Ternary Metastable Nitrides ϵ -Fe₂TMN ($TM = \text{Co, Ni}$): High-Pressure, High-Temperature Synthesis, Crystal Structure, Thermal Stability, and Magnetic PropertiesKai Guo,[†] Dieter Rau,[‡] Lorenzo Toffoletti,^{†,§} Carola Müller,^{†,⊥} Ulrich Burkhardt,[†] Walter Schnelle,[†] Rainer Niewa,[‡] and Ulrich Schwarz^{*,†}[†]Max-Planck-Institut für Chemische Physik fester Stoffe, Nöthnitzer Straße 40, 01187 Dresden, Germany[‡]Institut für Anorganische Chemie, Universität Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart, Germany

S Supporting Information

ABSTRACT: High-pressure, high-temperature synthesis gives access to ternary metastable nitrides ϵ -Fe₂TMN ($TM = \text{Co, Ni}$) as bulk materials for the first time. Both ϵ -Fe₂CoN and ϵ -Fe₂NiN crystallize isostructural to ϵ -Fe₃N as evidenced by X-ray powder diffraction data. The lattice parameters of the new compounds are slightly smaller than those of ϵ -Fe₃N owing to the reduced atomic radii of the metal atoms. Energy-dispersive X-ray spectroscopy of metallographic samples show homogeneous metal ratios corresponding to compositions Fe_{1.99(6)}Co_{1.01(6)}N and Fe_{1.97(2)}Ni_{1.03(2)}N. Extended X-ray absorption fine spectra indicate that cobalt and nickel occupy iron positions. Thermal analysis measurements reveal decomposition of both ternary nitrides above 920 K. ϵ -Fe₂CoN disintegrates into N₂ and iron–cobalt alloy, while ϵ -Fe₂NiN decays into N₂, iron–nickel alloy as well as α -Fe. The replacement of iron by cobalt or nickel essentially lowers the saturation magnetization from roughly 6.0 μ_B /f.u. for ϵ -Fe₃N to nearly 4.3 μ_B /f.u. for ϵ -Fe₂CoN and 3.1 μ_B /f.u. for ϵ -Fe₂NiN. In parallel, the Curie temperature decreases from 575(3) K for ϵ -Fe₃N to 488(5) K for ϵ -Fe₂CoN and 234(3) K for ϵ -Fe₂NiN. Calculations of the formation enthalpies illustrate that the phases ϵ -Fe₂TMN ($TM = \text{Co, Ni}$) are thermodynamically unfavorable at ambient conditions which is consistent with our experimental observations. The substitution of one Fe by Co (Ni) yields one (two) more electrons per formula unit which reduces the magnetic interactions. First-principles analysis indicate that the replacement has a negligible influence on the electron occupation numbers and spin moments of the N and unsubstituted Fe sites, but decreases the local magnetic moments on the substituted Fe positions because the extra electrons occupy the minority-spin channel formed by states of the TM atoms.

KEYWORDS: nitride materials, transition-metal substitution, high-pressure synthesis, magnetization, first-principles calculations

■ INTRODUCTION

Iron-rich nitrides play an essential role in the surface hardening of steel, a process which is applied worldwide to a significant fraction of the manufactured work pieces in order to improve fatigue endurance and corrosion resistance. Moreover, the discovery of advantageous magnetic properties in the binary iron nitrides (α'' -Fe₁₆N₂, γ' -Fe₄N and ϵ -Fe₃N) motivated numerous both experimental^{1–4} and theoretical studies^{5–8} for potential applications in high-density data recording. Many efforts were devoted to modifying or improving the magnetic properties by substituting iron with other transition metals.^{9,10} This holds especially for γ' -Fe₄N, forming a simple perovskite-type crystal structure and exhibiting outstanding chemical stability, which qualifies the compound as a suitable object for both fundamental research and industrial exploitation. Berthollide compounds with the general formula Fe_{4–x}M_xN ($x < 1$) and daltonide compounds with chemical formula Fe₃MN have been reported for almost all post-transition metals^{11–17} and some triel (main-group III) elements.^{18–21} Upon substitution, all metal atoms M except Mn and Co prefer to replace the Fe positions that are not coordinated to N

because of the relative affinity of M and Fe for nitrogen and, more important, the differences in atomic size.¹³

