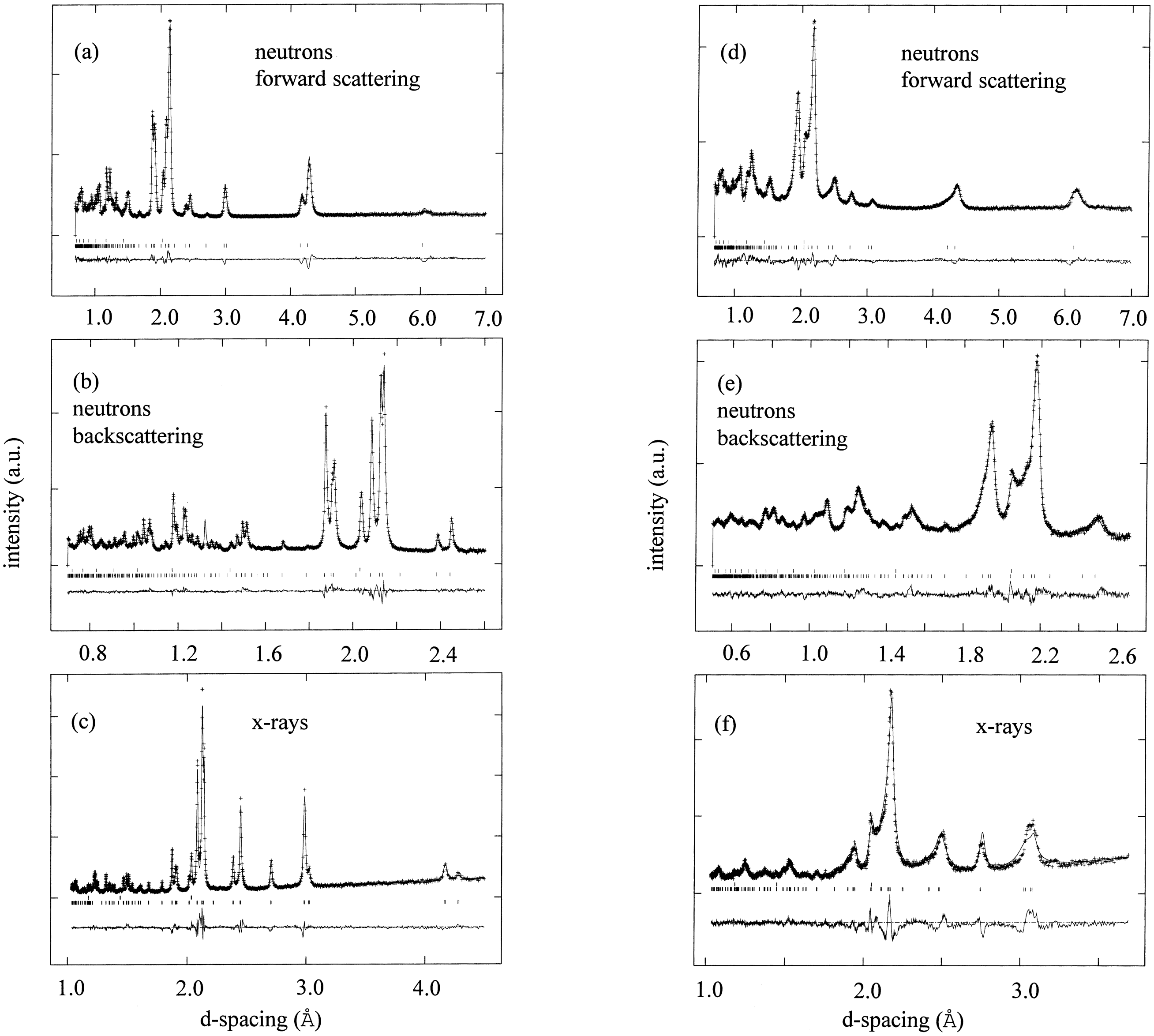

Fig. 1. Calculated (lines) and observed (crosses) neutron time of flight and X-ray powder diffraction patterns and difference plots (below) of $NdFe_{10.75}V_{1.25}$ (a)–(c) and $NdFe_{10.75}V_{1.25}N_{2.4}$ (d)–(f). (a) and (d): Neutron diffraction data from forward scattering with the detector center at $\Theta_{midpoint}=28.12°$. (b) and (e): Neutron diffraction data with the detector in backscattering position, $\Theta_{midpoint}=145°$. (c) and (f): X-ray diffraction data from the identical samples as used for neutron diffraction.

