Ordering of Nitrogen in Nickel Nitride Ni_3N Determined by Neutron Diffraction

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The metallic interstitial nitride Ni_3N was prepared from $Ni(NH_3)_6Cl_2$ and $NaNH_2$ in supercritical ammonia ($p(NH_3) \approx 2$ kbar) at 523 K. Its previously reported crystal structure, as determined from X-ray powder data, was confirmed by neutron powder diffraction: Ni_3N crystallizes in the hexagonal ϵ-Fe_3N-type structure ($P6_322$, $Z = 2$, $a = 4.6224$ Å and $c = 4.3059$ Å at room temperature). The N atoms on the octahedral sites of an *hcp* arrangement of Ni show virtually complete occupational order at ambient temperatures, which is preserved up to its thermal decomposition at $T \approx 600$ K. This behavior is in marked contrast to that of the isotypic iron nitride, ϵ-Fe_3N, which shows reversible partial disordering within the same range of temperatures. Possible reasons for the different behaviors of the two nitrides ϵ-Fe_3N and Ni_3N are discussed.

Introduction

The first reported synthesis of Ni_3N used Ni powder and flowing ammonia at 450 °C.[1] Another route starts from $Ni(NH_2)_2$ (obtained from Ni^{2+} and NH_2^- in liquid ammonia), which decomposes under intermediate formation of a probably amorphous Ni_3N_2, finally giving Ni_3N at about 200 °C.[2−4] Synthesis from Ni and N_2 has not yet been reported, and equilibrium pressures are expected to be very high.[1]

As with most other binary nitrides of 3d metals, Ni_3N can be regarded as a metallic interstitial compound:[5] these have an arrangement of metal atoms that is typical for a metal (mostly *fcc*, *hcp*, or *bcc*, not necessarily the same arrangement as for the pure metal) and N (or O, C, B, H) in interstices, in most cases on octahedral sites in a more or less ordered way. The metal−metal interactions are metal-like, and N is bonded covalently to the metal atoms. Bonding and electronic structure of interstitial nitrides are still a topic of many publications, also from a more or less chemical point of view.[6,7]

The crystal structure of Ni_3N[1,8] is based on an *hcp* arrangement of Ni in which N occupies octahedral sites, expanding the volume referring to nickel (the pure element is *fcc*) by 21%. The N atoms on the octahedral sites are ordered in such a way that the structure type of ϵ-Fe_3N[9] results. This has the space group symmetry $P6_322$ and unit cell dimensions increased by $3^{1/2} \times 3^{1/2} \times 1$ relative to the *hcp* cell (Figure 1). The ordered distribution of N may be understood in terms of a minimization of repulsive N···N interactions. Only corner sharing of octahedra NNi_6 is present.

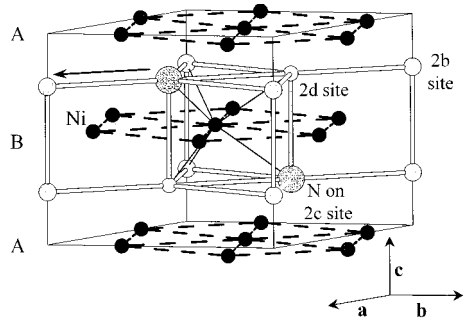

Figure 1. ϵ-Fe_3N-type structure of Ni_3N. Crystallographically different octahedral sites in $P6_322$ are labeled. Site 2c is the main site for N, and 2b is the main disorder site. The arrow indicates the reversible partial positional disordering of N at elevated temperatures as observed for ϵ-Fe_3N. The thick lines connecting the octahedral sites do not represent bonds but serve for orientation. The edges of one trigonal prism formed by a set of six octahedral sites as shown in Figure 5 are highlighted in gray. Broken lines indicate close-packed layers of Ni with |AB|AB| stacking. Ni atoms in addition to those located within the indicated unit cell are shown to clarify their *hcp* arrangement.

