Prediction and Characterization of the Marcasite Phase of Iron Pernitride under High Pressure

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Abstract:

Using the unbiased structure searching CALYPSO techniques and the first-principles calculations, we predicted a phase transition in iron pernitride (FeN_2) at 22 GPa from the hexagonal $R\bar{3}m$ structure to an orthorhombic $Pnnm$ structure. Although the $Pnnm$ structure is a well-known marcasite phase of transition-metal pernitrides, to our knowledge, this is the first report about the pressure-induced phase transition to the $Pnnm$ structure in the FeN_2 compound. The dynamically and mechanically stable for the $Pnnm$ phase are evaluated, further confirming this phase transition. By assessing the elastic property of the $Pnnm$ structure, the result indicates that it displays excellent brittle and hardness characters. Viewing its structure, a dinitrogen unit and a coordinating iron atom characterized by N-sharing six-fold FeN_6 octahedrons are found. Based on the quantum-chemical analysis, the dinitrogen unit was formulated as a quasi-molecular double-bonded N_2^{2-} and a mixed covalent N-N and Fe-N bonding nature was identified in the structure. These structural and covalent bonding characters play a crucial role to its excellent mechanical properties. The present results extend the well-known marcasite phase in other transition-metal pernitrides to the FeN_2 compound and provide a perspective toward the understanding of the synthesis and chemical bonding of N-rich FeN_2 under high pressure.

Keywords: Iron-nitrides compounds, Dinitrogen, High pressure, Particle Swarm Optimization

Introduction

The binary iron-nitrides (Fe-N) system has been investigated most intensively since 19 century [1]. A series of low nitrogen content compounds (Fe_2N , Fe_3N , Fe_4N , Fe_8N) successively synthesized starting from their constituent elements [2-4]. A N-rich FeN compound in which a nitrogen ratio is up to 50 % was reported by experimental studies [5]. These synthesis spurred the endeavors in search for N-rich Fe-N compounds. However, up to now, there no other Fe-N compound that its nitrogen content exceeds the FeN compound can be synthesized by experiment. Recently, an N-rich iron pernitride (FeN_2) crystallizing in the space group $R\bar{3}m$ at 17 GPa (1000 K) is predicted theoretically [6]. Its structural, electronic and dynamical stability have been further elaborated by Gupta using a spin polarized first-principles study [7]. This new crystalline phase of FeN_2 compound has been obtained by assuming the parent metal under the pressure conditions, which opens and arouses a research of exploring pressure-induced structural phases of FeN_2 .

The FeN_2 compound, as a member of transition-metal pernitrides family, is confirmed to have similar high-pressure phases of transition-metal pernitrides AN_2 ($\text{A} = \text{Os}$, Ru , Ir , and Pt) [8-9]. Due to Fe belonging to the same group as Os and Ru in the periodic table of elements, FeN_2 was recognized to also have a marcasite (orthorhombic, $Pnnm$) structure existing in the case of OsN_2 and RuN_2 at high pressure [10-12]. But, this viewpoint has not yet confirmed in theory or experiments.

In order to explore the stable high-pressure structure of FeN_2 , the phase stabilities of various stoichiometric $\text{Fe}_x\text{N}_{1-x}$ ($0 < x < 1$) compounds at 0 and 50 GPa are investigated systematically to obtain the formation enthalpy of FeN_2 . A combination of the unbiased structural search based on a particle-swarm optimization (PSO) algorithm [13] and the first-principles density functional total energy calculation is used to explore the entire configuration space. The effectiveness of the method has been demonstrated by recent successes in predicting the high-pressure structures of various systems [14-18]. The high-pressure insulating $Aba2\text{-}40$ (Pearson symbol $oC40$) structure of Li, the two low-pressure monoclinic structures of Bi_2Te_3 , and the orthorhombic $Imm2$ structure of FeTi_3O_7 predicted by this method have been confirmed by experiments [16-18]. Here we report a $Pnnm$ structure of FeN_2 as a well-known marcasite phase in the transition-metal pernitrides. Theoretical calculations reveal that the $Pnnm$ structure is more stable than the reported $R\bar{3}m$ structure at pressures above 22 GPa. A dinitrogen unit and a coordinating iron atom characterized by N-sharing six-fold FeN_6 octahedrons are found in the structure. The quasi-molecular double-bonded N_2^{2-} pernitride units and the mixed covalent N-N and Fe-N bonding nature were identified. By the calculations of bulk moduli, shear moduli, Young's moduli, Poisson's ratio and Vickers hardness, it indicates that the $Pnnm$ structure possesses excellent mechanical properties.

