

Prediction of Stable Iron Nitrides at Ambient and High Pressures with Progressive Formation of New Polynitrogen Species

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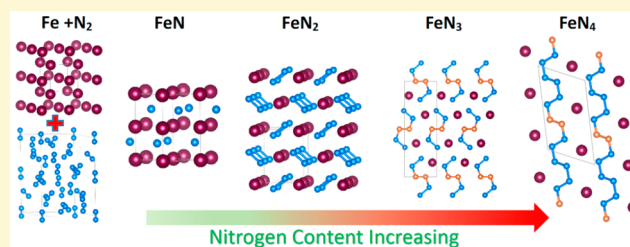
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Supporting Information

ABSTRACT: Nitride materials are of considerable interest due to their fundamental importance and practical applications. However, synthesis of transition metal nitrides often requires extreme conditions, e.g., high temperature and/or high pressure, slowing down the experimental discovery. Using global structure search methods in combination with first-principles calculations, we systematically explore the stoichiometric phase space of iron–nitrogen compounds on the nitrogen-rich side at ambient and high pressures up to 100 GPa. Diverse stoichiometries in the Fe–N system are found to emerge in the phase diagram at high pressures. Significantly, FeN₄ is found to be stable already at ambient pressure. It undergoes a polymerization near 20 GPa which results in a high energy density. Accompanying the polymerization, FeN₄ transforms from a direct band gap semiconductor to ferromagnetic metal. We also predict several phase transitions in FeN and FeN₂ at high pressure, and the results explain the previous experimental observations by comparing the X-ray diffraction patterns. Stepwise formation of polynitrogen species is observed following the increment of nitrogen content in the stoichiometry, from isolated N atoms in FeN, to the N₂ unit in FeN₂ and Fe₃N₈, to the N₆ unit in Fe₃N₈ and FeN₃, and to the N_∞ chain in FeN₄, FeN₆, and FeN₈. Ultra-incompressibility is found in marcasite-FeN₂, FeN₃, and FeN₄ along particular crystalline directions, while high energy density, 1.37–2.02 kJ g^{−1}, is expected for FeN₄, FeN₆, and FeN₈. Our results shed light on understanding the chemistry of transition metal polynitrides under pressure and encourage experimental synthesis of newly predicted iron nitrides in the near future.



INTRODUCTION

Nitrogen is one of the most abundant elements forming 78% of the Earth's atmosphere. At ambient conditions, nitrogen forms a very stable N₂ molecule bound by a triple bond. Metastable forms of nitrogen, in particular those rich in single N–N bonds, are good candidates for high-energy-density materials (HEDMs). Singly bond nitrogen species are efficient energy carriers, but they have low kinetic stability and are only accessible at high-pressure and high-temperature (HPHT) conditions.^{1,2} One way to strengthen the metastable nitrogen and ultimately lower the pressure of synthesis is through a moderate ionization by certain electron donors.³ On the basis of the consideration of formation enthalpy, materials of this type are expected to be found in N-rich polynitrides formed with certain metals. Currently, N-rich metal nitrides are being explored with increasing interest in both theory and experi-

ment, with a large candidate pool (alkali metal azides and pentazoles,^{4–13} alkaline earth metal polynitrides,^{14–16} and transition metal polynitrides^{17–21}). In particular, considerable recent progress has been made on the discoveries of novel pentazolate materials.^{22–28} One of the notable successes in this pursuit is the high-pressure synthesis^{5,6} of pentazolate salts containing an energetic cyclo-N₅[−] anion after a theoretical prediction.⁴ Similarly, WN₆ containing cyclo-N₆ species was also predicted to be stable above 16 GPa.¹⁷ Elemental nitrogen consisting of energetic N₆ or N₈ molecules was theoretically predicted to exist as well,^{29–31} but the pressures required for its formation are notably higher than the compound counterparts.

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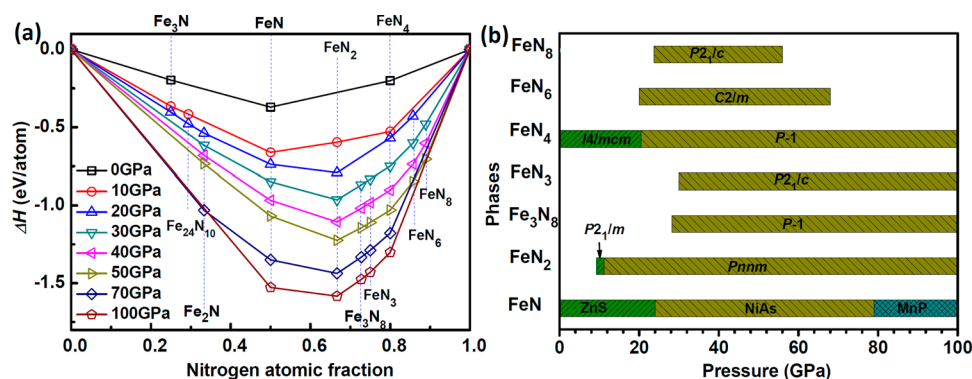


Figure 1. (a) Global stability convex hull of the Fe–N system at the pressure range 0–100 GPa. (b) Predicted pressure–composition phase diagram for the Fe–N system. Different phases are separated by colors.