In contrast to cubic γ' -Fe₄N, ideal ϵ -Fe₃N adopts an atomic pattern in which the Fe atoms are in a hexagonal closest-packed arrangement. In the idealized crystal structure, the N atoms occupy one-third of the octahedral voids in an ordered fashion, resulting in layers of NFe_{6/2} octahedra sharing common corners.²² Figure 1 depicts the idealized crystal structure with space group $P6_322$ in which the Fe atoms occupy Wyckoff position 6g and the N atoms are located at Wyckoff position 2c. Each iron atom is coordinated by two nearest-neighbor N atoms.

ϵ -Fe₃N exhibits expedient magnetic properties and good thermal stability, thereby attracting extensive attention in recent years.^{4,23–25} It was realized that the local magnetic moments of Fe in ϵ -Fe₃N were very close to those of the face-centered Fe atoms in γ' -Fe₄N. This finding is attributed to the similarity of

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Figure 1. Unit cell of the idealized ϵ -Fe₃N crystal structure ($P6_322$, $Z = 2$, $a = 4.6982(3)$ Å, $c = 4.3789(3)$ Å).²² Replacement of one iron per unit cell by a TM atom ($TM = \text{Co}$ or Ni) leaves five options for the second TM atom (see below).

the chemical environment in both compounds.⁵ Altering the nitrogen content^{23,26} or replacing Fe atoms by other transition metals TM ^{27–29} significantly influences the magnetic properties of ϵ -Fe₃N. With the exception of a few phases ($\text{Fe}_{3-x}\text{TM}_x\text{N}$, $x < 1$) in the form of fine particles, no ternary substitution phases like Fe_2TMN have been explored because of difficulties in the synthesis, evidenced by the observation that the replacement of iron by other transition metals induces the formation of impurity phases in the experimental process.^{27,28} In this sense, obtaining pure ϵ -phase compounds Fe_2TMN is a principle problem for further performance study. High-pressure, high-temperature (HPHT) synthesis provides a feasible path for preparing metastable iron nitride compounds since external forces are provided to cross the potential barrier and to modify the reaction path.^{30,31}

In the present paper, the ternary metastable nitrides ϵ -Fe₂TMN ($TM = \text{Co}, \text{Ni}$) have been synthesized via HPHT treatments for the first time. The crystal-structure determinations for as-obtained samples are based on X-ray powder diffraction data (XRPD). Phase homogeneity and compositions are studied by metallographic characterization and energy-dispersive X-ray spectroscopy (EDXS) in combination with chemical analyses (CA), respectively. Extended X-ray absorption fine spectra (EXAFS) are performed to probe the coordination environments of the metal atoms. Additionally, thermal stability is examined by thermogravimetry combined with differential thermal analysis (TG/DTA) and succeeded by calculations of the formation enthalpy according to the chemical reaction

Magnetization data are collected as a function of applied magnetic field and temperature in order to understand the magnetic properties of the new compounds ϵ -Fe₂CoN and ϵ -Fe₂NiN. Calculations of the density of states (DOS) and the local spin moments via first-principles computations considering spin polarization offer a profound understanding of the experimental results.

■ EXPERIMENTAL SECTION

High-Pressure, High-Temperature Synthesis. Microcrystalline samples of ζ -Fe₂N are prepared as starting materials for the HPHT reactions. Iron powder (99.9%, Johnson Matthey/Alfa) is treated with flowing NH_3 (99.98% NH_3) at 708 K, using a flow of 20 sccm (sccm is the gas volume flow in cm^3 under standard conditions, 1.013 bar, per minute) in a tube with an inner diameter of approximately 5 cm. Subsequently, transition-metal powders (Co, 99.9985%, Alfa; Ni,