Methods

The structure searching simulations were performed through the swarm-intelligence based CALYPSO method enabling a global minimization of free energy (at 0 K, it reduces to enthalpy) surfaces merging ab initio total energy calculations as implemented in the CALYPSO code [13]. The method is specially designed for global structural minimization unbiased by any known structural information, and has been benchmarked on various known systems [19-21]. To find the FeN_2 structure lying the lowest in energy, the structures of FeN_2 and its decomposition various $\text{Fe}_x\text{N}_{1-x}$ ($0 < x < 1$) compounds with simulation cell sizes of 1-4 formula units (f.u.) at 0 and 50 GPa were searched. The underlying ab initio electronic structure calculations and the geometry relaxations were performed in the framework of density functional theory (DFT) within the generalized gradient approximation and the frozen-core all-electron projector-augmented wave (PAW) method [22-23] implemented in the Vienna ab Initio Simulation Package (VASP) code [24]. The PAW pseudopotentials with $3d^7 4s^1$ and $2s^2 2p^3$ valence electrons were adopted for Fe and N, respectively. The kinetic energy cutoff for the plane-wave basis set is taken as 700 eV. The $11 \times 9 \times 17$, $16 \times 16 \times 4$ Monkhorst-Pack [25] grid for the k-points sampling are used for the $Pnnm$ and $R-3m$ structures, respectively. The convergence of these parameters is well checked, with the uncertainty in the total energy less than 1 meV per atom. The phonon calculations and the quasi-harmonic free-energy calculations were carried out by using a finite displacement approach through the PHONOPY code [26]. The macroscopic stress in the solid can be computed for a small strain by the use of the strain-stress method. The elastic moduli can be derived from the strain-stress relationship [27]. After obtaining the single-crystal elastic moduli, polycrystalline properties such as bulk moduli, shear moduli, and ductile/brittle are calculated by using the Voigt-Reuss-Hill approximation [27-28]. Vicker's hardness is formulated by Tian et al [29-31]. A quantum-chemical analysis is carried out by means of the crystal orbital Hamilton population (COHP) method³¹ using the LOBSTER program [32-33].

Results and discussions

Structural predictions for the FeN_2 compound was performed using the CALYPSO code with simulation cells containing 1-4 f.u. at 0-50 GPa. We typically generated several hundred structures to ensure the convergence of the global structural searches. In these structures, the energetic stable structures mainly contain dinuclear N_2 units. In this structural model, we not only successfully found the typical $R-3m$ structure of FeN_2 predicted by Richard Dronskowski [6] but also predicted an orthorhombic $Pnnm$ structure with lowest enthalpies at 50 GPa. By comparing the enthalpy curves in Figure 1a, it is found that the $Pnnm$ structure is even more stable than the $R-3m$ structure at pressures above 11 GPa (0 K).

As well known, magnetism plays a central role in iron and its compounds. Therefore it is necessary to check the role of magnetism on the affect of the energy balance between the $R-3m$ and $Pnnm$ structures. We therefore performed the enthalpy calculations after considering spin polarized mode in Figure 1b. As shown in the Figure 1b, the enthalpy difference curves show that the lowest-energy FeN_2 phase adopts $R-3m$ at low pressure (13–22 GPa) and transform into the $Pnnm$ structure at above 22 GPa. It found that the spin polarization effect shifted the phase transition pressure from 11 GPa to 22 GPa.