remains at this level with increasing nitrogen content, sites 8j and 8i are only 90% full at a nitrogen content of 2.4/f.u. This decrease is mainly due to a lowering of the V fractions on the Fe sites, with an emphasis on the 8i site as it was observed in the constrained refinement. The quality of the fit was somewhat better when the refinement was performed without constraint on the Fe/V occupation numbers, especially for the XRD data which is more sensitive to V.

The occupation number of nitrogen on the 2b site increases only little from 0.51 to 0.57 for the nitrogen contents 1.4/f.u. and 2.4/f.u., respectively. This is an interesting result because the remarkable change of peak shapes as well as peak positions with nitrogen content could easily be explained by an increasing occupation of interstitial sites by the nitrogen atoms. The 2b interstitial site is obviously not responsible for these changes. The 2b occupation number cannot be raised to one by means of the applied heat treatment. The attempt to find other interstitial nitrogen sites was not successful. No interstitial site apart from 2b has an outstanding nitrogen occupation of more than 5%. Anisotropic broadening of peaks of type (*h*,*k*,0) is strongly developed in the dataset of the sample with the highest nitrogen content. Two models, stacking faults and anisotropic strain, were used to interpret such a loss of periodicity along the *c*-axis. The strain model yields a much better agreement between observed and calculated intensities. In order to verify this result, we investigated a

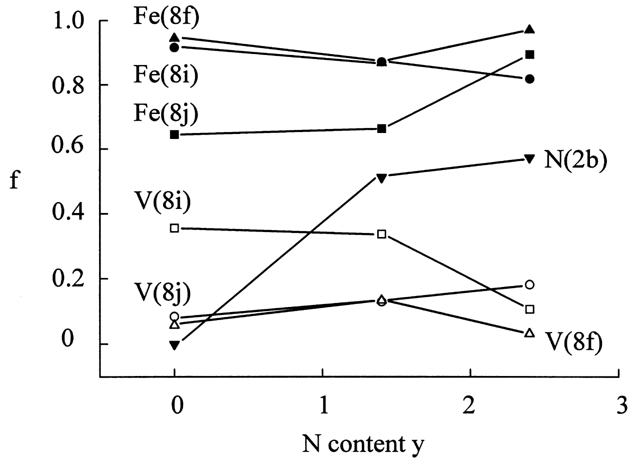

Fig. 2. Comparison of the Fe and V fractions f on the three Fe sites for different N contents. The total occupancy of the Fe and Nd sites was set to one. The N occupancies on the 2b site are also shown.

sample from bulk material before and after nitrogenation by TEM to look for the existence of stacking faults. The TEM examinations showed no increase of the number of stacking faults after the heat treatment in nitrogen. Since the TEM samples cannot be checked quantitatively for the amount of nitrogen absorbed by the sample, we carried out energy dispersive X-ray analysis (EDX) measurements in the TEM. These measurements showed qualitatively, that there is nitrogen in the $ThMn_{12}$-type structure, and that the nitrogen concentration was somewhat elevated at the grain boundaries. EDX also showed that the α-Fe impurities contained about 10% vanadium.