The ϵ-Fe_3N type or, for nonideal compositions and ordering of N, the "ϵ-type" structures[10,11] are quite common for binary nitrides of 3d metals.[5] However, in contrast to other ϵ-type carbides, nitrides, and oxides, including nitrides of earlier 3d elements, Ni_3N is restricted to its stoichiometric composition. There is only one report[12] that gives a composition of $Ni_3N_{1.16}$ for a hexagonal nickel nitride. However, its unit cell parameters are exactly those given elsewhere for the composition Ni_3N.[1−3,8] For other M−N systems (M = V−Co),[5] a considerable variation of unit cell parameters with composition is found. Therefore, it is probable that the composition $Ni_3N_{1.16}$,[12] deduced from chemical analysis (no details given), is wrong.

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Nickel is the last element of the 3d metals that forms interstitial nitrides. On going from Ni to Cu, one finds that the character of the only known copper nitride, Cu_3N,[13] changes: Cu_3N is a stoichiometric and semiconducting[14] compound and, like Ni_3N, has octahedral coordination of N. Together with the Cu atoms, the relatively open-packed *anti*-ReO_3-type structure results.

In the work presented here, Ni_3N was regarded as a model system to compare it with results obtained on the isotypic ϵ-Fe_3N.[15] For ϵ-Fe_3N at elevated temperatures, a reversible partial disordering of N on the octahedral sites was observed. By similar investigations on Ni_3N, the influence of the different metals on the ordering of N should result.

Experimental Section

Preparation, Chemical Analysis, X-ray Diffractometry, and Scanning Electron Microscopy. Severe problems in preparing large batches of Ni_3N by the reaction of Ni powder with flowing NH_3 are reported.[1] As a result, we chose a one-pot synthesis in supercritical ammonia including the formation of $Ni(NH_2)_2$ from $Ni(NH_3)_6Cl_2$ and $NaNH_2$ and its decomposition.

The starting material $Ni(NH_3)_6Cl_2$[16] was prepared by passing NH_3 gas (99.999%, Messer-Griesheim, Frankfurt, Germany) into a saturated aqueous solution of $NiCl_2 \cdot 6H_2O$ (purity > 97%, Merck, Darmstadt, Germany) along with some NH_4Cl (>99.8%, Merck). The product crystallized from this solution upon slow cooling and was filtered. $NaNH_2$ was prepared from Na (99.5 wt %, Merck) reacted with an excess of liquid NH_3 in a steel autoclave at 100 °C.[17]

$Ni(NH_3)_6Cl_2$ (6−7 g) and $NaNH_2$ (molar ratio 1:2.05) were mixed together in a glovebox under dry argon and filled in a high-pressure autoclave ($V = 15$ mL).[18] Especially sodium amide is very sensitive to moist air. The autoclave was filled with liquid NH_3 and heated to 100 °C within 3 h. Afterward, the temperature was increased to 250 °C by 30 °C/day, kept for 1 week at 250 °C ($p(NH_3) \approx 2$ kbar), and cooled to ambient temperatures by switching off the furnace.

After the NH_3 was released, the autoclave was opened. The gray reaction product (mostly a mixture of NaCl and Ni_3N) was stirred in ethanol, filtered, and washed with an aqueous solution of NH_4Cl/NH_3 (each 0.5 M), with water, and afterward with ethanol and ether. The washing liquids contained small amounts of Ni^{2+} and some very fine powder particles that passed the funnel. The overall yield was typically 60−70%.

X-ray diffraction patterns (Guinier camera FR552, Enraf-Nonius, Delft, The Netherlands, Cu$K\alpha_1$ radiation) showed the reported hexagonal cell with $a = 4.625(1)$ Å and $c = 4.306(1)$ Å. According to the X-ray patterns, some batches of pure Ni_3N were synthesized. However, some batches contained small amounts of Ni or NiO. Pure batches had an analytical N content (combustion analysis performed on an Elemental Analyzer 1106, Erba, Mailand, Italy) of 7.4% (theoretical content: 7.37%; ≤0.1% C and H were present). There are no hints in the literature that a considerable fraction of N can be replaced by O in interstitial nitrides of "late" 3d metals of Mn−Ni, including Ni_3N.