Figure 1. (a) Enthalpy curves (relative to the decomposition enthalpies of $\text{FeN} + 1/2 \text{N}_2$) of various structures as function of pressure in FeN_2 compound. Enthalpies are given per formula unit. (b) The enthalpy curves (relative to the decomposition enthalpies of $\text{FeN} + 1/2 \text{N}_2$) after considering spin polarized mode. (c) Formation enthalpies (ΔH) of various Fe-N compounds with respect to decomposition into constituent elemental solids at 0 and 50 GPa in the convex hull. The convex hulls are shown by solid lines. Dotted lines through the neighboring points residing above the convex hull are guides for the eye. (d) The Gibbs free energy–pressure diagram of FeN_2 ($T=1000$ K)

The estimation of the heat of formation is not trivial, thus we need to compare the enthalpy of the FeN_2 structure with its combination of possible starting materials Fe_4N , Fe_3N , Fe_2N , FeN_4 , FeN_6 with N_2 . The formation enthalpies of these compounds were calculated with respect to the decomposition into Fe and N, where the enthalpies are obtained for the most stable structures as searched by the CALYPSO

method at the desired pressures. The results were depicted to a convex hull shown in Figure 1c. The convex hull of the enthalpies of formation of Fe-N compound is constructed to account for all possible decompose routes at 0 and 50 GPa. Viewing the convex hull, it obviously shows that the most thermodynamically stable compound transforms from FeN at 0 GPa to FeN₂ at 50 GPa. The result confirms that the FeN₂ compound can be synthesized at 50 GPa.

To take account for the temperature effects, we performed quasi-harmonic Gibbs free energy calculations using the finite-displacement method. The Gibbs free energy–pressure diagram for the synthesis of FeN₂ at temperature of T=1000 K was performed and shown in Figure 1d. We found that the *Pnnm* phase synthesis of FeN₂ at 1000 K needs a higher pressure (> 34 GPa) than the value (~22 GPa) at 0 K. A similar trend of pressure dependence for the *R-3m* phase can be extracted from our data. These phenomenon manifest that temperatures have negative effect on FeN₂ synthesis.

It is known that the Gibbs free energy reduces to the enthalpy $H=U + PV$ at 0 K, where U , P and V are the static energy, pressure and volume per formula unit, respectively. The high-pressure competition between U and PV dominates the phase transitions. A sphere packing efficiency calculations show that the *Pnnm* structure (11.5%) is more densely packed than the *R-3m* structure (10.7%) at 50 GPa, with a less volume. The less volume is critical to the lower enthalpy for the stabilization of *Pnnm* phase. Moreover, dynamical structural stability of the *Pnnm* structure was investigated by calculating phonon dispersion curves. No imaginary frequency was found for the structure, which indicated that it is dynamically stable.

The *Pnnm* structural lattice constants generated in the optimization at 25 GPa are $a = 3.8015 \text{ \AA}$, $b = 4.5258 \text{ \AA}$, and $c = 2.4840 \text{ \AA}$, with Fe atoms on the Wyckoff sites $2c (0,1/2,1)$, being different from in a common $2a$ sublattice of metal atom in the marcasite type of AN₂ [34-35], and N atoms on the site $4g (x, y)$ with two internal parameters x and y ($x = 0.13016$, $y = 0.09678$). Thus it can be regarded as an iso-structure of the marcasite type. Calculations at different pressure confirm that there is no important effect of the pressure on the atomic positions of the atoms in the *Pnnm* structure. In the structure, it contains a dinitrogen unit with an N-N distance of $d_1 = 1.322 \text{ \AA}$, and the coordination of the Fe atoms is surrounded by the dinitrogen units (Figure 2a). Each Fe atom has two nearest and four next-nearest neighboring N atoms with Fe-N distances of $d_2 = 1.891 \text{ \AA}$ and $d_3 = 1.926 \text{ \AA}$, respectively. When the pressure is increasing to 50 GPa, the dinitrogen N-N distance is short to $1.317 \text{ \AA}$ and the Fe-N bond distances are compressed to $1.857 \text{ \AA}$ and $1.891 \text{ \AA}$, respectively. In the studied pressure range of Figure 2b, it is found that the dinitrogen N-N distance has a small change while the Fe-N distances decrease monotonically as pressure increases. This result manifests the pressure have an important effect on the Fe-N bond but less

effect the N-N bond. Polyhedral views (Figure 2a) of the $Pnnm$ structure is similar to the $R-3m$ structure with the same coordination number forming six-fold bond FeN_6 octahedron, but it contains longer dini-trogen units and closer-packed iron, in contrast with the cubic layers hexagonal $R-3m$ structure [6].