Structural parameters and magnetic moments derived from the RT neutron data with the constraint of total occupancies are given in Table 1. The moments obtained are very sensitive to other parameters like occupancies, and the errors of the moment values are quite high. However, it is possible to derive clear tendencies for the change of magnetic moments with nitrogenation. The Nd moment increases from 1.36 μ_B to 1.83 μ_B for $y=0$ and $y=2.4$, respectively, but has the small value of 1.08 μ_B for $y=1.4$. The moments of Fe on the three different sites show a strong dependency on the nitrogen content y. A strong variation of the magnetic moments with the different Fe sites was only observed in the case of $y=0$, where the 8i site has the biggest moment. The dependency of the Fe magnetic moments on the crystallographic sites decreases after nitrogenation, yet the moments are all increased. At $y=2.4$ the Fe moments are basically the same on sites 8f, 8i, and 8j. Table 1 also shows the moments reported in the literature obtained from neutron powder diffraction on $NdFe_{10}V_2$ [15], $NdFe_{10.05}V_{1.38}Al_{0.57}$ [16] and $YFe_{11}TiN_x$ [6]. Table 2

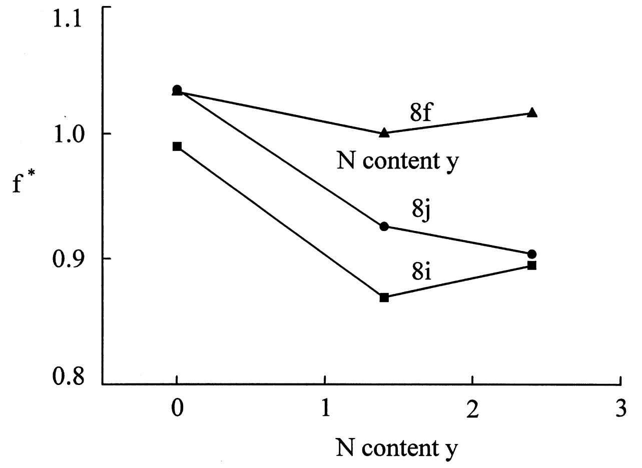

Fig. 3. Total occupancies f^* of the Fe sites for the three N contents investigated. The Fe and V occupancies were refined independently without constraint on the total occupancy. The decrease of these values is mainly due to a decrease of the V fractions on these sites. The Nd occupancy of the 2a site was fixed to one.

4. Discussion

The results on the occupancies of the three Fe sites show that there might be a decrease in the V fraction in $Nd(Fe,V)_{12}$ taking place during the nitrogenation process. Keeping in mind that V is an indispensable partner for stabilizing the $ThMn_{12}$-type structure, the V removal is a possible mechanism to explain the decomposition of $Nd(Fe,V)_{12}$ into α-Fe and an amorphous phase during nitrogenation which has been observed previously [4]. This amorphous phase represents a metastable state that is controlled by kinetic processes, the energetically lowest state, however, would be achieved by the formation of the nitrides, NdN and VN, and α-Fe. The remarkable broadening of the reflection peaks in the sample with 2.4 N atoms/f.u. indicates that this decomposition process may already be active at lower temperatures but with a reduced velocity. The same model could be applied to the Ti stabilized compounds with the $ThMn_{12}$-type structure, where this decomposition process has been observed for the first time [3]. The change of the Fe/V ratio in the $ThMn_{12}$-type phase can be explained by the continuous formation of a decomposition product [4].

The constant occupancy of only 0.5 of the 2b site by nitrogen could give an explanation for the remarkable anisotropic peak broadening. Rare earth and nitrogen atoms are aligned parallel to the *c*-axis in the $ThMn_{12}$-type structure, and for lack of every second N-atom on average strain may be caused along this direction.

The great discrepancy between the amounts of nitrogen determined by difference of mass or hot extraction and the amounts found by fitting the neutron diffraction data cannot be explained satisfactorily. The quality of the fit was somewhat better when other additional interstitial sites like 4d, 16l or 16m were assumed for N atoms, but their occupancies were found to be very small. The highest occupancy for those sites was found on the 4d site with

Table 1
Refined structural and magnetic paramters at RT of $NdFe_{10.75}V_{1.25}N_y$ [a]