For reasons of comparison, we reacted $Ni(NH_3)_6Cl_2$ with $NaNH_2$ in the absence of additional NH_3 in steel autoclaves[19] with a similar temperature program. According to X-ray diffraction, the product contained Ni_3N with large amounts of Ni as an impurity. The reflections of both phases were very broad compared to those from the materials obtained in liquid resp. supercritical NH_3.

SEM investigations were done on a S510 electron microscope (Scientific Instruments Ltd., Cambridge, U.K.).

Table 1. Selected Technical Details and Results of Rietveld Refinements of Neutron Diffraction Data of Ni_3N Taken at Room Temperature[b]

no. of background parameters	12/6/6
no. of profile parameters	4/5/4
min d spacing used for refinement, Å	1.40/0.65/0.50
cell parameters, Å	
a	4.6224[a]
c	4.3059
positional parameter of Ni, x_{Ni}	0.3279(1)
occupancy ρ(2b)	0.029(2)
$100u$(Ni), Å^2	0.517(4)
$100u$(N), Å^2	0.476(7)
distances,[a] Å	
d(Ni−Ni)	2×2.625, 4×2.633, 2×2.677, 4×2.691
d(Ni−N(2c))	6×1.890
cell parameter, Å	
a(NiO)	4.1826
a(Ni)	3.5229
wR_P	1.9/1.7/1.4
$R_{Bragg}(Ni_3N, F^2)$, 1σ	2.9/3.2/3.7

[a] Standard deviations resulting from Rietveld refinements are not reported here. They are insignificantly small (<0.0001 Å for lattice parameters, <0.001 Å for distances), which is frequently observed.[35] [b] Structural model: $P6_322$ (No. 182), $Z = 2$; Ni on 6g, x_{Ni}, 0, 0; N on 2c, 1/3, 2/3, 1/4, occupancy $1 - \rho$(2b); N on 2b, 0, 0, 0; vacancy on 2d, 2/3, 1/3, 1/4. Data on different detector banks are given for $2\theta =$ 35, 90, and 145°, respectively.

High-Temperature Neutron Diffraction. For neutron diffraction experiments, we combined several batches of Ni_3N. The final sample was 3.3 g of Ni_3N containing small amounts of impurities of NiO and Ni. The powder was placed into a vanadium cylinder of $r = 4$ mm and $h = 40$ mm.

Thermal decomposition of Ni_3N under evolution of N_2 is irreversible and kinetically controlled[1] and proceeds faster in a vacuum than under N_2.[20] High N_2 pressures are to be expected in a closed cylinder, which may lead to its destruction. Therefore, we only loosely closed the container with a gold wire as a closure ring. This was done in such a way that the ring was the weakest point in the system, and N_2 pressure is released upon growing too high. This ensures that the sample is not in a vacuum at the beginning of the measurements.

Neutron diffraction experiments were performed at the time-of-flight diffractometer POLARIS installed at the pulsed spallation source ISIS in the Rutherford Appleton Laboratory. Diffraction data were recorded independently on three different detector banks located at about $2\theta =$ 35, 90, and 135° covering different ranges of d spacings. Increased sample temperatures were generated by a furnace constructed with a vanadium shield and a continuously evacuated sample chamber. A manometer was used to monitor possible evolution of N_2 from decomposition of the sample. Each temperature step of $T \geq 373$ K took about 1 h, including change in temperature and for reaching thermal equilibrium.

Rietveld Refinement. For Rietveld refinement, the GSAS package of programs[21] was used. These programs allow a simultaneous evaluation of the data recorded on the different detector banks.

