

Theoretical Study of γ' -Fe₄N and ϵ -Fe_xN Iron Nitrides at Pressures up to 500 GPa

Z. I. Popov^{a,*}, K. D. Litasov^{b,c}, P. N. Gavryushkin^{b,c}, S. G. Ovchinnikov^a, and A. S. Fedorov^a

^a Kirensky Institute of Physics, Siberian Branch, Russian Academy of Sciences, Akademgorodok, Krasnoyarsk, 660036 Russia

* e-mail: zipcool@bk.ru

^b Sobolev Institute of Geology and Mineralogy, Siberian Branch, Russian Academy of Sciences, pr. Akademika Koptyuga 3, Novosibirsk, 630090 Russia

^c Novosibirsk State University, ul. Pirogova 2, Novosibirsk, 630090 Russia

Received December 23, 2014

The parameters of equations of state of stoichiometric and nonstoichiometric phases of the γ' -Fe₄N, ϵ -Fe₃N_{0.75}, ϵ -Fe₃N, ϵ -Fe₃N_{1.25}, and ϵ -Fe₃N_{1.5} iron nitrides in a pressure range up to 500 GPa have been determined using ab initio calculations. The points of the sharp drop and disappearance of the magnetic moment on iron atoms have been found. It has been shown that certain changes in the magnetic moment are accompanied by a change in the volume of a unit cell of the nitrides. The calculated parameters of equations of state demonstrate that the compressibility of both magnetic and nonmagnetic iron nitrides decreases monotonically with an increase in the content of nitrogen.

DOI: 10.1134/S0021364015060090

High-strength iron nitrides are wear-resistant materials with increased fatigue and corrosion resistances [1, 2]. They have a high magnetic moment (for Fe₄N, it is 2.7–2.0 μ_B). For this reason, the connection between the chemical bond and magnetism was analyzed in numerous works [3, 4]. Study of the stability and thermoelastic properties of iron nitrides is important, in particular, for geophysics, because they can exist in the inner and outer (liquid) core of the Earth [5, 6]. Nitrogen is one of the least studied elements regarding the composition of the Earth. Its content in the interior layers remains unknown [7].

The Fe–N system at 0.1 MPa includes a number of intermediate compounds from γ -Fe₄N (roaldite) to ζ -Fe₂N. The ϵ -Fe₃N_x include a series of isostructural nonstoichiometric compounds with $x = 0.75$ –1.4 [8, 9]. The stoichiometric compound ϵ -Fe₃N has the *P*6₃22 symmetry, but most of the other nitrides of this series has the *P*312 symmetry. The temperature dependent variations of the composition of ϵ -Fe₃N_x complicates the study of the equation of state and elastic properties of this nitride.

The experimental synthesis of ϵ -Fe₃N_x from γ -Fe₄N was performed at 8.5(8) GPa and 1373(150) K [10] and at 15(2) GPa and 1600(200) K [11]. The compressibility parameters of γ -Fe₄N, ϵ -Fe₃N_{1.05}, and ϵ -Fe₇N₃ were obtained with the diamond-cell method at pressures up to 70 GPa [5, 10, 12]. The compression of γ -Fe₄N in the diamond-anvil cell at 298 K results in the spontaneous formation of ϵ -Fe₃N_{0.75} at pressures

above 17 GPa. However, at a further compression to 33 GPa, the complete transformation was not observed [10, 13]. The parameters of the *P*–*V*–*T* equation of state of ϵ -Fe₃N_x ($x = 0.8$), which is stable in the Fe–N system at pressures up to 30 GPa and temperatures up to 1273 K, were determined in [14]. It was found that Fe₄N is unstable at high pressures and Fe₃N is unstable under the conditions of nitrogen deficit in the system. In the temperature range of 300–673 K and the pressure range of 20–30 GPa, the stable phase is ϵ -Fe₃N, rather than ϵ -Fe₃N_{0.8}. The results of these experiments stimulated theoretical studies of the elastic parameters of iron nitrides of different compositions, because it is difficult to experimentally reveal changes in the elastic properties of nitrides caused by a heating/cooling-induced change in their composition.