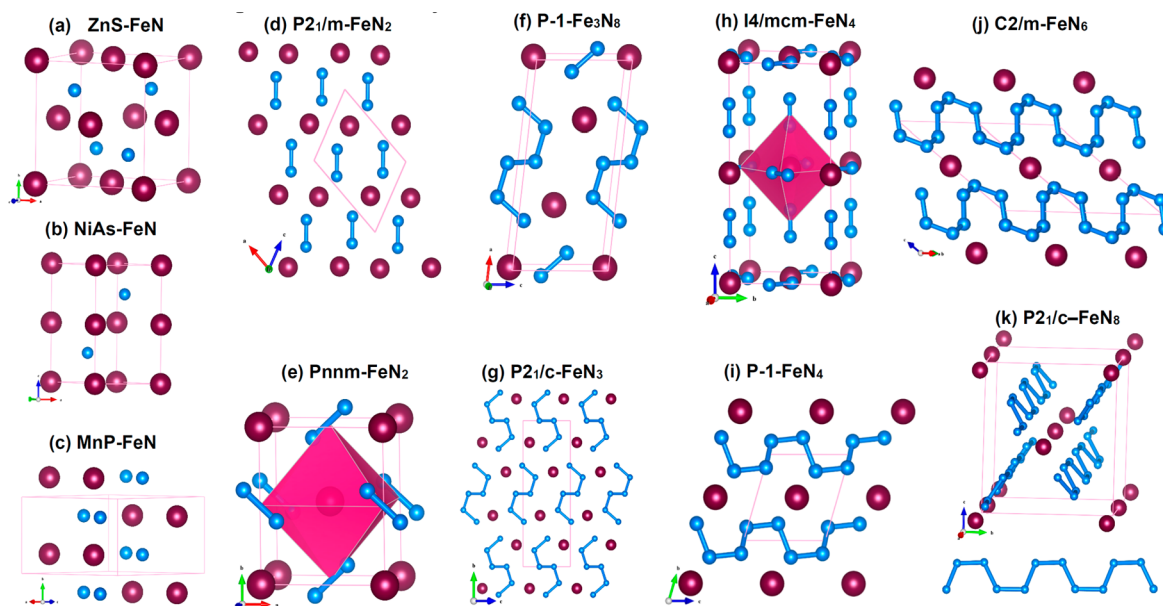


Figure 2. Crystal structures of iron polynitrides. The Fe and N atoms are shown by purple (large) and cyan (small) spheres, respectively. Stepwise formation of polynitrogen species can be seen following the increment of N content, from isolated atoms in FeN, to N₂ dimers in FeN₂ and Fe₃N₈, to N₆ units in Fe₃N₈ and FeN₃, and to N_∞ chains in FeN₄, FeN₆, and FeN₈.

In the present work, we expand the search for energetic nitrides to N-rich iron nitrides. Abundant in the Earth's crust, iron can form many compounds with nitrogen, such as Fe₁₆N₂, Fe₄N, Fe₃N_{1+y} ($y = 0–0.33$), Fe₂₄N₁₀, Fe₇N₃, Fe₂N, FeN_y ($y = 0.9–1.0$), and FeN₂.^{32–36} The majority of the known iron nitrides, however, are on the Fe-rich side, primarily for their applications in hardening coatings, magnetic recording media,³⁷ catalysis,^{38–41} and biomedical materials. The N-rich iron nitrides are relatively less explored,^{42–47} but we expect to find good candidates for energy applications on this front. In this group, FeN₂ is well-known with a common XN₂ stoichiometry for transition metal pernitrides (X = Pt, Pd, Ir, Os, Rh, Ru, Ti, and Co).^{48–55} FeN₂ has a marcasite structure with diatomic N₂ and is stable from ambient pressure to 72 GPa and 2200 K.⁴⁶ Another member may also exist, possibly having FeN₆ or FeN₉ stoichiometry,⁵⁶ but there is no structural information. One expects to discover more, hitherto unknown members in this group, in particular those with energetic nitrogen species. A reason could be the isolobal analogy of N₂ to CO: N₂ is isoelectronic to CO, and the latter can react with iron forming versatile compounds, i.e., Fe(CO)₅, Fe₂(CO)₉,

and Fe₃(CO)₁₂. Thus, we explored the material space of the Fe–N system using two global structure search methods in combination with first-principles electronic calculations. The search is primarily focused on new nitrides that can be synthesized under HPHT conditions. Significantly, our study unveils a new FeN₄ compound that is thermodynamically stable at ambient conditions and therefore synthesizable. The FeN₄ is among the first stable N-rich transition metal nitrides discovered at ambient conditions. This compound contains diatomic N₂ units, which undergo polymerization at about 20 GPa to form energetic infinite N_∞ chains. The calculated energy density of the polymerized FeN₄ is between 1.37 and 2.02 kJ g^{−1}, comparable to the energy densities of HEDMs. In addition, polymerized FeN₄ also possesses a directional incompressibility comparable to that of natural diamond. The mechanic strength of this compound is enhanced by the intrinsic stability of the nitrogen bonds. Other new iron nitrides, i.e., FeN₆ and FeN₈, were found to be stable in moderate pressure ranges which are well within the current reach of high-pressure synthesis.

RESULTS AND DISCUSSION

Structures and Stability. Structure searches for thermodynamically stable Fe–N compounds were performed with various stoichiometries using global structure search packages CALYPSO^{57,58} and USPEX.^{59,60} The search was conducted at high pressure up to 100 GPa. The results are presented in Figure 1a using the global stability tie lines in stoichiometric phase space, which are constructed from the formation enthalpy of all identified Fe–N compounds. On the Fe-rich side, Fe₃N, Fe₂₄N₁₀, and Fe₂N are found to be thermodynamically stable in different pressure ranges, while Fe₈N and Fe₄N are metastable. Because of the low nitrogen content, we do not expect significant energy density in these nitrides. In what follows, the structural, mechanical, and electronic properties and N–N distances for the proposed phases were all calculated at zero pressure and temperature unless otherwise noted.