99.99%, Alfa) are mixed with ζ -Fe₂N for 15 min in the ratio 1:1 in an argon-filled glovebox (H_2O and O_2 levels below 0.1 ppm). The mixtures (~30 mg) are put into crucibles machined from hexagonal boron nitride and placed in graphite tubes being enclosed in zirconia sleeves. These assemblies are transferred into MgO/Cr₂O₃ octahedra with an edge length of 14 mm. In the subsequent HPHT treatment, high pressures are generated in a Walkertype module, which is essentially a two-stage assembly with a central octahedral pressure chamber. The MgO/Cr₂O₃ octahedra are used in order to achieve quasihydrostatic pressure-distribution. Temperature is controlled by resistive heating of the graphite sleeve containing the sample crucible. Pressure and temperature calibration is completed prior to the HPHT treatments by analyzing the resistance changes of bismuth and lead and measuring setups equipped with a thermocouple, respectively. A typical HPHT synthesis requires pressure increase up to 15(2) GPa in 4.5 h, holding at the maximal pressure for 1.5 h followed by pressure decrease within 13 h. At the maximal pressure, the mixtures of ζ -Fe₂N and transition metal TM ($TM = \text{Co}, \text{Ni}$) are heated to 1473(200) K for 30 min and subsequently quenched to ambient temperature by switching off the heating current. The as-obtained ingots show metallic luster and conchoidal fracture.

Characterization. XRPD data are collected on a Huber G-670 diffractometer (Co $K_{\alpha 1}$ radiation, $\lambda = 1.788965$ Å). The lattice parameters are calculated using the software package WinCSD³² with silicon powder as internal standard. Composition and homogeneity are examined by metallographic studies with EDXS. Chemical analysis on O, N and H are performed by means of the carrier gas hot extraction (CGHE) method on a LECO analyzer TCH-600. EXAFS is realized at HASYLAB (Hamburg) on beamline C at room temperature. The measurements are carried out at the K edges of iron (7112 eV), cobalt (7709 eV) and nickel (8333 eV) in transmission mode. TG/DTA measurements are performed in argon atmosphere with a NETZSCH STA 449 C instrument using heating rates between 5 and 15 K min^{-1} in order to find the optimal combination of resolution and signal intensity. The magnetic properties of the samples are measured with a SQUID magnetometer (MPMS XL-7, Quantum Design) in the temperature range between 1.8 and 600 K and magnetic fields up to 7 T.

Calculations of the Electronic Structure. First-principles quantum mechanical calculations are performed within the CASTEP (Cambridge Serial Total Energy Package) code, which is based on density-functional theory (DFT) using the plane-wave pseudopotential method.³³ The electron-ion interactions are described by employing the preferred ultrasoft pseudopotential (USPP) which allows for calculations with a lower energy cutoff.³⁴ The exchange-correlation potential is treated in the scheme of the generalized gradient approximation (GGA) developed by Perdew-Burke-Ernzerhof (PBE).^{35,36} Special k -points with a $6 \times 6 \times 6$ grid in the Brillouin zone and an energy cutoff of 500 eV are chosen for all compounds ϵ -Fe₂TMN ($TM = \text{Co}, \text{Ni}$). In view of the high magnetization in ϵ -Fe₃N, spin polarization is considered. Upper limits for energy convergence tolerance, stress, ionic replacement and force on the atoms are selected to amount to 5.0×10^{-6} eV/atom, 0.01 eV Å⁻¹, 5×10^{-4} Å, and 0.02 GPa, respectively.

In the idealized crystal structure of the ϵ -phase, the metal atoms are arranged in the motif of a slightly distorted hexagonal closest packing (hcp) structure. Nitrogen atoms occupy voids of corner-sharing iron octahedra (Wyckoff position 2c in space group $P6_322$). Figure 1 shows the crystal structure of such an ideal ϵ -phase, in which each metal atom has two nearest-neighbor N atoms. To establish models for the atomic arrangement of the new compounds ϵ -Fe₂TMN ($TM = \text{Co}$ or Ni), two out of six Fe atoms are replaced by Co or Ni atoms ($Z = 2$). Replacing one Fe by a TM atom, there remain five options for the second TM atom. Calculations of the ground-state structure (Table 1) reveal a minimum of the total energy for configurations in which the TM atoms are located on the trans-position in half of the nitrogen-centered octahedra and in cis-position in the remaining half. After optimization of the atomic positions, the formation enthalpy, the density of states (DOS) and the magnetic moments are carefully investigated.