The elastic properties, equations of state, and electronic structure of individual iron nitrides were theoretically studied in [10–12, 14, 15]. The aim of this work is to simulate iron nitrides with different nitrogen contents using quantum chemical methods and to determine the most stable stoichiometry, the parameters of equations of state of iron nitrides, and their magnetic properties at pressures up to 500 GPa.

All calculations were performed by quantum-chemical simulation in the Vienna Ab Initio Simulation Package VASP 5.3 [16–18] based on the density functional theory (DFT) [19, 20] with the use of the plane wave basis within the PAW formalism [21, 22]. The generalized gradient approximation (GGA) with

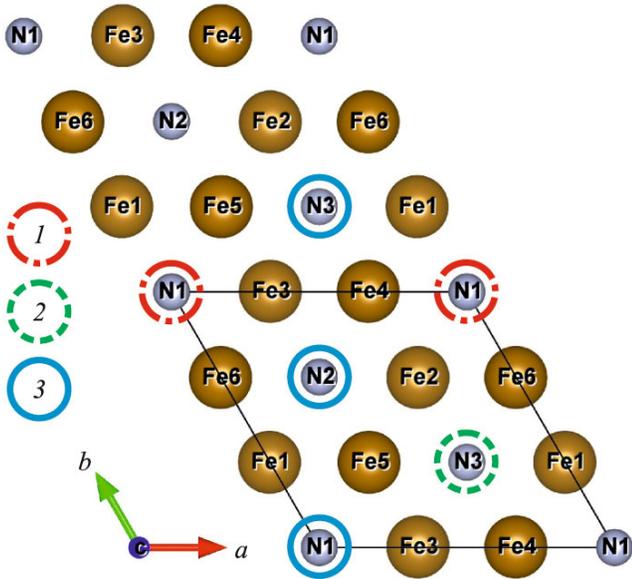


Fig. 1. (Color online) Supercell $1 \times 2 \times 1$ ϵ - Fe_2N . Digits mark the positions from which nitrogen atoms are removed for obtaining stoichiometry: (1) ϵ - $\text{Fe}_3\text{N}_{1.25}$, (2) ϵ - Fe_3N , and (3) ϵ - $\text{Fe}_3\text{N}_{0.75}$.

the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional was used in the calculations. A value of 700 eV was taken as the cutoff energy for plane waves. For the calculation of the electronic structure, we used a necessary (depending on the substance) number of k -points in the Brillouin zone, which is approximately $2000/N$, where N is the number of atoms in the unit cell, within the Monkhorst–Pack scheme [23].

We calculated the formation enthalpy, pressure dependence of the unit cell volume, and the magnetization of the following iron nitrides: γ' - Fe_4N ($Pm\bar{3}m$ symmetry), ϵ - $\text{Fe}_3\text{N}_{0.75}$ ($P312$), ϵ - Fe_3N ($P312$), ϵ - $\text{Fe}_3\text{N}_{1.25}$ ($P312$), and ϵ - $\text{Fe}_3\text{N}_{1.5}$ ($P312$). It is not trivial to obtain a nonstoichiometric structure for quantum-chemical calculations in a solid, because the higher the degree of nonstoichiometry, the larger the unit cell that should be used for calculations. This circumstance limits the choice of compositions. In this work, we used the $1 \times 2 \times 1$ $P312$ ϵ - Fe_2N supercell to obtain nonstoichiometric compounds. Further, removing some nitrogen atoms indicated in Fig. 1, we obtained nonstoichiometric compounds ϵ - $\text{Fe}_3\text{N}_{1.25}$, ϵ - $\text{Fe}_3\text{N}_{1.0}$, and ϵ - $\text{Fe}_3\text{N}_{0.75}$.