Figure 2. Crystal structures of the orthorhombic $Pnnm$ structure in FeN_2 , a structural unit of 6-fold bonded FeN_6 octahedra. The blue and purple spheres indicate Fe and N atoms, respectively.

In the following, we are going to study the mechanical stability of the $Pnnm$ structure under high pressure. Based on the Born criteria [36-37], the case of an orthorhombic crystal with six C_{ij} elastic moduli, the mechanical stability at zero pressure requires that

$$C_{11} > 0, C_{44} > 0, C_{55} > 0, C_{66} > 0$$

$$C_{11}C_{22} > C_{12}^2$$

$$C_{11}C_{22}C_{33} + 2C_{12}C_{13}C_{23} - C_{11}C_{23}^2 - C_{22}C_{13}^2 - C_{33}C_{12}^2 > 0 \quad (1)$$

To study the mechanical stability of the orthorhombic crystal under pressure, such Eqs. (1) have to be modified to include the particular case when the external load is different from zero. Referring to the reports [36-37] about a detailed explanation of how the Born stability criteria must be modified when the solid is subject to a external load, we obtain the general stability criteria valid when the orthorhombic crystal is subjected to an external hydrostatic pressure P in the following form (2):

$$C_{11} - P > 0, C_{44} - P > 0, C_{55} - P > 0, C_{66} - P > 0$$

$$(C_{11} - P)(C_{22} - P) > (C_{12} + P)^2$$

$$(C_{11} - P)(C_{22} - P)(C_{33} - P) + 2(C_{12} + P)(C_{13} + P)(C_{23} + P) - (C_{11} - P)(C_{23} + P)^2 - (C_{22} - P)(C_{13} + P)^2 - (C_{33} - P)(C_{12} + P)^2 > 0$$

Figure 3a shows the evolution of the calculated C_{ij} of the $Pnnm$ structure with pressure. It can be seen that all C_{ij} elastic moduli increase monotonically as pressure increases. In the studied pressure range, we

check the *Pnnm* structure whether satisfies Eqs. (2) for all pressures or not. It is found that all the above criteria are satisfied for the *Pnnm* structure. This fact indicates that the *Pnnm* phase is mechanically stable at the considered pressure, as expected.

We calculated the each axis of the *Pnnm* phase as a function of pressure to analyze the compressibility of each axis with pressure. As shown in Figure 3b, it is found that the *b* and *c* axis decrease as pressure increases while the *a* axis almost keeps a constant. The *a* axial compressibility (0.23%) is less than that of the *b* (0.35%) and *c* axis (0.34%) in the studied pressure range. This fact indicates that the *a* axis exhibits stronger resistance to linear compression than the *b* and *c* axis. In order to research the mechanical properties of the *Pnnm* structure, the elastic moduli (B, G, E) and Poisson's ratio (ν) have been calculated at 25 GPa in the Table 1. The bulk moduli (B) from the elastic constants is calculated to have a value of 385 GPa. In addition, a fit to the calculated E–V points (Figure 3c) using a Birch Murnaghan EOS [38] gives a bulk moduli (B') values of 357 GPa. This B' value compares well with the B value with small differences within the fitting errors. It is also important to notice that B/G=1.48. The critical B/G value for ductile and brittle materials is 1.75, indicating that the studied *Pnnm* structure of FeN₂ compound is brittle material. Regarding the effects of pressure on the brittleness of the *Pnnm* structure, we found that B/G increases under pressure reaching at 50 GPa values that is increasing to 1.55. This fact indicates that under compression the brittleness of *Pnnm* structure become weak. Additionally, we calculated the Poisson's ratio ν defined as $\nu = E/2G - 1$ which is an important physical quantity related to the stability of the crystal against shear. The calculated value ν is 0.22 a value smaller than the Poisson's ratio ~0.3 in cubic BN. It means that the stable of the *Pnnm* structure against shear can't be compatible to that of cubic BN.

