

A New Structure of the Environment-Friendly Material Fe₁₆N₂

Lei Feng^{a,b,*}, Dongmei Zhang^{a,b}, Fei Wang^c, Li Dong^b, Shuang Chen^b, Jie Liu^b, Xuesong Hui^b

^aMetallurgy and Energy College, North China University of Science and Technology, Tangshan, China

^bQian'an College, North China University of Science and Technology, Tangshan, China

^cInstitute of Power Source & Ecomaterials Science, Hebei University of Technology, Tianjin, China

feng_lei2000@163.com

In this paper, a new compound c-Fe₁₆N₂ is obtained using a new crystal structure prediction software CALYPSO (Crystal Structure Analysis by Particle Swarm Optimization). The compound has a structure of C_{2/m} (the twelfth space group), and a magnetic moment of 17 μ_B per unit cell. The enthalpy of c-Fe₁₆N₂ is -8.620 eV/atom, which is little to that of α''-Fe₁₆N₂ (-8.287 eV/atom), so the former is more stable from the view of energy. The average magnetic moment of c-Fe₁₆N₂ is 2.13 μ_B per iron atom which is small to that of α''-Fe₁₆N₂ (2.8 μ_B). The c-Fe₁₆N₂ is a new rare earth-free permanent magnet. No rare earth means no environmental pollution in the the rare earth mining. The α''-Fe₁₆N₂ has a highest saturation magnetic flux density, but it is difficult to mass production, because there are other several N-Fe iron compounds (such as Fe₃N, Fe₄N) in the obtained resultants. The newly found compound c-Fe₁₆N₂ may replace α''-Fe₁₆N₂ because the former can be easily obtained compared to the latter, and there maybe a new way to mass production of α''-Fe₁₆N₂ from c-Fe₁₆N₂.

1. Introduction

The magnetic material is an important functional material. At present, the permanent magnetic materials are all made of rare earth, such as SmCo, Sm₂Co₁₇ and Nd₂Fe₁₄B. Rare earth metal is non-renewable, and the source reserves is less and less. The mining, refining, recycling (Balintova et al., 2014) of rare earth metal are damaging to the environment (Elena et al., 2015). It is known that the rare earth mining is harmful to environment, and the purification of rare earth can generate air and water pollutions, so it is necessary to develop a new type of strong magnetic material which does not contain rare earth. In recent years, many attentions have been paid to nitriding magnetic materials. Iron nitride FeN (Rissanen et al., 1998), Fe₂₋₃N, Fe₃N, Fe₄N have high magnetization, and they are chemical stable. The discovery of these nitride magnetic materials makes researchers who study the magnetic materials have a great interest in N element. Jack (1951) first discovered α''-Fe₁₆N₂ and its high magnetization was reported by Kim and Takahashi (1972). The α''-Fe₁₆N₂ has the largest saturation magnetic field strength of 2.83T in all the magnetic materials.

The α''-Fe₁₆N₂ compound has a body centred tetragonal (bct) structure (I4/mmm space group) (Jack., 1995) which is illustrated in the Figure 1 (Benea et al., 2016), the lattice parameters are a = b = 5.72Å, c = 6.29Å, α = β = γ = 90° (Robert et al., 1994). The site positions of all the atoms in the α''-Fe₁₆N₂ crystal structure are listed in the Table 1. In the structure, Fe atoms occupy three different inequivalent Wyckoff sites (4e, 8h, 4d), and the N enters the 2a crystal site. The structure can be seen composing of a 2 × 2 × 2 super cell of bcc Fe with two additional N atoms locating at interstitial octahedral positions. The cell of bcc Fe is deformed, the length of c axis is twice of the α-Fe, so one unit cell of a α''-Fe₁₆N₂ is 205.8 Å³. The Fe atoms occupy the six vertexes of an octahedral structure, the upper and the lower vertexes are the 4e sites, and the horizontal vertexes are the 4h sites. The nearest neighbour of N atom is Fe2, and the furthest neighbour is Fe3.