Table 1. Differences in Total Energies (eV) upon Substitution of One Iron Atom Per Formula Unit (two per unit cell) with Transition Metal Atoms $TM = \text{Co}$ or Ni Yielding Ternary Phases $\epsilon\text{-Fe}_2\text{TMN}$ Adopting the Motif of $\epsilon\text{-Fe}_3\text{N}$ ^a

	Fe2 = Fe3	Fe4 = Fe5	Fe6
$\epsilon\text{-Fe}_2\text{CoN}$	0	−0.06	−0.02
$\epsilon\text{-Fe}_2\text{NiN}$	0	−0.15	−0.11

^aBy occupying the position of, for example, Fe1 with Co or Ni, the degeneracy of the iron sites is partially lifted. Fe2 and Fe3 remain equivalent, and the same holds for Fe4 and Fe5 since $d(\text{Fe1}-\text{Fe4}) = d(\text{Fe1}'-\text{Fe5}')$ and $d(\text{Fe1}-\text{Fe5}) = d(\text{Fe1}'-\text{Fe4}')$.

RESULTS AND DISCUSSION

The results evidence that metastable nitrides are well accessible by HPHT techniques. Under high-pressure conditions, the nitrogen content can be well-preserved with a diffusion controlled process triggered by high temperatures.^{37–39} Figure 2 shows the XRPD patterns for the starting material $\zeta\text{-Fe}_2\text{N}$

Figure 2. XRPD for (a) the starting material $\zeta\text{-Fe}_2\text{N}$, (b) the products $\epsilon\text{-Fe}_2\text{CoN}$ and $\epsilon\text{-Fe}_2\text{NiN}$. Silicon powders are used as internal standards for determinations of lattice parameters. Weak reflections originating from small BN impurities (crucible material) are indicated by asterisks.

and products $\epsilon\text{-Fe}_2\text{CoN}$ and $\epsilon\text{-Fe}_2\text{NiN}$ after HPHT treatments. The calculated lattice parameters of $\zeta\text{-Fe}_2\text{N}$ ($a = 5.5242(4) \text{ \AA}$, $b = 4.8301(4) \text{ \AA}$, $c = 4.4251(3) \text{ \AA}$) are in good agreement with earlier results.⁴⁰ For the ternary substituted products, positions and intensities of the diffraction peaks indicate atomic patterns being isostructural to $\epsilon\text{-Fe}_3\text{N}$ (ICSD_79983).²² Shifts of the line positions in direction of higher angles suggest smaller unit cells in agreement with smaller atomic radii of the TM atom

(Co: 1.252 $\text{\AA}$, Ni: 1.244 $\text{\AA}$) in comparison to iron (Fe: 1.260 $\text{\AA}$).⁴¹ Lattice parameters of $\epsilon\text{-Fe}_2\text{CoN}$ and $\epsilon\text{-Fe}_2\text{NiN}$ are listed in Table 2 together with the values obtained by electronic structure calculations.

The surface morphology and phase homogeneity of as-synthesized samples is studied by optical microscopy (Figure 3). No obvious grain boundaries are observed after polishing the samples. Uniform composition of the samples is also evidenced by EDXS results (Table 3). The compositions determined in three independent analyses yield atomic ratios Fe:Co of 1.99(6):1.01(6) and Fe:Ni of 1.97(2):1.03(2). Chemical analysis is carried out to quantify the nitrogen contents as well as to search for oxygen and hydrogen impurities. The measured contents of hydrogen are below the limits of detection (0.02 wt %). Contents of nitrogen as well as oxygen impurities are determined by 3 independent measurements to evaluate average values. Combining the results leads to experimental compositions $\text{Fe}_{1.99(6)}\text{Co}_{1.01(6)}\text{N}_{0.91(4)}$ and $\text{Fe}_{1.97(2)}\text{Ni}_{1.03(2)}\text{N}_{1.07(6)}\text{O}_{0.03(1)}$. Within experimental error, these findings are consistent with the idealized compositions $\epsilon\text{-Fe}_2\text{CoN}$ and $\epsilon\text{-Fe}_2\text{NiN}$, respectively, which will be used in the following discussions.