Site	Element	N content y	Fraction f	Wyckoff letter x	m [μ_B]	m [μ_B] ([15])	m [μ_B] ([16])	m [μ_B] ([6])
2a	Nd	0	1.0	0.0	1.36(13)	1.4(1)	1.8(2)	
		1.4	1.0	0.0	1.08(20)			
		2.4	1.0	0.0	1.83(22)			
8f	Fe	0	0.943(2)	0.25	1.00(8)	1.4(1)	2.0(1)	
		1.4	0.867(3)	0.25	2.20(8)			2.181
		2.4	0.969(3)	0.25	1.84(8)			
	V	0	0.057(2)	0.25				
		1.4	0.133(3)	0.25				
		2.4	0.031(3)	0.25				
8i	Fe	0	0.645(1)	0.3600(1)	1.68(7)	2.6(1)	2.2(2)	
		1.4	0.663(3)	0.3598(3)	2.22(9)			2.284
		2.4	0.894(4)	0.3577(1)	1.90(8)			
	V	0	0.355(1)	0.3600(1)				
		1.4	0.337(3)	0.3598(3)				
		2.4	0.106(4)	0.3577(1)				
8j	Fe	0	0.916(1)	0.2721(1)	1.65(7)	1.7(1)	2.4(3)	
		1.4	0.871(4)	0.2733(1)	1.98(15)			2.798
		2.4	0.818(5)	0.2703(2)	1.90(22)			
	V	0	0.084(1)	0.2721(1)				
		1.4	0.129(4)	0.2733(1)				
		2.4	0.182(5)	0.2703(2)				
2b	N	0	0	0				
		1.4	0.512(8)	0				
		2.4	0.573(10)	0				

[a] Estimated standard deviations are given in parentheses. The magnetic moments are compared with values obtained from powder neutron diffraction data on $NdFe_{10}V_2$ ([15]), $NdFe_{10.05}V_{1.38}Al_{0.57}$ ([16]) and $YFe_{11}TiN_x$ ([6]).

5%. However, these sites cannot explain the high nitrogen contents. Apart from areas like grain boundaries or particle surfaces, the decomposition product that has already been used to explain the change of the Fe/V ratio in the $ThMn_{12}$-type structure gives the only possible explanation for the whereabouts of the surplus nitrogen atoms.

The value of the iron moment varies for the three different crystallographic sites in the non-nitrided case, but is practically equal for $y=2.4$. This is in qualitatively good agreement with the results of neutron powder diffraction experiments and Mössbauer spectroscopy [15,17], however, in our study the 8i and 8f moments have smaller values. A dominant magnetic moment that would be expected on the 8i site because of a higher number of Fe neighbours [18] was not observed. The discrepancy between the Fe moments for $y=0$ listed in ref. [14] and found by us might be due to different Fe and V fractions on the three Fe sites. In ref. [14] the V atoms were restricted to the 8i site, whereas we allowed V to occupy all Fe sites. The magnetic moment of iron in $NdFe_{11}TiN_x$ [6], also derived from neutron diffraction, corresponds to the values we found for $y = 1.4$ on sites 8f and 8i, but locates a higher moment on site 8j. The increase of the Fe magnetic moments is confirmed by magnetic measurements performed at 10 K, where an increase of the saturation magnetization after nitrogenation was observed [19]. Regarding the continuous expansion of the lattice and the beginning decomposition of the crystal structure, it can be assumed that the local atomic environment of the Fe atoms is changed on average in the sample with $y=2.4$, which is known to change the value of the Fe moment [20].

Table 2
Weighted reliability factors R(wp) for the datasets of neutron diffraction in forward (nfs) and backscattering (nbs) position, respectively, and X-ray diffraction (xrs) [a]

y	R(wp) % nfs	 nbs	 xrs	a [Å]	c [Å]	V [$Å^3$]	$\Delta V/V$ [%]	M_s [μ_B/f.u.]
0	3.72	4.05	8.10	8.5570(1)	4.7725(1)	349.45(1)		15.5
1.4	4.15	5.51	10.64	8.6320(3)	4.8452(6)	361.02(5)	3.31	21.5
2.4	4.63	4.31	10.17	8.6935(4)	4.8348(11)	365.40(13)	4.56	22.0

[a] Unit cell parameters and magnetic moment per formula unit (f.u.) of $NdFe_{10.75}V_{1.25}N_y$ at RT, calculated from the results of neutron diffraction, are also shown.