The calculated formation enthalpies were compared by the formula

$$\Delta E(\text{Fe}_x\text{N}) = E(\text{Fe}_x\text{N}) + yE(\text{Fe}) - E(\text{Fe}_{(x+y)}\text{N}), \quad (1)$$

where $\text{Fe}_{(x+y)}\text{N}$ corresponds to Fe_4N and $E(\text{Fe})$ is the enthalpy of hcp Fe, which is the most stable phase of iron under the PT conditions in the inner core of the Earth [24]. The transition from the bcc to fcc phase of iron is observed at pressures above 15 GPa [25]. The found ΔE values are shown in Fig. 2. It is seen that the transition of γ' - Fe_4N to ϵ - $\text{Fe}_3\text{N}_{0.75}$ occurs at a pressure of 7 GPa in agreement with the theoretical results obtained in [11] and corresponds to the experimentally observed transition at 8.5(8) GPa and 1373(150) K [10]. The transition from γ' - Fe_4N to ϵ - Fe_3N occurs at a pressure of about 1 GPa. The ϵ - Fe_2N compound has the lowest energy at pressures above 25 GPa (Fig. 2). The transition from ϵ - Fe_3N to

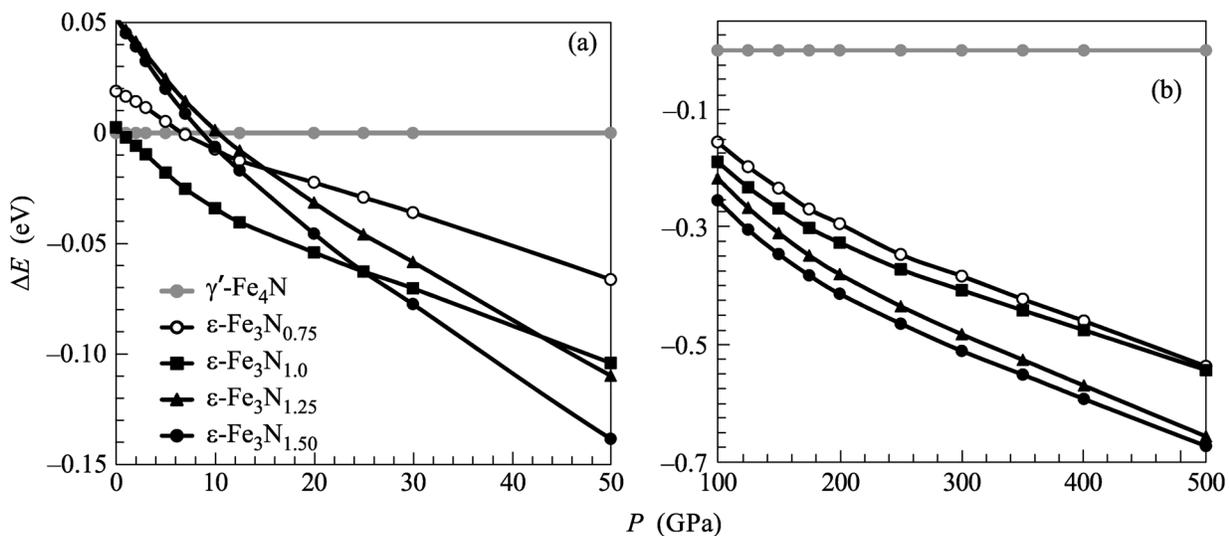


Fig. 2. Difference of the formation enthalpy of the iron nitrides from that for γ' - Fe_4N at pressures of (a) 0–50 and (b) 100–500 GPa.

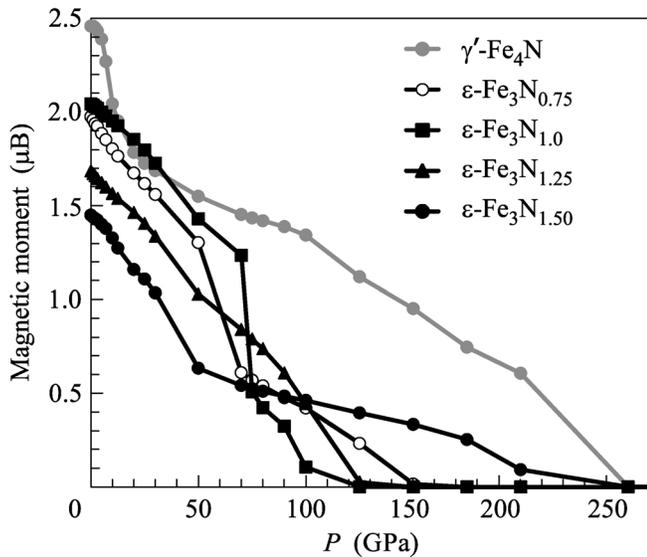


Fig. 3. Pressure dependence of the magnetic moments.