The coordination environments of the transition metals in the phases $\epsilon\text{-Fe}_2\text{CoN}$ and $\epsilon\text{-Fe}_2\text{NiN}$ are investigated by EXAFS measurements with synchrotron radiation. Figure 4 shows the normalized X-ray absorption spectra of $\epsilon\text{-Fe}_2\text{CoN}$ and $\epsilon\text{-Fe}_2\text{NiN}$ at the transition-metal K edges at room-temperature.

For comparison, all edges are shifted to 0 eV, and normalized EXAFS data of references like Fe (body-centered cubic, bcc), Co (face-centered cubic, fcc) and Ni foil (fcc) are provided. The similarity of the data for elemental Co and Ni evidence similar distributions of peaks in E - as well as k -space which are attributed to the realization of the same fcc metal substructure with only a tiny discrepancy in cell volume.^{42,43} The essential differences in the patterns of Fe are assigned to dissimilar coordination environments in the body-centered cubic arrangement.⁴⁴ In the case of $\epsilon\text{-Fe}_2\text{TMN}$ ($TM = \text{Fe}, \text{Co}, \text{and Ni}$), all EXAFS data are very similar, indicating that the transition metals in these compounds have the same coordination environments. Minute shifts of the maxima result from subtle differences of the interatomic distances. Quantitative analyses by calculating the Fourier transforms are in progress to reveal coordination numbers, interatomic distances and local environments.

In the band-structure calculations, Fe1 and Fe5 are replaced by Co or Ni atoms in the structure models for $\epsilon\text{-Fe}_2\text{CoN}$ and $\epsilon\text{-Fe}_2\text{NiN}$, respectively (Figure 1, Table 1). Subsequently, atomic positions and lattice parameters were relaxed by geometry optimization. In comparison with the experimental values, the lattice parameters from electronic structure calculations are slightly underestimated with GGA as the exchange-correlation potential (Table 2). The deviations from the experimental values are smaller than 2% and fall, thus, certainly into the range that can be accepted for further calculations of the electronic and magnetic properties. In order to model the thermodynamic stability of $\epsilon\text{-Fe}_2\text{CoN}$ and $\epsilon\text{-Fe}_2\text{NiN}$, formation enthalpies according to the chemical reaction 1 are calculated in eq 2.

$$\Delta E(\epsilon\text{-Fe}_2\text{TMN}) = E(\epsilon\text{-Fe}_2\text{TMN}) - E(\zeta\text{-Fe}_2\text{N}) - E(TM) \quad (2)$$

Table 2. Lattice Parameters of Phases ϵ -Fe₂TN and Formation Enthalpies of the Chemical Reactions ζ -Fe₂N + TM $\rightarrow$ ϵ -Fe₂TMN (see 1) for TM = Fe, Co, Ni

	lattice parameters (Å)			formation enthalpy (0 GPa)(kJ/mol)
	electronic structure calculations	experimental	deviation (%)	
Fe ₂ CoN	$a = 4.621$	$a = 4.6759(5)$	-1.2	10.1
	$c = 4.302$	$c = 4.3776(5)$	-1.7	
Fe ₂ NiN	$a = 4.609$	$a = 4.6698(4)$	-1.2	12.0
	$c = 4.335$	$c = 4.3699(4)$	-0.8	
ϵ -Fe ₃ N	$a = 4.623$	$a = 4.6982(3)^{22}$	-1.6	-16.3
	$c = 4.300$	$c = 4.3789(4)^{22}$	-1.8