For the FeN compound, we correctly identified the stable ZnS-type structure (*F* $\bar{4}$ 3*m*) at ambient pressure and a phase transition to the NiAs-type structure (*P*6₃/*mmc*) at about 24 GPa (Figure 1b), which agrees well with a previous study.⁴² We also predicted a new phase transition from the NiAs-type structure to the MnP-type structure (*Pnma*) at about 79 GPa. The MnP-type structure is a common structure for mononitrides MPn (M = VIII B transition metal; Pn = P or As), and the predicted transition has been known in a number of compounds.⁶¹ In all three FeN structures, the N atoms are not paired but intercalated with the Fe atoms (Figure 2). The ZnS-type structure is a typical covalent motif in which the two elements occupy alternating diamond lattice sites. In this structure, each N atom is tetrahedrally coordinated by four Fe atoms. The NiAs-type structure on the other hand has a hexagonal close-packed lattice of Fe with N atoms in octahedral sites, in which the NFe₆ octahedrons distorted to become trigonal prismatic. In this structure, the N coordination is increased to six, as expected under high pressure. The MnP type is a common derivative of the NiAs type. In this structure, the hexagonal lattice is distorted into a C-centered orthorhombic lattice, in which the N atoms are displaced in the plane perpendicular to the hexagonal axis, and the Fe atoms are shifted along the axis forming zigzag chains. The NiAs and MnP structures are related by the group–subgroup relation, which allows for a continuous displacive transition. The closest distance between two N atoms is decreased from 2.99 Å in ZnS–FeN, to 2.78 Å in NiAs–FeN, and to 2.74 Å in MnP–FeN.

FeN₂ has been predicted to exist only at high pressures. Previous theoretical studies suggest that this compound forms at a pressure of 17 GPa in an *R* $\bar{3}$ *m* structure and then transforms to a marcasite-type structure (*Pnnm*, denoted as *o*-FeN₂) at 22 GPa.^{43,62} However, our structure search reveals a new *P*2₁/*m* structure (denoted as *m*-FeN₂) that has notably lower enthalpy than the *R* $\bar{3}$ *m* structure, e.g., by 37 meV atom^{−1} at a lower formation pressure of 9.3 GPa. The modified phase sequence for FeN₂ is thus *m*-FeN₂ between 9.3 and 11.2 GPa and *o*-FeN₂ at pressures above to at least 100 GPa (Figure 1b). As shown in Figure 2, both *m*-FeN₂ and *o*-FeN₂ have diatomic N₂ units. The *m*-FeN₂ can be viewed as a sandwich structure with alternating layers of Fe atoms and slightly buckled N₂ units. The closest N–N distances in *m*-FeN₂ and *o*-FeN₂ are 1.326 and 1.360 Å, respectively. These distances are comparable to that in TiN₂ (1.383 Å),⁵² but shorter than those in PtN₂ (1.41 Å)⁶³ and OsN₂ (1.43 Å).⁵⁰ Mayer bond

orders (MBO)^{64,65} analysis reveals that the N–N bond orders are 1.34 and 1.25 for *m*-FeN₂ and *o*-FeN₂, respectively, within the range of single and double bonds. Clearly, the nitrogen bonds in FeN₂ are softened at high pressures because of enhanced Fe–N₂ interactions and electron transfers. Bader charge analysis⁶⁶ reveals an average of 1.2 e[−] loss by each Fe atom in these two structures. Electrons acquired by N₂ units reduce the electron sharing between two N atoms which lower the bonding order. Another way to look at the FeN₂ structures is that each N atom is coordinated to three Fe atoms and one N atom in a distorted tetrahedron, where the Fe–N distances are much greater than the N–N distances showing distorted sp³ hybridization. The two neighboring N atoms have their respective N–N and N–Fe bonds arranged in a staggered conformation to minimize the repulsions between neighboring lone pairs. The Fe atoms on the other hand are coordinated to six N atoms in both structures forming FeN₆ octahedrons (Figure S1). The octahedrons in *m*-FeN₂ are interconnected by edge-sharing to form 2D octahedral slabs, while in *o*-FeN₂, they are more 3D close-packed by mixed edge- and corner-sharing. The newly predicted FeN₂ structures are accessible at moderate pressures well within the current reach of high-pressure apparatuses. Because of the intrinsic stability of the N₂ units, this compound once formed may be recovered to ambient conditions. Previously, CaN₂ with a similar structural motif has been realized at about 12 GPa and recovered at ambient conditions.^{67,68}

Remarkably, for the FeN₄ stoichiometry, our structure search reveals a stable tetragonal phase (*I*4/*mcm*, denoted as *te*-FeN₄) at ambient pressure (Figure 1). This is one of the first N-rich transition metal nitrides that are thermodynamically stable at ambient conditions. The *te*-FeN₄ consists of N₂ units separated by Fe atoms (Figure 2). There are two types of N₂ units in the structure, one aligned and alternating with Fe atoms along the *c* direction, and the other planed with Fe atoms on the plane perpendicular to the *c* direction. The first type has a bond length of 1.179 Å, slightly larger than that of a triple bond (1.10 Å) in ethyne. The second type has a longer bond length of 1.262 Å, similar to the double bond (1.25 Å) in ethylene. Moreover, the ∠N–N–Fe angle in the second type is 121.9°, which is also close to the atomic arrangement in ethylene (∠H–C–C is 121.3°) (Figure S1). In the unit cell, the two groups are arranged in an octahedron centered by an Fe atom, with the two “ethyne N₂” pointing in head-on and four “ethylene N₂” siding on (Figure S1). The calculated bond orders are 1.84 and 2.11 for the ethylene- and ethyne-like N–N bond, respectively, suggesting that they are close to or greater than the double bond. This N₂ arrangement is similar to that in *m*-FeN₂; however, with higher nitrogen content, FeN₄ can be stabilized at ambient pressure. Near 20 GPa, a triclinic *P* $\bar{1}$ -type FeN₄ (denoted as *tr*-FeN₄ hereafter) becomes more energetically favorable than *te*-FeN₄, and persists to at least to 100 GPa, the highest pressure investigated here (Figure 1). Interestingly, we immediately noticed that our predicted structure is similar to a synthesized FeN₄ reported by Bykov et al.⁶⁹ during the review of our manuscript. The slight difference is contributed to a finer tolerance of atomic positions selected for our calculation. The formation enthalpy of our predicted structure is about 42 meV f.u.^{−1} (f.u., formula unit) lower than that reported by Bykov et al. at 135 GPa.⁷⁰ The predicted lattice parameters of *a* = 2.511, *b* = 3.525, *c* = 3.567 Å, α = 74.97°, β = 69.40°, and γ = 91.90° and cell volumes 28.27 Å³ at 135 GPa match well with those of *a* = 2.5089(4), *b* =