$\epsilon\text{-Fe}_3\text{N}_{1.25} + 0.75\text{Fe}$ is possible at a pressure of about 42 GPa. The transition from $\epsilon\text{-Fe}_3\text{N}_{0.75}$ to $\epsilon\text{-Fe}_3\text{N}_{1.5} + 1.5\text{Fe}$ occurs at 10 GPa.

For compounds with a lower content of nitrogen, a high magnetic moment on iron atoms is observed. The magnetization of $\epsilon\text{-Fe}_3\text{N}_{0.75}$ almost coincides with the magnetization of $\epsilon\text{-Fe}_3\text{N}$ because of the compensation effect [10]. With an increase in the concentration of nitrogen atoms in the series $\epsilon\text{-Fe}_3\text{N}_{0.75}$, Fe_3N , $\text{Fe}_3\text{N}_{1.25}$, and $\text{Fe}_3\text{N}_{1.5}$, the magnetic moment decreases from 2.01 to 1.47 μ_B . The calculated pressure dependence of the magnetic moment (per iron atom) is shown in Fig. 3. The behaviors of the magnetic moment as a function of the pressure are different for different compositions of nitrides. The magnetic moment $\gamma'\text{-Fe}_4\text{N}$ drops at a pressure of about 10 GPa and then decreases monotonically to the complete disappearance at 250 GPa, where the magnetic moments of all nitrides under study vanish. The magnetic moments of $\epsilon\text{-Fe}_3\text{N}_{0.75}$ and $\epsilon\text{-Fe}_3\text{N}$ nitrides drop at pressures of 50–70 GPa and vanish completely at 150 and 125 GPa, respectively. The magnetic moment calculated for $\epsilon\text{-Fe}_3\text{N}_{1.25}$ nitride decreases monotonically and vanishes at 125 GPa. The magnetic moment for $\epsilon\text{-Fe}_3\text{N}_{1.5}$ drops at 40–50 GPa and vanishes completely only at 250 GPa.

Sharp jumps in the magnetic moment of nitrides are manifested in a change in the volume of the unit cell (Fig. 4). The largest changes in the volume are associated with the drop of the magnetic moment for $\epsilon\text{-Fe}_3\text{N}_{0.75}$ and $\epsilon\text{-Fe}_3\text{N}$ at 50–70 GPa, where the decrease in the volume is 2–3%. A decrease in the magnetic moment of $\gamma'\text{-Fe}_4\text{N}$ at 5–10 GPa is also responsible for a strong decrease in the volume of the cell. The other nitrides demonstrate quite smooth

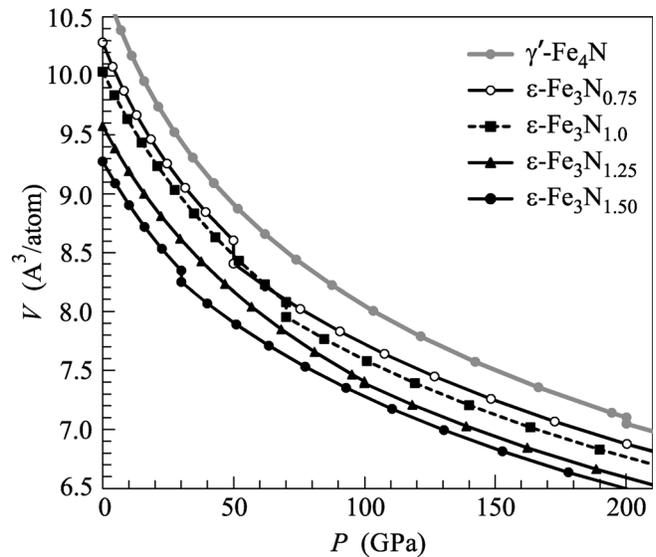


Fig. 4. Pressure dependence of the unit cell volume of the iron nitrides calculated with the Birch–Murnaghan equation of state [27].

compressibility curves and do not deviate from the main trend at a large change in the magnetic moment (Fig. 4).