The preparation methods of α''-Fe₁₆N₂ are mainly the following several kinds. The first method is the nitriding annealing method, this is the earliest method for preparing α''-Fe₁₆N₂ (Huang et al., 1994) and is also the main method for the preparation of bulk α''-Fe₁₆N₂ material. This method is also used in the preparation of α''-

Fe₁₆N₂ thin films. At about 750 °C, α-Fe is nitrided in nitrogen to form a nitrogen austenite phase, and then quenched at a temperature below 0 °C to obtain a martensitic α' phase and anneal at about 120 °C for an hour to obtain α''-Fe₁₆N₂ phase (Jack, 1994). The second method is implanting the N₂⁺ ion into the iron film (Leroy et al., 1995). The third is the vapor phase epitaxy method. The iron nitride film is grown by molecular beam epitaxy in NH₃ / H₂ to prepare α''-Fe₁₆N₂.

But up to now, the reported coercive force of α''-Fe₁₆N₂ compound was still too small to practical use. The low coercive force is attributed to inappropriate grain size which is with obvious grain boundaries. Unfortunately, the grain size and the grain boundaries in the compound are hard to control by traditional methods. As we said above, the structure of α''-Fe₁₆N₂ is a martensite structure, its structure is sensitive to temperature changes, and stable only under 214 °C. But according the literature, the lowest temperature to obtain α''-Fe₁₆N₂ is 350 °C, so the traditional annealing method is not applicable for α''-Fe₁₆N₂. So, a low-temperature approach is needed to prevent the martensitic phase breaking down.

Recently, Jiang et al. (2015) invented a new method to prepare α''-Fe₁₆N₂. They firstly used ball milling method to prepare α''-Fe₁₆N₂ powder, the ratio of ball mass to sample mass was 10:1, the ammonium nitrate (NH₄NO₃) was used to as nitrogen source in the reaction during ball milling, the experiment was carried out in a nitrogen gas environment inside a glove box, the ball mill rotation speed was 600 rpm in planetary mode. After 60 h of milling, the α''-Fe₁₆N₂ was obtained with a purity of 70 %, the saturation magnetization was up to 210 emu/g, and the coercivity was 854 Oe at room temperature. A strained-wire method of production of α''-Fe₁₆N₂ was proposed in 2016 (Jiang et al., 2016). First, the bulk iron was melted with a prefixed ratio of urea, second, the FeN mixture was heated to 660°C for 4 h, then quenched into water at room temperature, after that, 0.2 - 0.3 mm² and 10 mm long samples which were cut from the mixture were strained using a loading device to apply an external force which could elongate the length of the lattice. The prepared FeN magnet was with a coercivity of 1,220 Oe, and the saturation magnetization at the 2-T field was 220 emu/g. But the prepared sample was a mixture of Fe₁₆N₂, Fe₈N, Fe₄N, and Fe.

In this article, by using a new crystal structure prediction software CALYPSO, a new compound c-Fe₁₆N₂ is obtained, and it is different to α''-Fe₁₆N₂ which is difficult to mass production. The c-Fe₁₆N₂ has a lower enthalpy than α''-Fe₁₆N₂, so the former is more stable than the latter in energy, in other words, the former can be easily obtained compared to the latter. The c-Fe₁₆N₂ is also a magnet with large magnetic moment, so it can replace the α''-Fe₁₆N₂ and is an important rare earth-free permanent magnet. There is no rare earth in c-Fe₁₆N₂, so there is no occurrence of environmental pollution in the production of this compound.

Table 1: The site positions of the Fe and N in α''-Fe₁₆N₂ crystal structure

Site	Site symmetry	x/a	y/b	z/c	First [second] coordination
Fe1	4d	0	1/2	1/4	8 Fe3, 2.55 Å; [4 Fe2, 2.86 Å] 2 N, 3.26 Å
Fe2	4e	0	0	0.31	1 N, 1.95 Å, 4 Fe3, 2.33 Å, 1 Fe2, 2.39 Å [4 Fe3, 2.80 Å, 4 Fe1, 2.86 Å]
Fe3	8h	0.25	0.25	0	1 N, 2.01 Å, 2 Fe2, 2.33 Å, 4 Fe1, 2.55 Å 1 [2 Fe2, 2.80 Å, 4 Fe3, 2.84 Å]
N	2a	0	0	0	2 Fe2, 1.95 Å, 4 Fe3, 2.01 Å [8 Fe1, 3.24 Å]