The nuclear scattering lengths used were $b(Ni) = 1.03 \times 10^{-12}$ cm, $b(N) = 0.936 \times 10^{-12}$ cm, and $b(O) = 0.5805 \times 10^{-12}$ cm.[22] The background was fitted by a shifted Chebishev function for each multidetector bank. The reflection profiles were refined using an exponential pseudo-Voigt convolution as implemented in GSAS.

Absorption due to the sample and its environment was refined by a model for linear absorption. The coefficients for each bank were

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Table 2. Results of Rietveld Refinements of High-Temperature Neutron Diffraction Data Taken of Ni_3N (Further Technical Details Are Those Given for Data Taken at Ambient Temperatures (Table 2))

T, K	a,[a] Å	c,[a] Å	ρ(2b)	x_{Ni}	100u(Ni), Å^2	100u(N), Å^2	content of NiO[b]	content of Ni[b]	$R_{Bragg}(Ni_3N)$
298	4.6224	4.3059	0.029(2)	0.3279(1)	0.517(4)	0.476(7)	0.0132(3)	0.0266(4)	3.7/2.9/3.2
373	4.6264	4.3100	0.029(2)	0.3281(1)	0.658(5)	0.558(8)	0.0137(3)	0.0264(4)	2.8/3.2/4.1
423	4.6290	4.3126	0.029(2)	0.3282(1)	0.753(6)	0.629(8)	0.0148(3)	0.0257(4)	3.0/3.6/4.5
473	4.6317	4.3154	0.028(2)	0.3284(1)	0.859(6)	0.704(9)	0.0157(3)	0.0259(4)	3.9/3.8/4.8
498	4.6329	4.3171	0.023(2)	0.3286(2)	0.930(6)	0.777(9)	0.0187(3)	0.0254(5)	4.7/4.2/5.4
523	4.6339	4.3187	0.017(2)	0.3290(2)	0.984(7)	0.82(1)	0.0226(3)	0.0262(5)	5.7/3.8/5.8
548	4.6348	4.3202	0.011(2)	0.3292(2)	1.041(7)	0.86(1)	0.0251(3)	0.0419(6)	6.2/4.8/4.6
573	4.6363	4.3217	0.015(2)	0.3295(2)	1.082(9)	0.89(1)	0.0278(4)	0.199(1)	6.9/4.4/5.8
598	4.6380	4.3230	0.021(4)	0.3294(4)	1.12(2)	0.89(2)	0.0331(5)	0.460(2)	8.2/4.9/7.0

[a] Standard deviations resulting from Rietveld refinements are not reported here. They are insignificantly small (<0.0001 Å), which is frequently observed.[36] [b] Content referring to the number of Ni atoms.

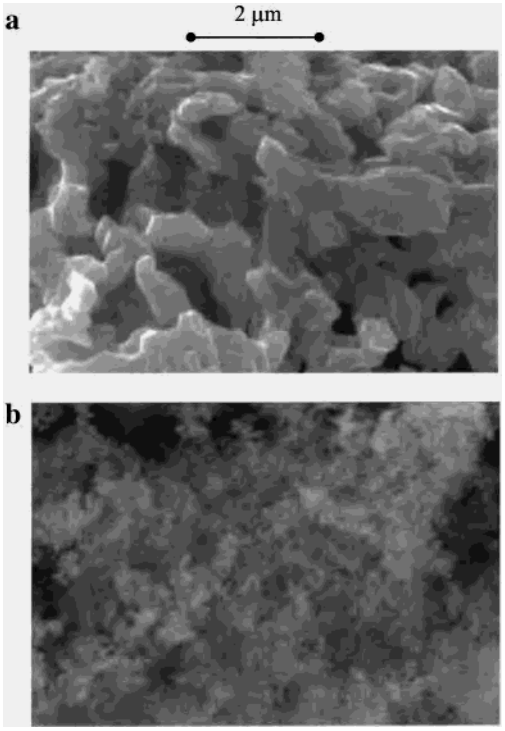

Figure 2. SEM photographs of Ni_3N (magnification = 16000×, black line corresponds to 2 μm): (a) material synthesized in supercritical NH_3 ($p(NH_3) \approx 2$ kbar) and (b) material from the direct reaction of $Ni(NH_3)_6Cl_2$ with $NaNH_2$. Each of the materials was produced at 250 °C.