3.5245(13), $c = 3.5409(5)$ Å, $\alpha = 105.08(2)$, $\beta = 110.260(14)$, and $\gamma = 92.03(2)^\circ$ and cell volume 28.1 Å³ at 135 GPa. In *tr*-FeN₄, N atoms form infinite armchair N_∞ chains, which are extended along the [0 0 1] direction with various N—N bond lengths: 1.351, 1.386, and 1.500 Å (at zero pressure, see Figure S1), corresponding to MBO values of 1.08, 1.25, and 0.98, respectively. The calculated N—N bond lengths of 1.309, 1.322, and 1.405 Å in the N_∞ chains are in good agreement with $\sim 1.29(5)$, $1.30(3)$, and $1.43(4)$ Å in experiment at 135 GPa. Significantly, the shorter bond lengths are between single (1.45 Å) and double (1.25 Å) bonds, while the longest one is comparable to a single bond. The two dihedral angles in the chains are 109.8° and 106.1°, respectively, which are close to the tetrahedral angle (109.8°). Infinite N_∞ chains with similar geometries were previously predicted to exist in RuN₄,²⁰ CaN₄,¹⁶ and MgN₄,¹⁴ and carbon nanotubes.⁷¹ In FeN₄, one-half of the N atoms in the chains adopt sp³ hybridization coordinated by two Fe and two N atoms, while others have sp² by a near-planar triangular coordination with one Fe and two N atoms, in good agreement with the calculated MBO values. The FeN₆ octahedrons in *tr*-FeN₄ therefore exhibit 1D arrangement by edge-sharing in the (1 1 1) direction, in which the neighboring octahedrons are connected together by single N—N bonds.

Other predicted stable N-rich iron polynitrides include Fe₃N₈, FeN₃, FeN₆, and FeN₈; each has a specific pressure range of stability (Figure 1). FeN₃ has the *P2*₁/*c* symmetry at pressures above 30 GPa. In this structure (Figure 2 and Figure S1), the N atoms form zigzag N₆ units with three bond lengths, e.g., 1.420 Å (×2), 1.378 Å (×2), and 1.352 Å (×1) with the MBO values of 1.12, 1.08, and 1.23, respectively. Previously, open N₆ units were proposed for RuN₃ and AlN₃ in their high-pressure phases.^{20,72} Fe₃N₈ is predicted to be thermodynamically stable with the *P1* symmetry from 28 to at least 100 GPa (Figure 1b). In Fe₃N₈, the N atoms are separated into N₆ (similar to those in FeN₃) and N₂ units. These two species form two different layers, namely, (FeN₃)₂ and FeN₂, and stack alternatively. The bond lengths (Figure S1) in the N₆ (1.407 Å (×2), 1.383 Å (×2), and 1.351 Å) and N₂ (1.368 Å) units are close to those in FeN₃ and FeN₂, respectively. A similar trend is also found for the MBO values. The FeN₆ is predicted to have the *C2*/*m* symmetry between 20 and 68 GPa (Figure 1b). In FeN₆ the N atoms form infinite N_∞ chains (Figure S1) along the *b*-axis with two alternating bond lengths (1.338 and 1.377 Å). Each N atom is coordinated to two neighboring N atoms and one Fe atom, with two N—N—N angles of 117.3° and 116.6°. These bond lengths and angles reveal distorted sp² hybridization analogous to the infinite carbon chains proposed in Ca₂C₃.⁷³ Since the FeN₆ stoichiometry is already fulfilled by FeN₆ octahedrons, there is no edge-sharing or corner-sharing of the octahedrons; instead they are connected by N—N σ bonds. The MBO values in the N_∞ chains are 1.05 and 1.17, which are close to the N—N single bond, and weaker than the N=N double bond. The most N-rich phase, FeN₈, is predicted to have the *P2*₁/*c* symmetry between 24 and 60 GPa (Figure 1b). In this structure, N atoms form distorted armchair N_∞ chains similar to those in *tr*-FeN₄ (Figure 2). The N_∞ chains propagate along the [1 0 0] direction with the bond lengths varying between 1.329 and 1.369 Å with MBO values ranging between 1.10 and 1.23, and N—N—N angles between 112.5° and 117.3°. In these chains 6 out of 8 N atoms have two neighboring N atoms and one Fe atom, similar to that in FeN₆, whereas the other two N atoms are only neighboring

with two adjacent N atoms, isolated from the FeN₆ octahedrons (Figure S1).