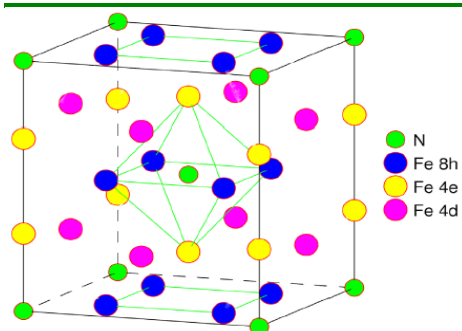


Figure 1: The structure of the α''-Fe₁₆N₂ compound

2. Method and calculation details

CALYPSO is a short name of “Crystal Structure Analysis by Particle Swarm Optimization” (Wang et al., 2015), it has been developed by professor Ma and his team in Jilin university (Su et al., 2017). It is designed to predict crystal structures of materials ranging from 0-dimensional (0D) to 1D, 2D, and 3D (Wang et al., 2017). In the software, the Particle Swarm Optimization (PSO) algorithm is applied, and this algorithm is inspired by team organization pattern of a bird flock which can be regarded as a distributed algorithm in multidimensional searching and can be seen as an unbiased global optimization method. This algorithm can quickly search for all the potential energy surface, overcome the energy barrier, and not cause the loss of the smallest energy structure. The software can employ the structure relaxation software such as Vasp, Pwscf, Castep, Gaussian, etc. In the prediction of structures of a material, the CALYPSO can randomly generate a group structures according to the material formula and take care of the symmetry requirements, a few random structures can be generated in every generation, the number of generation can be set according to the number of atoms, for each structure, the geometry optimization will be make, the number of the geometry optimization is usually set as three or four, the reasonable structures will be reserved and make further optimization, the unreasonable will be discarded, and this procedure will be repeat many times. The software can also be used to search for functional materials according to a few parameters, such as semiconductors, superconductor, superhard materials, lithium-ion battery materials, and study the binary phase diagram, clusters (Liu et al., 2016), crystal structures under high pressure (Harran et al., 2016), and so on.

The preparation of Fe_{16}N_2 involves α -Fe to α' -N-martensite as one adds N atoms gradually in the structure and tempers it. But the prepared sample is always a mixture. So, the more stable phase of Fe_{16}N_2 should be explored and the CALYPSO software was used to study other new structures of Fe_{16}N_2 .

For Fe_{16}N_2 , the number of element specie, name of the element Fe, N, the atom numbers, the number of formula, an estimate volume of the formula and the distance of the atoms were all supplied to the CALYPSO software, and the maximum step of the revolution in the procedure was 30.

The density of states (DOS) and bands structures were obtained using a generalized-gradient approximation (GGA) method proposed by Perdew et al. (1996).

3. Results and discussions

According the computational results, a new monoclinic structure (C_2/m space group) of Fe_{16}N_2 was found, the lattice parameters are $a = 5.0716 \text{ \AA}$, $b = 7.3262 \text{ \AA}$, $c = 5.0404 \text{ \AA}$, $\alpha = \gamma = 90^\circ$, $\beta = 92.5146^\circ$, and the volume is 187.0985 \AA^3 . The site positions of all the atoms in the crystal structure are listed in the Table 2. The structure is illustrated in the Figure 2.

The N atoms are all in the centre of four plane, the N atoms in the up and lower plane have four nearest Fe atoms, the N atoms in the left and right plane have two first nearest Fe atoms and four second nearest Fe atoms. Two Fe1, Fe5, Fe7 atoms in the body centre of the structure form an octahedron.

Table 2: The site positions of the atoms in Fe_{16}N_2 with C_2/m crystal structure

Site	Site symmetry	x/a	y/b	z/c
Fe1	4h	0	0.7568	0.5
Fe3	4g	0	0.2454	0
Fe5	4i	0.7681	0	0.7674
Fe7	4i	0.2440	0	0.7615
N1	2d	0	0.5	0.5

The calculated total density of states (DOS) are presented in Figure 3. For the total DOS, the states are mainly between $-10 \sim 17 \text{ eV}$, the shapes of the upper and lower halves are asymmetry, especially around the Fermi level, and there are two leading peaks below and above the Fermi level.