Figure 3. Typical optical micrographs of (a) ϵ -Fe₂CoN and (b) ϵ -Fe₂NiN prepared by HPHT reactions.**Table 3.** Compositions Detected by EDXS in Various Areas That Are Shown in Figure 3

nominal composition	EDXS	avg composition
ϵ -Fe ₂ CoN	Fe _{1.931} Co _{1.069} N _x	Fe _{1.99(6)} Co _{1.01(6)} N _x
	Fe _{2.020} Co _{0.980} N _x	
	Fe _{2.019} Co _{0.981} N _x	
ϵ -Fe ₂ NiN	Fe _{1.976} Ni _{1.024} N _x	Fe _{1.97(2)} Ni _{1.03(2)} N _x
	Fe _{1.952} Ni _{1.048} N _x	
	Fe _{1.973} Ni _{1.027} N _x	

Here, $\Delta E(\epsilon\text{-Fe}_2\text{TMN})$ expresses the formation energies of products $\epsilon\text{-Fe}_2\text{TMN}$ at zero temperature, and $E(\epsilon\text{-Fe}_2\text{TMN})$, $E(\zeta\text{-Fe}_2\text{N})$, $E(\text{TM})$ refer to the total energies for $\epsilon\text{-Fe}_2\text{TMN}$, $\zeta\text{-Fe}_2\text{N}$, and elemental transition metal, respectively. At $T = 0$ K and $P = 0$ Pa, the formation enthalpy ΔH corresponds to the calculated energy, i.e., $\Delta H(\epsilon\text{-Fe}_2\text{TMN}) = \Delta E(\epsilon\text{-Fe}_2\text{TMN})$ when the zero-point vibration contribution is neglected.⁴⁵ Within this approximation, the formation enthalpy for the well-characterized compound $\epsilon\text{-Fe}_3\text{N}$ is negative, indicating that the calculations are reasonable. Positive values of the formation enthalpy for $\epsilon\text{-Fe}_2\text{CoN}$ and $\epsilon\text{-Fe}_2\text{NiN}$ imply that they are metastable phases at ambient pressure. Figure 5 depicts the pressure-dependent evolution of the enthalpy differences for $\epsilon\text{-Fe}_2\text{CoN}$ and $\epsilon\text{-Fe}_2\text{NiN}$ and for competing phases. The ternary phases $\epsilon\text{-Fe}_2\text{TMN}$ remain less stable by ~ 16 kJ/mol than $\zeta\text{-Fe}_2\text{N}$ plus TM in the pressure range up to 10 GPa. This is taken as an indication that the reactions are driven by temperature rather than pressure. However, high pressure does play an important role in the synthesis by preserving the nitrogen content. In this sense, HPHT conditions, such as 15(2) GPa and 1473(200) K, support the formation of compounds $\epsilon\text{-Fe}_2\text{TMN}$ by stabilizing the ternary products and by suppressing any loss of nitrogen in the synthesis.

The estimation given above is supported by the experimental findings of TG/DTA measurements at ambient pressure and elevated temperatures (Figure 6). For both $\epsilon\text{-Fe}_2\text{CoN}$ and $\epsilon\text{-Fe}_2\text{NiN}$, the mass losses above 750 K as evidenced by the TG curve strongly suggest a decomposition reaction involving the loss of nitrogen. Quantitative mass losses of 6.78% and 7.75%

Figure 4. Selected EXFAS measurements close to the transition-metal K edges of $\epsilon\text{-Fe}_3\text{N}$, $\epsilon\text{-Fe}_2\text{CoN}$ and $\epsilon\text{-Fe}_2\text{NiN}$ at room-temperature together with the absorption spectra of elemental Fe, Co and Ni foils as reference. (a) For the sake of comparison, all the Fe (7112 eV), Co (7709 eV), and Ni (8333 eV) K edges are moved to 0 eV in energy space, (b) resulting oscillations in k space ($k = ((2m(E - E_0))/\hbar^2))^{1/2}$).