Table 1. Calculated the bulk moduli B (GPa), shear moduli G (GPa), young's moduli E (GPa), Vickers hardness H_v (GPa) and Poisson's ratio (ν) from the elastic constants and the bulk moduli B' (GPa) using a Birch-Murnaghan EOS for the *Pnnm* phase at 25 GPa

Structure	B	B'	G	B/G	E	H_v	ν
<i>Pnnm</i>	385	357	259	1.48	634	26.3	0.22

As known, most common hard transition-metal pernitrides crystallize have bulk moduli comparable with those of the traditional superhard materials. For example, the measured bulk moduli (B = 428 GPa) of IrN₂ is second only to that of diamond (K = 440 GPa) [39]. The bulk moduli or shear moduli can be a measure of the hardness in an indirect way. Note that the high bulk moduli for the *Pnnm* phase of FeN₂ indicates it is likely to be hard materials. The value is close to the bulk moduli (B = 368 GPa) of

$\text{Fe}_3\text{Mo}_3\text{N}$, thus pointing to a very similar resistance to plastic deformations [38]. Employing the Simunek's Method, a theoretical Vickers hardness of 26.3 GPa for the $Pnnm$ phase is estimated, which is close to that of ternary nitrides ($\text{Ni}_2\text{Mo}_3\text{N}$, $\text{Fe}_3\text{Mo}_3\text{N}$) and other transition-metal pernitrides AN_2 such as OsN_2 [34-35, 38]. Such excellent mechanical properties would like to relate the incompressible with the dinitrogen units as found in other transition-metal pernitrides AN_2 . As charge transfer from A to N controls the length of the N-N bond, resulting in a quite incompressible N-N bond, dominantly by providing Coulomb repulsion between the pairing N atoms.

Figure 3. (a) Pressure dependence of the theoretical elastic moduli of the $Pnnm$ structure at 25 GPa. (b) Calculated the each axis of the $Pnnm$ phase as a function of pressure. (c) Total-energy versus volume from *ab initio* calculations for the $Pnnm$ structure.

Return to the dinitrogen units, we note that it's N-N distance (~ 1.32 Å) in the $Pnnm$ structure is longer than the double bond (1.27 Å) in the $R-3m$ structure [6] and the $\text{N}\equiv\text{N}$ triple bond (1.10 Å) in the neutral N_2 , and smaller than the N—N single bond (1.47 Å) that is presumably present in N_2^{4+} of PtN_2 and OsN_2 [9-10]. The N-N distance is nearly identical to the single C-C bond (1.31 Å) of the C_2^{4+} unit in ThC_2 [40], which directly shows that the $Pnnm$ structure of FeN_2 compound maybe have the N_2^{4+} unit.

However, a similar N–N distance (1.34–1.35 Å) of N_2^{2-} units was found in the dubbed $\text{Li}_2\text{Ca}_3\text{N}_6$ [41]. Even if the N–N distance increases to 1.46 Å for TiN_2 , the N_2^{2-} units still present in the compound. Therefore it is not safely to regard the dinitrogen units of the $Pnnm$ structure as an N_2^{4-} or N_2^{2-} unit only judging from the N–N distances. The charge distribution is more appropriate to judge the dinitrogen units as $\text{Fe}^{2+}\text{N}_2^{2-}$ or $\text{Fe}^{4+}\text{N}_2^{4-}$. The Bader charge analysis [42] reveals that about 1.6 e from Fe atom transfers to the dinitrogen units in the $Pnnm$ structure, which is close to the value (approximately 1.5 e) of the $R\bar{3}m$ structure. The non-integer charges are due to the fact that the charges are calculated by partitioning space according to its zero-flux surfaces. The same situation is found in a typical ionic crystal Na^+Cl^- , in which the Na transfer charge is around 0.8 e using the Bader charge analysis. Therefore, it is plausible to recognize that the N_2^{2-} units is present in the $Pnnm$ structure.