The calculated total magnetic moment of Fe_{16}N_2 with C_2/m crystal structure is $17\mu_B$ per unit cell, $2.13 \mu_B$ per Fe atom, this result is small to that of α' - Fe_{16}N_2 obtained by Kim and Takahashi (1972), and their result is $2.8 \mu_B$. The magnetic moment of one N atom is $-0.02 \mu_B$, which is little and anti-parallel with the other Fe atoms. The enthalpy of c- Fe_{16}N_2 is -8.620 eV/atom , which is little to that of α' - Fe_{16}N_2 (-8.287 eV/atom), so the former is more stable from the view of energy.

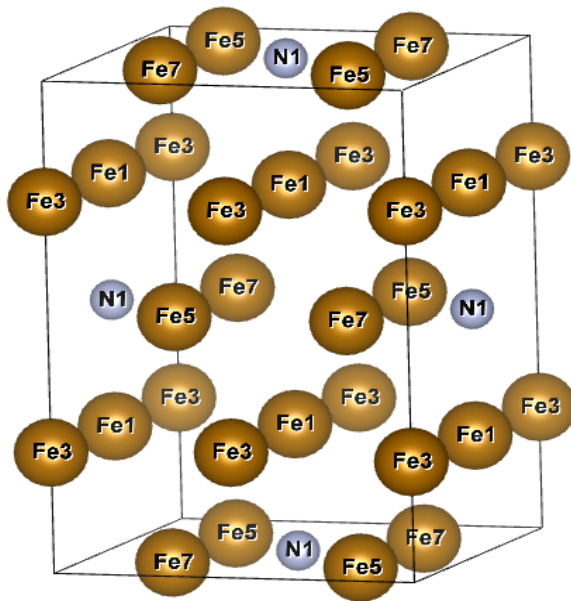


Figure 2: The structure of the Fe₁₆N₂ with C₂/m crystal structure

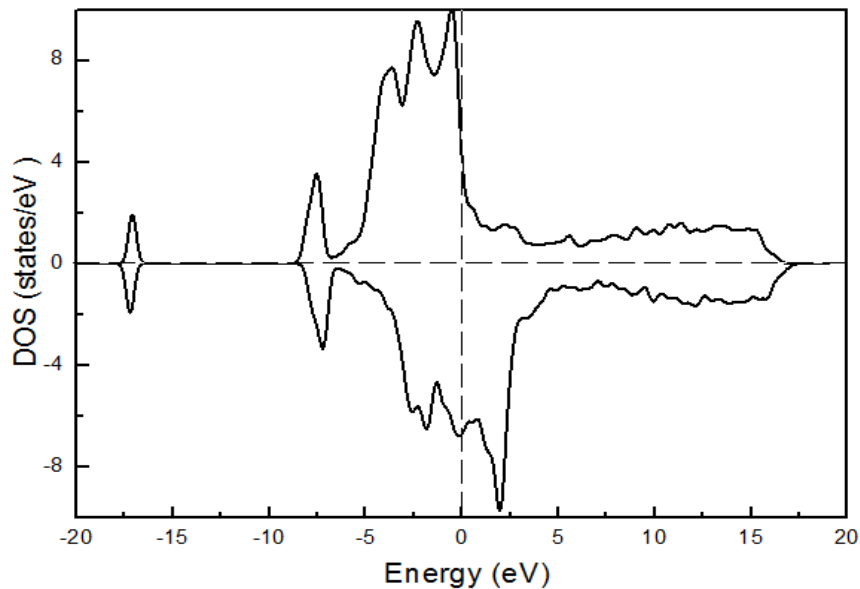


Figure 3: The total density of states of Fe₁₆N₂ with C₂/m crystal structure

The spin-dependent energy bands along high-symmetry directions in the Brillouin zone for Fe₁₆N₂ with C₂/m crystal structure are shown in Figure 4. The band structures distribute in the range of -8 eV to 17 eV, and very dense in the range of -5 eV to the Fermi level, implies that the electron in this range is rather local, and the effective mass is relatively large. The bands below -5 eV are relatively wide, the shapes look like parabolas, so they are *sp*-like bands. The valence bands intersect with the conduction bands.