In the structures described above, the basic nitrogen species are single N, N₂, N₆, and N_∞ chain. Increasing the N content in the compound tends to encourage the formation of polynitrogen species. This process is illustrated in Figure 3,

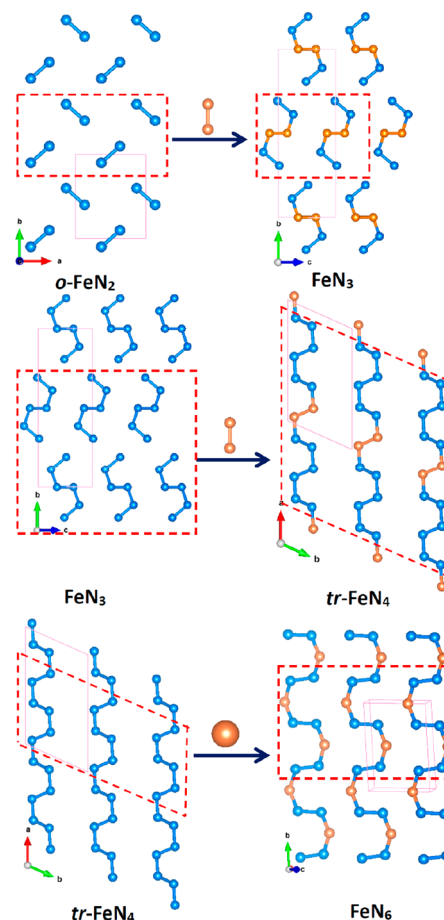


Figure 3. Scheme of the stepwise formation of polynitrogen species from *o*-FeN₂ to FeN₆.

stepwise: two neighboring N₂ units in *o*-FeN₂ being linked by another N₂ and resulting in a zigzag N₆ unit in FeN₃; linking the N₆ units with single N atoms resulting in armchair N_∞ chains in *tr*-FeN₄; and adding a single N atom at each turn of the armchair chain resulting in a bent chain in FeN₆. Finally in FeN₈, the N_∞ chain can be viewed as a periodically repeating N₈ segment resulting from adding two more N atoms to each N₆ segment in FeN₆. In FeN₈, however, the two additional N atoms do not belong to any FeN₆ octahedrons, so they hardly interact with the Fe atoms. This point was later verified by the Bader charge analysis, which shows that these two N atoms have nearly zero electron gain/loss.

Mechanical Properties. Transition metal nitrides often exhibit extraordinary mechanical properties. Thus, the elastic moduli of the predicted iron nitrides are examined (Figure 4a). The general trend is that both bulk (*B*) and shear (*G*) moduli increase from FeN to FeN₂, and then decrease gradually to FeN₈. The marcasite FeN₂ is calculated to have the largest bulk modulus (333 GPa) among all iron nitrides, which agrees well with the experiment (344 GPa)⁴⁶ and is comparable to those of OsN₂ (358 GPa)⁷⁴ and RuN₂ (330 GPa).⁵³ The bulk

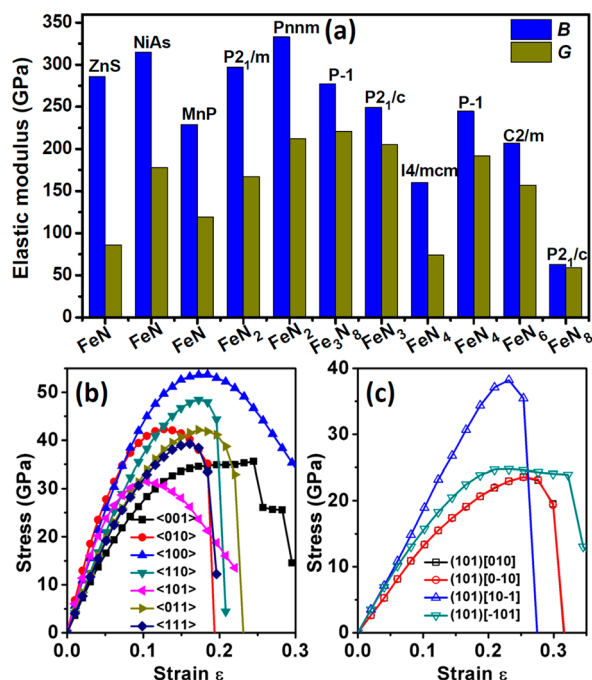


Figure 4. (a) Calculated bulk (*B*) and shear (*G*) moduli for iron polynitrides. (b) Calculated tensile stress–strain relations for *o*-FeN₂. (c) Shear stress–strain relations for *o*-FeN₂ in the (101) easy cleavage plane.

modulus of FeN increases from the MnP to ZnS and to NiAs type, among which the latter exhibits the second largest value (315 GPa) after *o*-FeN₂. The bulk moduli of *m*-FeN₂ (297 GPa), Fe₃N₈ (277 GPa), FeN₃ (249 GPa), and *tr*-FeN₄ (245 GPa) are comparable or greater than those of RhN₂ and CoN₂. In terms of the shear modulus, Fe₃N₈ has the highest value (221 GPa), followed by *o*-FeN₂ (212 GPa), FeN₃ (205 GPa), and *tr*-FeN₄ (192 GPa), which are comparable to those of OsN₂ (234 GPa,⁷⁵ 220 GPa⁴⁸), IrN₂ (217 GPa),⁴⁹ and PtN₂ (187 GPa).⁷⁶

The calculated elastic constants for predicted iron nitrides are summarized in Table S3. The elastic constants of marcasite FeN₂ are in good agreement with a previous report.⁴³ According to the Born–Huang criterion, all these nitrides are elastically stable at ambient pressure. Significantly, three of them show higher incompressibility along a particular direction than diamond, e.g., *C*₁₁ (918 GPa) in *o*-FeN₂, *C*₂₂ (858 GPa) in FeN₃, and *C*₃₃ (933 GPa) in *tr*-FeN₄ (Figure S3a–d). The high incompressibility of *o*-FeN₂ is due to the intrinsic stability of the N₂ units in the structure. However, the angle between the N₂ units and the *ac* plane is 41.8°, less than the angle 48.2° between the N₂ units and the *bc* plane, which results in a higher incompressibility along the *b*-axis. Similarly, strong bonding in the infinite N_∞ chains in FeN₃ and *tr*-FeN₄ is crucial for the incompressibility along the *b* and *c* direction, respectively. For a better understanding of the preferred strength direction, a three-dimensional surface representation of the Young's moduli (*E*) of *o*-FeN₂ and *tr*-FeN₄ was calculated (Figure S3e,f). Here, the deviation of the shape from a sphere measures the degree of strength anisotropy. Clearly, significant anisotropy is seen in both structures. The calculated maximum-to-minimum Young's moduli ratio (*E*_{max}/*E*_{min}) for *tr*-FeN₄ is 3.74, much larger than that of *o*-FeN₂ (2.32), indicating a more prominent anisotropy in the former.