Acknowledgements

This work has been supported by the BMBF, project numbers 13N6613 and 03WI4BO3. The authors want to thank Dr. habil. H.-D. Bauer for the TEM investigations.

References

[1] Y.Z. Wang, G.C. Hadjipanayis, J. Appl. Phys. 70(10) (1991) 6009–6011.
[2] Y.C. Yang, X.D. Zhang, S.L. Ge, Q. Pan, L.S. Kong, H. Li, J.L. Yang, B.S. Zhang, Y.F. Ding, C.T. Ye, J. Appl. Phys. 70(10) (1991) 6001–6005.
[3] L. Schultz, C. Kuhrt, K. Schnitzke, J. Wecker, M. Katter, Trans. Mat. Res. Soc. Jpn. 16A (1994) 63–68.
[4] Ph. Oleinek, G. David, K.H. Müller, A. Handstein, N. Mattern, L. Schultz, Mater. Lett. 35 (1998) 126–129.
[5] Y.Z. Wang, G.C. Hadjipanayis, A. Kim, D.J. Sellmyer, W.B. Yelon, J. Magn. Magn. Mater. 104–107 (1992) 1132–1134.
[6] Y.C. Yang, X.D. Zhang, L.S. Kong, Q. Pan, S.L. Ge, J.L. Yang, Y.F. Ding, B.S. Zhang, C.T. Ye, L. Jin, Solid State Commun. 78 (1991) 313–316.
[7] H. Sun, Y. Morii, H. Fujii, M. Akayama, S. Funahashi, Phys. Rev. B 48 (1993) 13333–13339.
[8] E. Tomey, O. Isnard, A. Fagna, C. Desmoulins, S. Miraglia, J.L. Soubeyroux, D. Fruchart, J. Alloys Comp. 191 (1993) 233–238.
[9] H. Fujii, Y. Miyazaki, K. Tatami, H. Sun, Y. Morii, M. Akayama, S. Funahashi, J. Magn. Magn. Mater. 140–144 (1995) 1089–1090.
[10] T. Goto, Y. Takahashi, S. Abe, J. Magn. Magn. Mater. 140–144 (1995) 1021–1022.
[11] T. Hahn, International Tables for Crystallography, vol. C, Kluwer Academic Publishers, 1995, p. 391.
[12] H.M. Rietveld, J. Appl. Crystallogr. 2 (1969) 65–71.
[13] A.L. Larson, R.B. Von Dreele, GSAS General Structure Analysis System, LANCE, MS-H805 Los Alamos National Laboratory, Los Alamos, New Mexico, 1994.
[14] R.B. Helmholdt, J.J.M. Vleggaar, K.H.J. Buschow, J. Less-Common Metals 144 (1988) 209–214.
[15] W.G. Haije, J. Spijkerman, F.R. De Boer, K. Bakker, K.H.J. Buschow, J. Less-Common Metals 162 (1990) 285–295.
[16] Z. Hu, W.B. Yelon, W.J. James, J. Appl. Phys. 79(8) (1996) 6315–6317.
[17] C.J.M. Denissen, R. Ceohoorn, K.H.J. Buschow, J. Magn. Magn. Mater. 87 (1990) 51–56.
[18] R.B. Helmholdt, J.J.M. Vleggaar, K.H.J. Buschow, J. Less-Common Metals 138 (1988) L11–L14.
[19] Ph. Oleinek, unpublished results.
[20] R. Fruchart, P. L'Heritier, P. Dalmas de Reotier, D. Fruchart, P. Wolfers, J.M.D. Coey, L.P. Ferreira, R. Guillen, P. Vulliet, A. Yaouanc, J. Phys. F: Met. Phys. 17 (1987) 483.