In this article, the crystal structure and the electric structure were studied using GGA method. If one who had the experimental condition could try to prepare the alloy c-Fe₁₆N₂. Because X-ray diffraction method is usually used to confirm the crystal structure, so the calculated X-ray diffraction was done, and the data are plotted in the Figure 5.

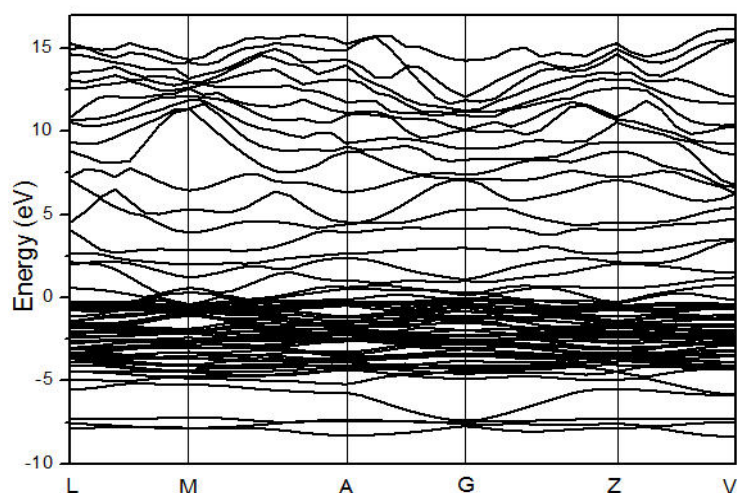


Figure 4: The majority spin band structures of Fe_{16}N_2 with C_2/m crystal structure

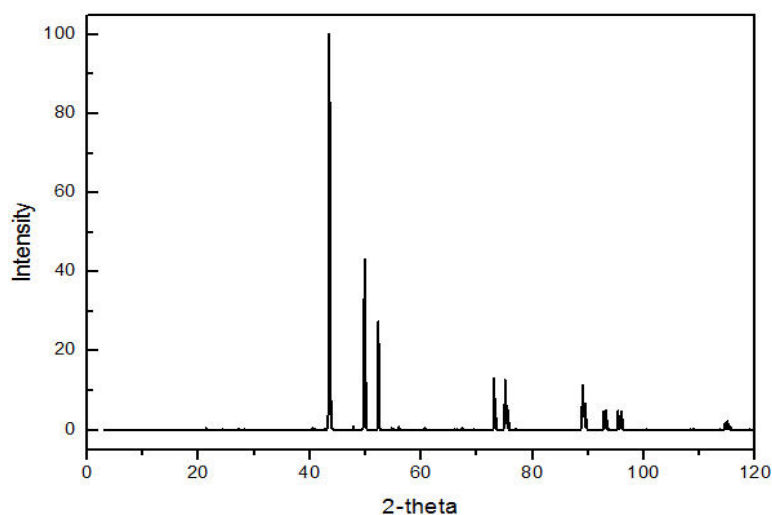


Figure 5: The x-ray diffraction result of Fe_{16}N_2 with C_2/m crystal structure

4. Conclusions

In this paper, using a new crystal structure prediction software CALYPSO, a new compound of $c\text{-Fe}_{16}\text{N}_2$ is obtained which is different to $\alpha''\text{-Fe}_{16}\text{N}_2$. It has a C_2/m symmetry, and the $c\text{-Fe}_{16}\text{N}_2$ is a new magnet with a magnetic moment of $17 \mu_B$. The density of states and the band structures are all obtained using GGA method. The x-ray diffraction simulation result of $c\text{-Fe}_{16}\text{N}_2$ is also obtained. The newly found compound $c\text{-Fe}_{16}\text{N}_2$ may replace $\alpha''\text{-Fe}_{16}\text{N}_2$ as a new rare earth-free permanent magnet. There is no rare earth in the compound, implying no occurrence of environmental pollution in the the rare earth mining. The magnetic moment of $c\text{-Fe}_{16}\text{N}_2$ is smaller than that of $\alpha''\text{-Fe}_{16}\text{N}_2$, and this may limit some applications of this material.