Another indirect way to subject to proof the N_2^{2-} units is given by a quantum-chemical analysis of the extended $Pnnm$ structure of FeN_2 indeed yields the antibonding states within the quasi-molecular nitrogen dimer. Figure 4 offers the COHPs for the Fe–Fe, Fe–N and the N–N bonding inside FeN_2 . In the N–N combination, the antibonding states are found between -4 and +0.5 eV, which differs from that in PtN_2 completely filled [43]. Just like for BaN_2 , the nitrogen- π_p^* levels in FeN_2 are half-filled so that the per-nitride unit can be formulated as N_2^{2-} , as above already suggested by the charge analysis. By comparing with the $R\bar{3}m$ structure, the $R\bar{3}m$ structure with the N_2^{2-} units has similar COHP feature [6], which supported that the dinitrogen units of the $Pnnm$ structure is regard as the N_2^{2-} unit. Moreover, the strong bonding states also exist in the $Pnnm$ structure. Besides a strongly bonding N–N bond behavior below the -4.5 eV, there is a Fe–N combination bonding state in the entire occupied region. These bonding states of the occupied crystal orbitals reveal a mix Fe–N and N–N chemical bonding in the $Pnnm$ structure.

Figure 4. Crystal orbital Hamilton population (COHP) analysis of Fe—Fe, Fe—N, and N—N bonding interactions within the $Pnnm$ structure

The electronic band structure and partial density of states (PDOS) of the $Pnnm$ structure were calculated (Figure 5). The result shows that FeN_2 exhibit metallic features. This is in agreement with the OsN_2 and RuN_2 , but differs from IrN_2 and PtN_2 which are nonmetallic. From PDOS of Figure 5, we noticed that Fe d orbital has hybridization with N p orbital, indicating a covalent bonding between Fe and N. Fe belongs, like Os, Ru, to the transition metal series and just has electrons less than Os and Ru, so a same metallic character would be compatible with electron counting arguments. To probe the role of Fe played in the electronic structures, we calculated the band structure of a hypothetical Fe_0N_2 system by removing Fe out of the lattice, where N sublattice remains unchanged. A uniform compensated background charge ($8e/\text{Fe}$) is applied to preserve the total valence electrons of the system. The resultant band structure (red dash lines in Figure 5) isn't essentially similar to the realistic one of FeN_2 . The indication is that the Fe atoms not only act as electron donors but also bond with N, consistent with the analyses of COHP and PDOS as described above. One might conclude that the correlations the mechanical properties with the Fe action: acting as electron donors to the antibonding orbital help stretch the N-N covalent bond; acting bond with N increase the covalence of system, which involving covalency are the source of the mechanical properties. This reasoning can be also found to hold true for other transition-metal carbides and nitrides [31, 44-45].

Figure 5. Electronic band structure and PDOS for the *Pnnm* phase at 25 GPa. In the left panel, the black solid lines are electronic band structure of FeN_2 ; the red dashed lines represent the band structure of the N sublattice (Fe_0N_2) with a uniform compensated background charge; the Γ (0 0 0), Z (0 0 0.5), T (-0.5 0 0.5), Y (-0.5 0 0), S (-0.5 -0.5 0), X (0 0.5 0), U (0 0.5 0.5) and R (-0.5 0.5 0.5) are high symmetry points in the Brillouin zone. The right panels present the DOS of *Pnnm* structure projected on the Fe-*d* and N-*p* orbitals.

Conclusion

In summary, the stable structures and possible stoichiometries in the Fe-N system at high pressure are explored by first-principles crystal structure prediction based on PSO algorithm. The *Pnnm* structure of FeN_2 , a well-known marcasite phase in the case of transition-metal pernitrides AN_2 , is predicted to be more stable than the *R-3m* structure at pressures above 22 GPa. Moreover, its dynamical and mechanical stability under pressure are also verified. The COHP and PDOS analyses demonstrate the pernitride unit is formulated as $(\text{N}=\text{N})^{2-}$ and the mixed covalent N-N and Fe-N bonding nature are present in the structure. The mechanical properties including bulk moduli, shear moduli, Young's moduli, Poisson's ratio and Vickers hardness have been further computed, revealing that *Pnnm* structure exhibits excellent mechanical properties, which are correlated with the dinitrogen units.

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