are identified for $\epsilon\text{-Fe}_2\text{CoN}$ and $\epsilon\text{-Fe}_2\text{NiN}$, respectively, which are in good agreement with the nitrogen contents of the compounds determined by chemical analysis ($\epsilon\text{-Fe}_2\text{CoN}$, $6.92 \pm 0.32\%$; $\epsilon\text{-Fe}_2\text{NiN}$, $8.08 \pm 0.45\%$). DTA curves demonstrate that these mass losses result from distinguishing processes. A pronounced exothermic peak at 855 K in Figure 6a indicates that the disintegration of $\epsilon\text{-Fe}_2\text{CoN}$ is exothermic. XRPD measurements (see the Supporting Information) after the TG/DTA measurements show the formation of iron–cobalt alloy and γ' -phase nitride at 820 K, as well as the formation of pure iron–cobalt alloy at 920 K for $\epsilon\text{-Fe}_2\text{CoN}$. Thus, the

Figure 5. Calculated values for the enthalpy as a function of pressure for (a) ϵ -Fe₂CoN and (b) ϵ -Fe₂NiN and some competing phases.

decomposition from ϵ -Fe₂CoN into γ' -phase nitride and further into iron–cobalt alloy occurs in the same temperature range. However, in the case of ϵ -Fe₂NiN, an exothermic peak at 831 K and an endothermic peak at 884 K are observed. Only γ' -phase nitride is identified besides the residual ϵ -phase at 820 K. Iron–nickel alloy and α -Fe are found when the temperature is increased above 920 K. Thus, it is deduced that the first exothermic effect can be attributed to the formation of γ' -phase nitride and the second endothermic peak originates from the decomposition of γ' -phase nitrides into nitrogen-poorer Fe–Ni alloys and α -Fe. Both ϵ -Fe₂CoN and ϵ -Fe₂NiN remain metastable until 750 K at ambient pressure.

The magnetic properties of ϵ -Fe₂CoN and ϵ -Fe₂NiN are characterized by isothermal magnetization curves $M(\mu_0 H)$ at 1.8 K up to applied fields $\mu_0 H_{\max} = 7.0$ T and as a function of temperature $\sigma(T)$ ($1.8 \text{ K} < T < 600 \text{ K}$) in applied fields $\mu_0 H = 0.1$ and 1.0 T (Figure 7). The characteristic of rapid increase of the magnetization below a certain (Curie) temperature and the large value of M at low temperatures indicates ferromagnetic ordering of both compounds (Figure 7a, c). The absence of significant hysteretic loops in the magnetization isotherms at $1.8 \text{ K} \ll T_C$ classifies ϵ -Fe₂CoN and ϵ -Fe₂NiN as soft ferromagnetic materials, similar to the iron nitrides ϵ -Fe₃N_{1+x}.²³ The Curie temperatures T_C are determined from the linear extrapolation of the steepest slope of $M(T)$ in 0.1 and 1 T to the paramagnetic value (Figure 7b, d). ϵ -Fe₃N exhibits a large saturation moment of about $6 \mu_B/\text{f.u.}$ and a Curie point of $575(3) \text{ K}$.⁴ For ϵ -Fe₂CoN, the saturation moment and T_C both decrease to values of $4.3 \mu_B/\text{f.u.}$ and $488(5) \text{ K}$, respectively, and

Figure 6. TG/DTA curves of (a) ϵ -Fe₂CoN (heating rate 5 K min^{-1}) and (b) ϵ -Fe₂NiN (heating rate 15 K min^{-1}). The temperatures given in the figures correspond to maxima, the onset temperatures of the exothermal effects amount to 836 and 809 K for Fe₂CoN and Fe₂NiN, respectively.

Figure 7. Magnetization as a function of temperature (1.8–600 K) and the applied magnetic field (0–7 T) in (a, b) ϵ -Fe₂CoN and (c, d) ϵ -Fe₂NiN.

for ϵ -Fe₂NiN, values of $3.1 \mu_B/\text{f.u.}$ and $234(3) \text{ K}$ are obtained. As expected, the introduction of one or two extra electrons per formula unit decreases the average ordered magnetic moments per TM and leads to a concomitant lowering of the ordering temperatures.