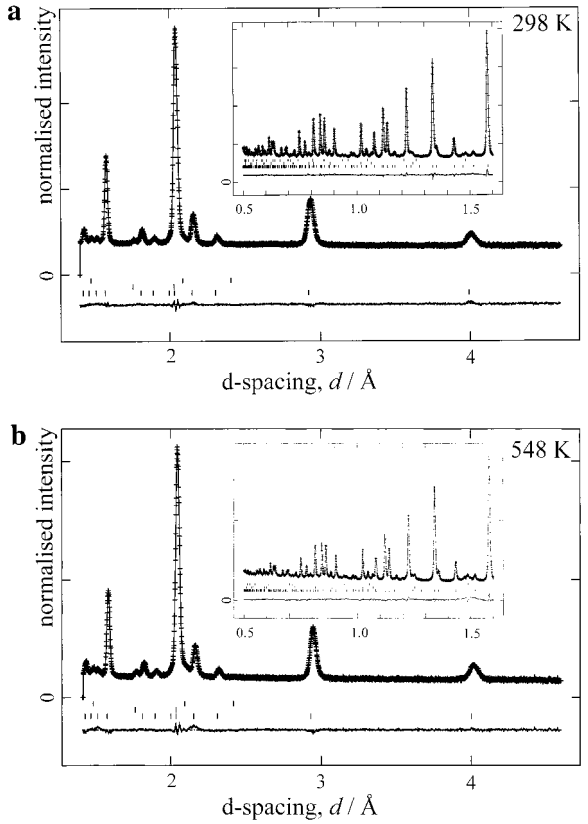

Figure 3. Neutron powder diffraction patterns of Ni_3N (POLARIS (ISIS), detector bank at $2\theta = 35°$): (a) ambient temperatures and (b) 548 K. The insets show the 0.5Å < d < 1.6Å range of the backscattering bank ($2\theta = 135°$). Reflection markers: NiO, Ni, and Ni_3N (from the top).

determined from a simultaneous refinement of data taken at ambient temperatures and 548 K. The obtained coefficients were used as fixed values for all other measuring temperatures.

The nuclear structure used for refinement is based on the ϵ-Fe_3N ideal structure with fixed composition Ni_3N and with allowance for partial disorder of N using a second octahedral site (top of Table 2). Further on, this is called a "disorder" site. It assumes a disorder similar to that found for ϵ-Fe_3N at elevated temperatures.

The presence of NiO and Ni impurities in the sample of Ni_3N was considered by multiphase refinements. Thermal displacement parameters of Ni and O were fixed to those of Ni and N of the Ni_3N phase, respectively, except for the measurements taken at 573 and 598 K. For these, the metallic Ni phase was present in larger amounts and a separate thermal displacement parameter was considered. Furthermore, for all phases, we used one set of profile parameters for each pattern from a particular detector bank.

Results

SEM. Figure 2 shows SEM images of Ni_3N synthesized (a) in supercritical ammonia and (b) by direct solid-state reaction of powdered $Ni(NH_3)_6Cl_2$ with $NaNH_2$. Clearly, the first material is more compact. Transport phenomena within the NH_3 solvent may be responsible for the increased particle size, although attempts to grow single crystals of Ni_3N from NH_3 using various mineralizers including amides have not been successful.[4]

In contrast, the solid-state reaction is difficult to control. Solid $NaNH_2$ seems to act partially as a reductant to Ni^{2+}, before the amide is formed. Ni_3N, once formed, should not decompose to Ni at the reaction temperatures.