The ideal strength is a measure of macroscopic mechanical properties of materials. Schematic of tensile/shear deformation and the ideal strength for *o*-FeN₂ are obtained from the stress–strain relationships along different crystallographic directions (Figure 4b). Clearly, marcasite FeN₂ exhibits the strongest stress response (53.7 GPa) along the [100] direction, which is consistent with the largest elastic constant *C*₁₁ and Young's modulus. The weakest tensile strength for *o*-FeN₂ is 31.5 GPa along the [101] direction, comparable to that of PtN₂ (~30 GPa)⁷⁷ along the [100] direction. Since the plastic deformation usually occurs by shearing, the shear stress responses in the (101) easy cleavage plane of marcasite FeN₂ are evaluated (Figure 4c), which exhibit a large anisotropy. The ideal shear strength of 23.6 GPa is found in the (101)[010]/(101)[0 $\bar{1}$ 0] slip system at a strain of 0.25, comparable to those of PtN₂⁷⁷ (25 GPa in the (111)[$\bar{1}$ 12] slip system) and hcp-Si₃N₄⁷⁸ (19–25 GPa in the (10 $\bar{1}$ 0)[0001] slip systems), but higher than that of TiN₂⁷⁹ (14.9 GPa in the (110)[111] slip systems). The advanced mechanical properties of *o*-FeN₂ may find potential technological applications, such as cutting tools or wear-resistant coatings.

The hardness of iron nitrides considered in this work was estimated using an empirical model by Chen et al.,⁸⁰ *H_v* = 2.0(*k*²*G*)^{0.585} – 3.0. The estimated hardnesses of NiAs–FeN and *o*-FeN₂ are 18.3 and 24.1 GPa, respectively. The new proposed phases are expected to have greater hardness: Fe₃N₈ (33.1 GPa), FeN₃ (32.9 GPa), *tr*-FeN₄ (29.6 GPa), and FeN₆ (24.9 GPa), which are higher or comparable to those of OsN₂ (27 GPa)⁴⁸ and RuN₃ (23.4 GPa).⁸¹ Therefore, these compounds can be classified into hard materials but not superhard materials.

High Energy Density. Decomposition of polynitrides at ambient pressure usually produces gaseous N₂ and lower nitrides. This process has a high exotherm due to the large energy difference between single N–N bond (160 kJ mol^{–1}) in nitrides and triple N≡N bond (954 kJ mol^{–1}) in N₂.³³ For this reason, the polynitrides are often investigated as HEDM. As depicted in Figure 5, the calculated energy densities for *tr*-FeN₄, FeN₆, and FeN₈ are approximately 1.37, 1.83, and 2.02 kJ g^{–1}, which are lower than modern explosives (i.e., RDX and HMX),⁸² cg-N₂,¹ LiN₃,⁴ BeN₄,¹⁵ B₃N₅,⁸³ and MgN₃,¹⁴ but comparable to XeN₆,⁸⁴ CO-N₂,⁸⁵ and MgN₄.¹⁴ Obviously,

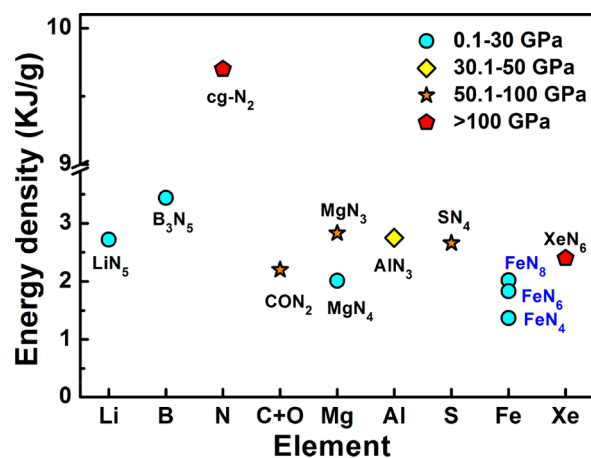


Figure 5. Energy density of FeN₄, FeN₆, and FeN₈ in comparison with nitrogen allotropes and compounds.^{1,4,14,15,72,82–85,89,90} The results are calculated at zero pressure and 0 K.