With respect to the occupation of the spin channels, an almost equal occupation of both spin directions indicate negligible moments on the nitrogen atoms, whereas pronounced differences are evidenced for the Fe 3d states, implying high local magnetic moments of the iron atoms in ϵ -Fe₂TMN (see Figure 8). This situation is similar to the

Figure 8. Total and partial DOS for majority-spin and minority-spin electrons at the Fe and the TM sites ($TM = \text{Co}$ or Ni) in (a) $\epsilon\text{-Fe}_2\text{CoN}$ and (b) $\epsilon\text{-Fe}_2\text{NiN}$. The dashed line indicates the Fermi level positioned at 0 eV.

unsubstituted binary $\epsilon\text{-Fe}_3\text{N}$.⁷ The substitution of Fe by TM has little impact on the local moments of the N atoms and the Fe atoms. However, in contrast to $\epsilon\text{-Fe}_3\text{N}$, the minority-spin channel of the Co d-states is half-filled and that of the Ni atoms is almost completely occupied. Hence, the resulting magnetic moments differ significantly.

According to the data in Table S1 (see the Supporting Information), the electron occupation numbers for Fe and N remain basically unchanged upon substitution of iron with TM because the extra electrons remain more or less completely localized in the minority-spin 3d channels of the transition-metal atoms (~ 2.2 for Fe, ~ 3.2 for Co, and ~ 4.2 for Ni). Herein, the magnetic moments of about $2.1 \mu_{\text{B}}$ and $-0.1 \mu_{\text{B}}$ were identified for Fe and N atom in both phases, respectively. The increase in minority-spin 3d channels associated to the TM atoms reduces the differences between majority-spin and minority-spin channels. In this way, the local magnetic moments of the metal atoms decrease gradually from roughly $2.1 \mu_{\text{B}}$ for Fe to almost $1 \mu_{\text{B}}$ for Co and nearly $0.1 \mu_{\text{B}}$ for Ni. Therefore, it is concluded that the substitution with TM ($TM = \text{Co}, \text{Ni}$) causes the decrease of the magnetic moments from $\epsilon\text{-Fe}_3\text{N}$ ($\sim 6 \mu_{\text{B}}/\text{f.u.}$) to Fe_2NiN ($4.23 \mu_{\text{B}}/\text{f.u.}$), which is in agreement with the DOS analysis (see Figure 8). The

remaining differences to the experimental measurements are probably attributed to the overestimation in magnetization with GGA, and the idealized, fully ordered model of the crystal structure which was used in the calculations.

CONCLUSIONS

The metastable nitrides $\epsilon\text{-Fe}_2\text{CoN}$ and $\epsilon\text{-Fe}_2\text{NiN}$ have been systematically investigated by experimental and electronic structure calculation methods. Pure and homogeneous compounds $\epsilon\text{-Fe}_2\text{CoN}$ and $\epsilon\text{-Fe}_2\text{NiN}$ are obtained by high-pressure, high-temperature synthesis. EXAFS measurements indicate successful replacement of iron by Co or Ni, respectively, in the $\epsilon\text{-Fe}_3\text{N}$ -type atomic arrangements. Combined thermal analysis and X-ray powder diffraction results indicate that both compounds are metastable phases which decompose above 750 K. The transition-metal substitutions essentially reduce the magnetization from $\sim 6 \mu_{\text{B}}/\text{f.u.}$ for $\epsilon\text{-Fe}_3\text{N}$ to $4.3 \mu_{\text{B}}/\text{f.u.}$ for $\epsilon\text{-Fe}_2\text{CoN}$ and further to $3.1 \mu_{\text{B}}/\text{f.u.}$ for $\epsilon\text{-Fe}_2\text{NiN}$. In parallel, the Curie temperatures decrease from 575(3) K for $\epsilon\text{-Fe}_3\text{N}$ to 488(5) K for $\epsilon\text{-Fe}_2\text{CoN}$ and 234(3) K for $\epsilon\text{-Fe}_2\text{NiN}$.

■ ASSOCIATED CONTENT

■ Supporting Information

XRPD data of ϵ -Fe₂CoN and ϵ -Fe₂NiN after TG/DTA measurements as well as calculated electron occupation numbers and magnetic moments. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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