The table presents the parameters K_0 and K' calculated for the magnetic phases of iron–nitrogen compounds with the use of the Vinet [26] and Birch–Murnaghan [27] equations of state. Smooth variations of the magnetic moment complicate the calculation of the elastic parameters in the spin-polarized case. For this reason, we calculated K_0 and K' both for the entire pressure range of 0–500 GPa and for ranges where the magnetic moment vanishes and decreases strongly. The bulk modulus obviously increases monotonically with an increase in the content of nitrogen in nitride in agreement with the experimental data summarized in [6]. This behavior was established for both magnetic and nonmagnetic iron nitrides (in the calculations for the spin-polarized and spin-unpolarized systems).

To summarize, systematic ab initio studies have been performed for $\gamma'\text{-Fe}_4\text{N}$, $\gamma\text{-Fe}_3\text{N}_{0.75}$, $\epsilon\text{-Fe}_3\text{N}$, $\epsilon\text{-Fe}_3\text{N}_{1.25}$, and $\epsilon\text{-Fe}_3\text{N}_{1.5}$ iron nitrides in the pressure range to 500 GPa. The points of the sharp drop and disappearance of the magnetic moment on iron atoms have been found. It has been shown that certain changes in the magnetic moment are accompanied by a 2–3% change in the volume of a unit cell of the nitrides. The calculated parameters of equations of state demonstrate that the compressibility of both magnetic and nonmagnetic iron nitrides decreases monotonically with an increase in the content of nitrogen. For nonmagnetic nitrides from $\gamma'\text{-Fe}_4\text{N}$ to $\epsilon\text{-Fe}_3\text{N}_{1.5}$, the bulk elastic modulus increases from 285 to 304 GPa.

Parameters of the (BM) Birch–Murnaghan [27] and (V) Vinet [26] equations of state of Fe_xN compounds and the magnetic moment per iron atom M at $P = 0$ GPa as calculated for (F) ferromagnetic (spin-polarized) and (N) nonmagnetic compounds in the indicated pressure range

Nitride	P , GPa	E_0 , eV/atom	M , μ_B	V_0 , $\text{\AA}^3/\text{atom}$	BM		V	
					K_0 , GPa	K'	K_0 , GPa	K'
γ' - Fe_4N (F)	0–500	–8.47	2.46	10.82	161(2)	5.03(5)	148(2)	5.81(4)
	0–200				152(4)	5.41(17)	147(3)	5.88(13)
γ' - Fe_4N (N)	0–500	–8.20		9.85	285(1)	4.38(1)	278(2)	4.73(10)
ε - $\text{Fe}_3\text{N}_{0.75}$ (F)	0–500	–8.45	1.97	10.28	158(4)	5.71(16)	157(2)	6.04(4)
	0–100				181(4)	4.49(19)	179(5)	4.78(22)
	0–50				179(1)	4.96(8)	178(1)	5.16(8)
ε - $\text{Fe}_3\text{N}_{0.75}$ (N)	0–500	–8.30		9.55	295(1)	4.37(1)	281(1)	4.93(1)
ε - Fe_3N (F)	0–500	–8.50	2.04	10.03	178(3)	5.26(8)	165(3)	5.98(7)
	0–70				214(3)	3.80(12)	214(3)	3.91(15)
ε - Fe_3N (N)	0–500	–8.33		9.37	298(1)	4.38(1)	284(1)	4.94(1)
ε - $\text{Fe}_3\text{N}_{1.25}$ (F)	0–500	–8.44	1.68	9.57	210(2)	4.95(3)	197(1)	5.65(3)
	0–100				224(1)	4.30(5)	222(2)	4.54(7)
ε - $\text{Fe}_3\text{N}_{1.25}$ (N)	0–500	–8.32		9.11	303(1)	4.38(1)	289(1)	4.93(1)
ε - $\text{Fe}_3\text{N}_{1.5}$ (F)	0–500	–8.45	1.45	9.27	232(2)	4.90(4)	218(1)	5.57(3)
	0–175				212(1)	5.59(6)	207(1)	5.95(5)
	0–30				226(3)	4.36(27)	226(3)	4.46(28)
ε - $\text{Fe}_3\text{N}_{1.5}$ (N)	0–500	–8.40		8.96	304(1)	4.42(2)	290(1)	4.98(2)
hcp-Fe		–8.36		10.08	318(2)	4.36(3)	305(3)	4.89(4)

All calculations were performed on the cluster of the Supercomputer Center, Novosibirsk State University. This work was supported by the Russian Science Foundation (project no. 14-17-00601), by the Council of the President of the Russian Federation for Support of Young Scientists and Leading Scientific Schools (project nos. MD-500.2013.5 and NSh-2886.2014.2), by the Ministry of Education and Science of the Russian Federation (project no. 14.B25.31.0032), and by the Presidium of the Russian Academy of Sciences (project no. 2.16).