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References

- Benea D., Isnard O., Pop V., 2016, Electronic structure and magnetic properties of the Fe₁₆N₂ doped with Ti, *Journal of Magnetism and Magnetic Materials*, 420, 75-80.
- Balintova M., Holub M., Stevulova N., Cigasova J., Tesarcikova M., 2014, Sorption in acidic environment – biosorbents in comparison with commercial adsorbents, *Chemical Engineering Transactions* 39, 625-630.
- Iannicelli Zubiani E., Cristiani C., Dotelli G., Gallo Stampino P., Pelosato R., 2015, Recovery of rare earths and precious metals from waste electrical and electronic equipment by acid leaching and immobilized chelating agents, *Chemical Engineering Transactions*, 43, 2413-2418.
- Huang M.Q., Wallace W.E., Simizu S., Sankar S.G., 1994, Magnetism of α' -FeN alloys and α'' -Fe₁₆N₂ nitrides, *Journal of Magnetism and Magnetic Materials*, 135, 226-230.
- Harran I., Wang H.M., Chen Y.Z., Jia M.Z., Wu N.N., 2016, Exploring high-pressure FeB₂: Structural and electronic properties predictions, *Journal of Alloys and Compounds*, 678, 109.
- Jack K. H., 1995, The synthesis and characterization of bulk α'' -Fe₁₆N₂, *Journal of Alloys and Compounds*, 222, 160-166.
- Jack K. H., 1951, The Iron-Nitrogen System: The preparation and the crystal structures of nitrogen-austenite and nitrogen-martensite, *Proceedings of the Royal Society A*, 208, 200-215.
- Jack K. H., 1994, The synthesis, structure, and characterization of α'' -Fe₁₆N₂, *Journal of Applied Physics*, 76, 6620-6625.
- Jiang Y.F., Liu J.M., Suri P.K., Kennedy G., Thadhani N.N., Flannigan David J., Wang J.P., 2015, Preparation of an α'' -Fe₁₆N₂ magnet via a ball milling and shock compaction approach, *Advanced Engineering Materials*, 18, 1009-1016.
- Jiang Y.F., Dabade V., F. Allard L., Lara-Curzio E., James R., Wang J.P., 2016, Synthesis of α'' -Fe₁₆N₂ compound anisotropic magnet by the strained-wire method, *Physical Review Applied*, 6, 024013-024023.
- Kim T.K., Takahashi M., 1972, New magnetic material having ultrahigh magnetic moment, *Applied Physics Letters*, 20, 492-494.
- Leroy E., Mariadassou C.D., Bernas H., Kaitasov O., Krishnan R., 1995, The road to Fe₁₆N₂ formation in N⁺ implanted Fe enriched films, *Applied Physics Letters*, 67, 560-562.
- Liu L., Hu C., Tang M., Chen X., Cai L.C., 2016, Ab initio investigation of structure, stability, thermal behavior, bonding, and infrared spectra of ionized water cluster (H₂O)₆⁺, *Journal of Chemical Physics*, 145, 154307.
- Perdew J.P., Burke K., Ernzerhof M., 1996, Generalized gradient approximation made simple, *Physica Review Letters*, 77, 3865-3868.
- Rissanen L., Neubauer M., Lieb K.P., Schaaf P., 1998, The new cubic iron-nitride phase FeN prepared by reactive magnetron sputtering, *Journal of Alloys and Compounds*, 274, 74-82.
- Robert M. M., Bao X.H., 1994, Magnetism of a α'' -Fe₁₆N₂, *Journal of Applied Physics*, 76 (10), 6626-6631.
- Su C.X., Lv J., Li Q., Wang H., Zhang L.J., Wang Y.C. and Ma Y.M., 2017, Construction of crystal structure prototype database: methods and applications, *Journal of Physics: Condensed Matter*, 29, 16.
- Wang Y., Lv J., Zhu L., Lu S., Yin K., Li Q., Wang H., Zhang L., Ma Y., 2015, Materials discovery via CALYPSO methodology, *Journal of Physics Condensed Matter*, 27(20), 203203.
- Wang Z., Li Y., Li H., Harrana I., Jia M., Wang H., Chen Y., Wang H., Wu N., 2017, Prediction and characterization of the marcasite phase of iron pernitride under high pressure, *Journal of Alloy and Compounds*, 702, 132-137.