Crystal Structure. The high-temperature neutron diffraction experiments were started with a measurement taken at ambient temperatures (Figure 3). Rietveld refinement indicates that the crystal structure is virtually ideal with respect to the distribution of N. The occupied octahedral sites correspond to the position of N in the ϵ-Fe_3N ideal structure. Only about 3% of the N atoms are found on the disorder site 2b (Table 2). The impurities of Ni and NiO are less than 5% (referring to Ni atoms) of the sample.

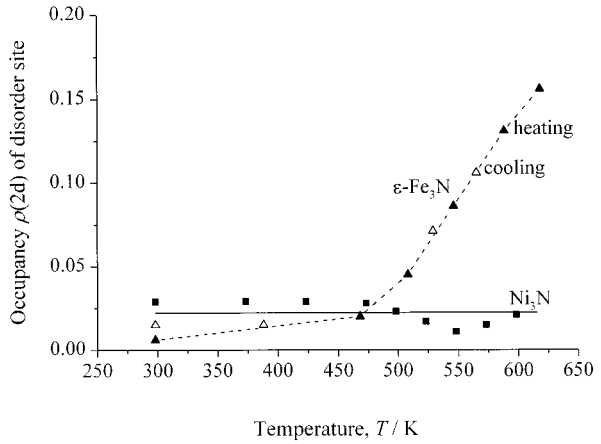

Figure 4. Occupancy of N on the disorder site 2b in $P6_322$ as a function of temperature for Ni_3N and ϵ-Fe_3N.[15] Lines are not fitted and only give the trend.

As the sample temperature is increased stepwise, the diffraction patterns visually show no changes up to 548 K (Figure 3). Starting from 573 K, the intensity of the reflections for the metallic Ni phase becomes stronger with increasing temperatures. This is accompanied by an increase in pressure in the dynamically evacuated sample chamber. Obviously, Ni_3N decomposes under formation of Ni and N_2. Up to the maximum sample temperature of 598 K, the Ni content increases strongly whereas the NiO content remains unchanged (Table 2). The reported phase contents are, however, only averages during the data collection period. Cubic Ni_4N[20,23] was not observed as an intermediate phase.

Rietveld refinement (Table 2) of the high-temperature diffraction data does not show significant changes in the distribution of N with increasing temperatures. These results have to be compared with what has been observed for ϵ-Fe_3N.[15] In Figure 4, the occupancy of the disorder site 2b by N is plotted for ϵ-Fe_3N and Ni_3N. In contrast to Ni_3N, significant disorder is found for ϵ-Fe_3N with a maximum measuring temperature of about 600 K. For ϵ-Fe_3N, the significant disorder is readily detected from visual inspection of the diffraction patterns.

Order−disorder phenomena in interstitial compounds can be regarded as being driven by configurational entropy, which, at increased temperatures, may overcome a state of lowest enthalpy leading to disorder.[24] The comparison of the data of the isotypic compounds obviously indicates that repulsive interactions between the N atoms, the reason for the ordered occupation of one-third of the octahedral sites, may be higher in Ni_3N than in isotypic ϵ-Fe_3N.

A physical reason for this may be the shorter interatomic distances of N···N in Ni_3N compared to those in ϵ-Fe_3N: moving with increasing atomic numbers of the metals from Fe_3N to Ni_3N, one observes a considerable contraction of the unit cell parameters (from 4.694 to 4.622 Å for *a*, and from 4.375 to 4.306 Å for *c*). In the simplest models, the interactions of N···N (like some kind of Coulomb repulsion between ions, but the main mechanisms governing the pair interactions for N in intersitial compounds are probably the so-called strain-induced interactions)[24,25] should increase as their distances are reduced with decreasing unit cell parameters. Therefore, the disordering of N should be more difficult for Ni_3N than for ϵ-Fe_3N.