REFERENCES

- H. Jacobs, D. Rechenbach, and U. Zachwieja, *J. Alloys. Compd.* **227**, 10 (1995).
- N. I. Kardonina, A. S. Yurovskikh, and A. S. Kolpakov, *Metalloved. Termich. Obrab. Met.* **10**, 5 (2010).
- B. Eck, R. Dronskowski, M. Takahashi, and S. Kikawa, *J. Mater. Chem.* **9**, 1527 (1999).
- M. Sifkovits, H. Smolinski, S. Hellwig, and W. Weber, *J. Magn. Magn. Mater.* **204**, 191 (1999).
- J. F. Adler and Q. Williams, *J. Geophys. Res. Solid Earth* **110**, B01203 (2005).
- K. D. Litasov, A. F. Shatskiy, S. G. Ovchinnikov, Z. I. Popov, D. S. Ponomarev, and E. Ohtani, *JETP Lett.* **98**, 805 (2013).
- W. F. McDonough, in *Treatise on Geochemistry*, Ed. by H. D. Holland and K. K. Turekian (Elsevier–Pergamon, Oxford, 2003), Vol. 2, p. 547.
- K. H. Jack, *Proc. R. Soc. London A* **208**, 200 (1951).
- H. A. Wriedt, N. A. Gokcen, and R. H. Nafziger, *Bull. Alloy Phase Diagrams* **8**, 355 (1987).
- K. Guo, D. Rau, J. von Appen, Y. Prots, W. Schnelle, R. Dronskowski, R. Niewa, and U. Schwarz, *High Press. Res.* **33**, 684 (2013).
- R. Niewa, D. Rau, A. Wosylus, K. Meier, M. Wessel, M. Hanfland, R. Dronskowski, and U. Schwarz, *J. Alloys Compd.* **480**, 76 (2009).
- R. Niewa, D. Rau, A. Wosylus, K. Meier, M. Hanfland, M. Wessel, R. Dronskowski, D. A. Dzivenko, R. Riedel, and U. Schwarz, *Chem. Mater.* **21**, 392 (2009).
- A. Leineweber, H. Jacobs, F. Huning, H. Lueken, and W. Kockelmann, *J. Alloys Compd.* **316**, 21 (2001).
- Y.-J. Shi, Y.-L. Du, and G. Chen, *Comput. Mater. Sci.* **67**, 341 (2013).

15. W. Zhang, Z. Lv, Z. Shi, S. Sun, Z. Wang, and W. Fu, *J. Magn. Magn. Mater.* **324**, 2271 (2012).
16. G. Kresse and J. Furthmuller, *Phys. Rev. B* **54**, 11169 (1996).
17. G. Kresse and J. Hafner, *Phys. Rev. B* **47**, 558 (1993).
18. G. Kresse and J. Hafner, *Phys. Rev. B* **49**, 14251 (1994).
19. P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964).
20. W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133 (1965).
21. P. E. Blochl, *Phys. Rev. B* **50**, 17953 (1994).
22. G. Kresse and D. Joubert, *Phys. Rev. B* **59**, 1758 (1999).
23. H. J. Monkhorst and J. D. Pack, *Phys. Rev. B* **13**, 5188 (1976).
24. S. Tateno, K. Hirose, Y. Ohishi, and Y. Tatsumi, *Science* **330**, 359 (2010).
25. R. Taylor, M. Pasternak, and R. Jeanloz, *J. Appl. Phys.* **69**, 6126 (1991).
26. P. Vinet, J. Ferrante, J. H. Rose, and J. R. Smith, *J. Geophys. Res.* **92**, 9319 (1987).
27. F. Birch, *J. Geophys. Res.* **57**, 227 (1952).

Translated by R. Tyapaev