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Review

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*-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 it's 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.

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1. 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

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iron pernitride (FeN_2) crystallizing in the space group *R*-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 (A = 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 $Fe_xN_{1\text{-}x}$ ($0 < x < 1$) 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 *Aba*2-40 (Pearson symbol *oC*40) structure of Li, the two low-pressure monoclinic structures of Bi_2Te_3, and the orthorhombic *Imm*2 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*-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.

2. 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 $Fe_xN_{1\text{-}x}$ ($0 < x < 1$) 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 $3d^74s^1$ and $2s^22p^3$ 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*-3*m* 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 mouduli, 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) method [31] using the LOBSTER program [32,33].

3. Results and discussions

Structural predictions for the FeN_2 compound was performed using the CALYPSO code with simulation cells contaning 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*-3*m* 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 Fig. 1a, it is found that the *Pnnm* structure is even more stable than the *R*-3*m* 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*-3*m* and *Pnnm* structures. We therefore performed the enthalpy calculations after considering spin polarized mode in Fig. 1b. As shown in Fig. 1b, the enthalpy difference curves show that the lowest-energy FeN_2 phase adopts *R*-3*m* 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.

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 Fig. 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 FeN_2 at 50 GPa. The result confirms that the FeN_2 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 FeN_2 at temperature of $T = 1000$ K was performed and shown in Fig. 1d. We found that the *Pnnm* phase synthesis of FeN_2 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*-3*m* phase can be extracted from our data. These phenomenon manifest that temperatures have negative effect on FeN_2 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*

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