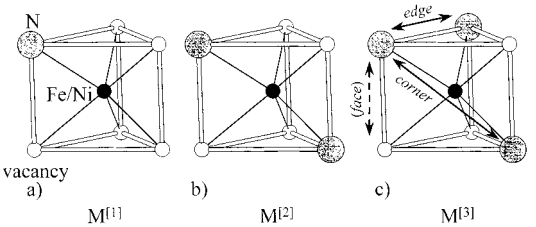

Figure 5. (a−c) Coordination spheres $M^{[1]}$, $M^{[2]}$, and $M^{[3]}$ relevant for the discussion of the disordering of N in ϵ-Fe_3N and Ni_3N. The first three closest possible distances of N···N are depicted, which correspond to NM_6 octahedra sharing common corners (distance in Ni_3N at ambient temperatures: 3.43 Å), edges (2.67 Å) and faces (2.15 Å). Face sharing does not occur for the three coordination spheres shown here.

This can be examined more closely on a local scale. In an *hcp* arrangement of M, each M is "coordinated" by six octahedral sites forming a trigonal prism. In the ϵ-Fe_3N-type structure, two of these sites are occupied by N. This is illustrated in Figure 5b and shows that NM_6 octahedra share only corners. This coordination will be called $M^{[2]}$ as suggested to assign coordination numbers.[26]

Statistical considerations show that the occupation of site 2b, as occurring in ϵ-Fe_3N at elevated temperatures, leads to a partial formation of the environments $Fe^{[1]}$ and $Fe^{[3]}$ depicted as $M^{[1]}$ (Figure 5a) and $M^{[3]}$ (Figure 5c), respectively. Mössbauer spectroscopy is able to detect separate signals for the different environments and shows that only $Fe^{[2]}$ is present for slowly cooled ϵ-Fe_3N; $Fe^{[1]}$ and $Fe^{[3]}$ are additionally observed for samples quenched from elevated temperatures.[27] The environment $Fe^{[3]}$ is accompanied by the presence of octahedra NM_6 sharing common edges. The disordering can than be described on a local scale as a "disproportionation" $2Fe^{[2]} \rightleftarrows Fe^{[1]} + Fe^{[3]}$. Furthermore, $Fe^{[3]}$ is also needed to achieve N contents higher than that of Fe_3N, i.e., ϵ-Fe_3N_{1+x} ($x \leq 0.48$).[8,28] ζ-Fe_2N[29,30] contains only $Fe^{[3]}$.

Ni_3N, however, has no significant range of homogeneity (Ni_3N_{1+x} is restricted to $x = 0$). This is in contrast to other hexagonal interstitial compounds with "ϵ-type" structure,[5] including the ϵ-type nitrides of the metals Fe and Co,[31,32] followed by Ni in the periodic table. This means that in Ni_3N, both processes which would generate $Ni^{[3]}$ (N contents higher in composition than Ni_3N and disordering of N in Ni_3N) are somehow suppressed. The formation of an environment $Ni^{[3]}$ can only be achieved by NNi_6 octahedra sharing common edges. This seems to be unfavored for nickel, e.g., because of the geometric reasons as given above.

For simplicity, we discussed here the ordering of N in terms of deviations from the ϵ-Fe_3N ideal structure and not in terms of order parameters. The latter has been done previously[11,28,33] for different ϵ-type nitrides of 3d metals using concepts and formalisms[10,11] and will be done in full together with data from structurally similar manganese nitrides.[34]

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Finally, it should be pointed out that the higher stability of ordering in Ni_3N compared to that in ϵ-Fe_3N seems to be in contrast to its lower stability toward thermal decomposition under loss of N_2. ϵ-Fe_3N_{1+x} starts to decompose at about 670−770 K,[35] whereas Ni_3N begins at 570 K as observed here. This shows that the ordering energy is only a small part of the overall energy of formation of these nitrides.

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Supporting Information Available: X-ray crystallographic file in CIF-format for the Rietveld refinement of the high-temperature neutron diffraction data on Ni_3N. This material is available free of charge via the Internet at http://pubs.acs.org.

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