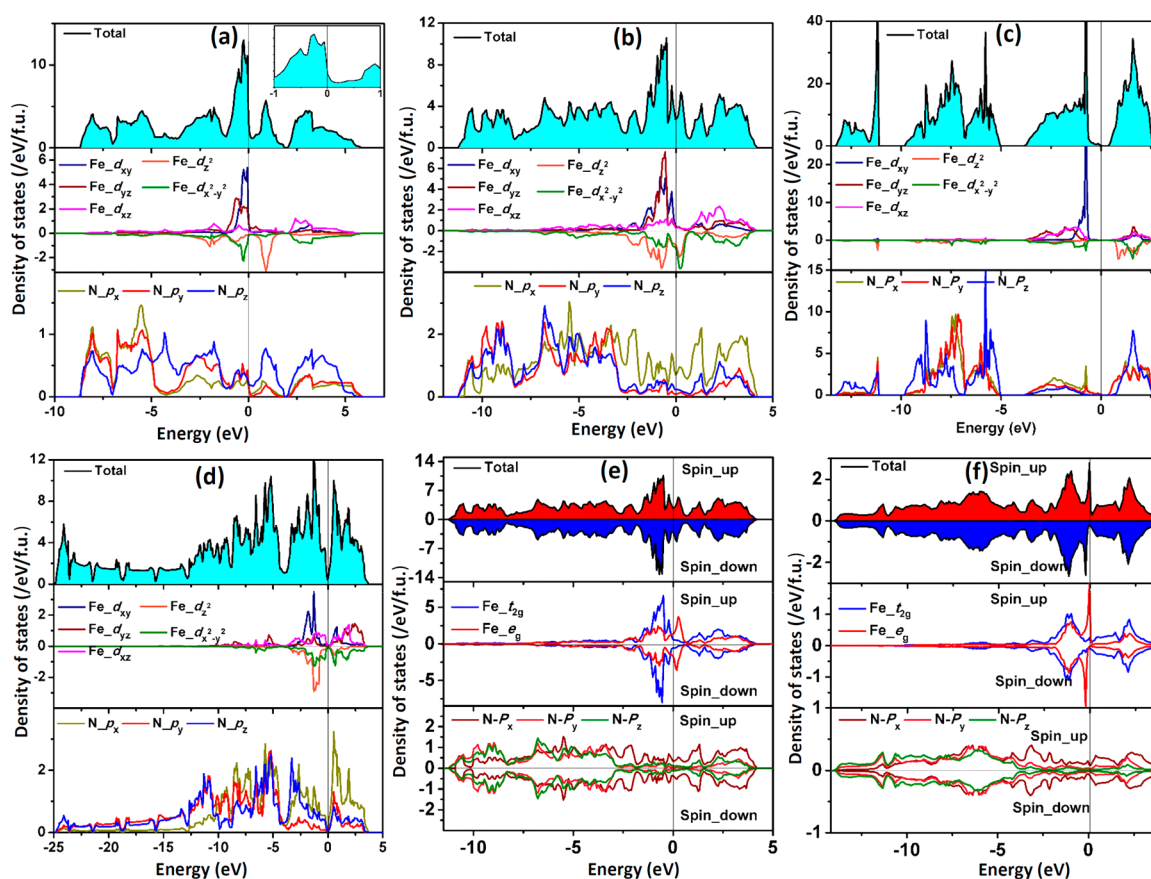


Figure 6. Spin-polarized projected density of states calculated for (a) *o*-FeN₂, (b) Fe₃N₈, (c) *te*-FeN₄, (d) FeN₆, (e) FeN₃, and (f) *tr*-FeN₄.

there is a correlation between the energy density and the number of single bonds in the compound. All predicted iron polynitrides are thermodynamically stable at 20–24 GPa, which is within the current capability of high-pressure synthesis. Other advantages of iron nitrides, compared to LiN₅ and magnesium polynitrides, are environmentally friendly decomposition processes and low cost for starting materials.

Electronic Structure. The electronic band structures of the predicted iron polynitrides are calculated using the Heyd–Scuseria–Ernzerhof screened hybrid functional.⁸⁶ This functional incorporates a fraction of Hartree–Fock (HF) exchange into the short-range exchange interaction which was found to precisely reproduce the electronic properties of several strong correlated systems. The results are shown in Figures S4 and S5. The *te*-FeN₄ and FeN₆ are found to be semiconductors with a band gap of 1.41 and 0.63 eV, respectively. Notably, both band gaps are direct and within the visible light spectrum, indicating that these two nitrides may potentially have photovoltaic applications. On the other hand, all other iron polynitrides were found to be metallic, including FeN, FeN₂, Fe₃N₈, FeN₃, *tr*-FeN₄, and FeN₈. The metallic feature may explain the absence of Raman spectrum of *tr*-FeN₄ in experiment,⁶⁷ among which the band structures of ZnS- and NiAs-type FeN and *o*-FeN₂ agree very well with previously reported results. Moreover, from the spin-polarized projected density of states (DOS) (Figure 6 and Figure S6), the ZnS-type FeN, *m*-FeN₂, *o*-FeN₂, Fe₃N₈, *te*-FeN₄, FeN₆, and FeN₈ are all nonmagnetic, while the MnP-type FeN, NiAs-type FeN, FeN₃, and *tr*-FeN₄ should be ferromagnetic. The results of FeN are consistent with previous theoretical and experimental results.^{42,87,88} For

ferromagnetic FeN₃ and *tr*-FeN₄ (Figure 6e,f), there are almost equal occupations in both spin channels by the electrons of the N atoms, suggesting that N atoms' contributions to the magnetic moment are negligible. The magnetic moments in these two nitrides are primarily from the Fe atoms, as shown by the pronounced differences between the two Fe *t*_{2g} channels at the Fermi level in FeN₃, and the differences between the two Fe *e*_g channels at the Fermi level in *tr*-FeN₄. In general, the *t*_{2g} and *e*_g electrons in FeN₃ and *tr*-FeN₄, respectively, are the major contributors to the ferromagnetism in these two nitrides. The electronic states at the lower energy range of the valence bands are mainly contributed by N p orbitals, while Fe 3d orbitals dominate near the top of valence bands to the Fermi level. The states at the Fermi level are mostly occupied by the Fe 3d electrons, with some contribution from N 2p electrons. Intuitively, strong covalent bonding features may be concluded in iron nitrides, namely, from the 2p–3d orbital hybridization in a wide energy window (−8, 0) eV, which suggests a mixed covalent and ionic bonding between the Fe and N atoms.

XRD Pattern Examinations. It is important to examine the newly predicted iron polynitrides with respect to the results of experimental synthesis at similar pressure and temperature conditions. Previously, Laniel et al.^{45,46} reported the X-ray diffraction (XRD) patterns from the products of direct reaction of elemental Fe with excess N₂ in a laser-heated diamond anvil cell up to 91 GPa and 2200 K. The XRD patterns were compared with structure data of iron nitrides available at that time. Here, we simulate the XRD patterns of all stable iron nitrides including those predicted in the present study and compare them with the experimental data. As shown in Figure

7 and Figure S7, the majority of the experimental XRD pattern obtained during the compression process at 30.5 GPa can be

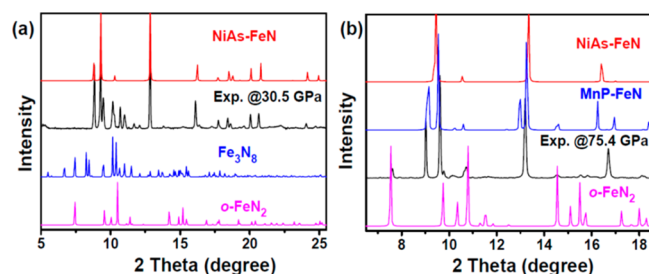


Figure 7. Simulated X-ray diffraction patterns for iron polynitrides at (a) 30.5 GPa and (b) 75.4 GPa in comparison with the previously reported experimental results.^{45,46}

well-matched to the NiAs-type FeN. For the XRD pattern obtained at 74.5 GPa, our results show that it matches better to the MnP-type FeN than NiAs-type FeN. This interpretation also agrees with the predicted NiAs- to MnP-type transition near 79 GPa. Thus, the FeN is the major component of the synthesized iron nitrides. Moreover, the simulated XRD patterns indicate that *o*-FeN₂ may be a minor component, which shows a good match to weak peaks in the experimental XRD patterns at both 30.5 and 74.5 GPa. This is consistent with the stable pressure range (11.2–100 GPa) of *o*-FeN₂. In addition to FeN and FeN₂, there are also some weak diffraction peaks appearing between 10 and 13° at 30.5 GPa, which should be from N-rich nitrides rather than Fe-rich nitrides because of the excessive nitrogen in the synthesis. As marked in Figure 7 and Figure S7, the simulated XRD patterns of Fe₃N₈, *tr*-FeN₄, FeN₆, and FeN₈ all bear a similarity to the experimental data, and therefore one or more of them may correspond to the minor components in the products. A more detailed examination of the XRD pattern at 74.5 GPa (Figure S7) suggests that Fe₃N₈ and *tr*-FeN₄ can also match well to the experimental XRD pattern, but FeN₆ and FeN₈ are unlikely, which is in a general agreement with the prediction that Fe₃N₈, *tr*-FeN₄, FeN₆, and FeN₈ are stable in the pressure range 28–100, 20.5–100, 20–68, and 24–60 GPa, respectively. Finally, we compared the simulated XRD patterns with the experimental XRD pattern obtained in the product recovered at ambient pressure (Figure S7). In general, the NiAs-type FeN and *m*-FeN₂ are more likely to be present in the product, although Fe₃N₈, *tr*-FeN₄, and FeN₈ cannot be completely ruled out. Thus, the predicted global stability tie lines in the Fe–N stoichiometric phase (Figure 1) are in good agreement with the experimental results and may be used as a guide for future synthesis of iron nitrides. During the synthesis, multiple phases of FeN, FeN₂, Fe₃N₈, FeN₄, FeN₆, and FeN₈ may coexist in the product under HPHT conditions. Our findings may lead to the discovery of new iron nitrides, especially on the N-rich side of the phase diagram, expanding this family to new members with more diverse and useful properties.

CONCLUSION

In summary, a thorough exploration of stable iron polynitrides (FeN_{*x*}, 1 ≤ *x* ≤ 8) was carried out at ambient and high pressures up to 100 GPa with the CALYPSO and USPEX structure search packages. A series of FeN_{*x*} compounds that are thermodynamically stable at ambient or high pressure were predicted for the first time. Most remarkably, a new FeN₄

compound was found to be thermodynamically stable at ambient pressure, which was recently synthesized by Bykov et al.⁶⁹ This prediction adds a new member to the family of stable iron polynitrides, along with ZnS-type FeN and ϵ -Fe₃N. Significantly, FeN₄ undergoes a polymerization near 20 GPa which results in a high energy density. Accompanying the polymerization the FeN₄ transforms from a direct band gap semiconductor to a ferromagnetic metal. For FeN and FeN₂, we predicted a NiAs- to MnP-type phase transition near 79 GPa and a *P*₂₁/*m* to marcasite phase transition near 11.2 GPa, respectively, which agree well with previous experimental observations by comparing experimental and simulated X-ray diffraction patterns. In addition, Fe₃N₈, FeN₃, FeN₆, and FeN₈ were predicted to be stable in the pressure ranges 28–100, 30–100, 20–68, and 24–60 GPa, respectively. Stepwise formation of polynitrogen species is observed following the increment of N content in the stoichiometry, from isolated N atoms in FeN, to the N₂ unit in FeN₂ and Fe₃N₈, to the N₆ unit in Fe₃N₈ and FeN₃, and to the N_∞ chain in FeN₄, FeN₆, and FeN₈. Directional ultra-incompressibility comparable to that of diamond is found in marcasite FeN₂, FeN₃, and FeN₄, while high tensile and shear strengths are found exclusively in marcasite FeN₂. Significantly, FeN₄, FeN₆, and FeN₈ are highly exothermic (1.37, 1.83, and 2.02 kJ g^{−1}, respectively) upon decomposition at ambient pressure, making them efficient energy carriers. The outstanding properties of the predicted iron polynitrides will encourage immediate experimental efforts in their synthesis. Note added: During the publishing of our present work, a new allotrope of nitrogen (*l*-N₂) was reported by Turnbull et al. at 56 GPa and ambient pressure,⁹¹ which suggests the importance of understanding of nitrogen chemistry under high pressure.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.8b02972.

Computational methods, crystal structure, phonon spectrum, incompressibility, band structure, density of states, and X-ray diffraction pattern examination (PDF)

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Notes

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