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Analysis of magnetic structures of iron nitrides by Landau's theory of second-order phase transitions

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The magnetic structures of iron nitrides are studied by Landau's theory of second-order phase transitions. It is found that the magnetization direction of ϵ -Fe₃N must be parallel to the c-axis of the hexagonal structure, which may conclude the debates on the easy axes of ϵ -Fe₃N in this field. The easy axes of α'' -Fe₁₆N₂ are turned out to be along [001], or [100], or [110] direction, with the former two cases already found by the experiments. The magnetization along [111] is forbidden, which solves rigorously the puzzle why the easy axes of the α'' -Fe₁₆N₂ on InGaAs and Fe are different from each other. Finally, the magnetic structure of γ' -Fe₄N is also determined, and the result shows that there are three possibilities for the magnetization: parallel to the axial, or the body diagonal, or the face diagonal direction of the cubic structure, among which the first case has been found in experiments. © 2013 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [<http://dx.doi.org/10.1063/1.4817589>]

Iron nitrides have received attention for many years. Early interest on iron nitrides came from their ability to improve surface hardness and wear resistance.¹ In the last decade, the iron nitrides films have been widely investigated since they show a variety of structures and magnetic properties.²⁻⁶ Among all the iron nitrides, only three materials have been found to be ferromagnetic, they are ϵ -Fe₃N, α'' -Fe₁₆N₂ and γ' -Fe₄N. Those compounds are attractive magnetic functional materials for applications such as magnetic recording media and data storage devices. Recently, with the rapid development of spintronics, ϵ -Fe₃N has been considered as a potential material for spintronic devices due to its large spin polarization.⁷ It has been reported that highly oriented nitride-based crystalline α -Fe/AlN/Fe₃N trilayer structures are realized on Si substrates by MBE.^{8,9}

However, the literatures up to now have not definitely classified the magnetic structures of the three iron nitrides yet.

With the sample grown by MBE, Yamaguchi *et al.* reported that the magnetization of ϵ -Fe₃N was perpendicular to the c-axis through M-H curves.⁸ The same result is also obtained by Leineweber *et al.*, using TOF neutron diffraction.¹⁰ On the contrary, Robbins and White found the magnetization of ϵ -Fe₃N directed parallel to the c-axis from neutron diffraction.¹¹ This result is further supported by Rochegude and Foct,¹² whose Mössbauer data suggests indirectly that the c-axis should be the easy axis of ϵ -Fe₃N. Such a point of view is also confirmed theoretically by Siberchicot *et al.*, based on their band structure calculation.¹³ Therefore, it is still under debate whether the easy axis of ϵ -Fe₃N is parallel or perpendicular to the c-axis. We shall try to solve this debate, which is just the first aim of this letter.

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With respect to $\alpha''\text{-Fe}_{16}\text{N}_2$, it can be grown on two different substrates: InGaAs and Fe. Ref. 14 found that the easy axes of the samples on InGaAs can be along [010] or [100] whereas the easy axis of the samples on Fe was along the [111] direction. Just as pointed out by Sugita *et al.*,¹⁴ these two results conflict with each other and thus form a puzzle. This puzzle has not been clarified theoretically yet. We shall try to resolve this puzzle, which is the second aim of this letter.

For $\gamma'\text{-Fe}_4\text{N}$, Wood *et al.* found that the easy axis was along [100] from Mössbauer spectrum.¹⁵ Afterwards, the same result has also been reported by many other literatures, using various methods of measurement.^{16–22} This experimental result poses a theoretical problem why the magnetization can occur along the [100] direction. We shall try to answer this problem, which is the third aim of this letter.

To this end, we shall invoke Landau's theory of second-order phase transitions to study the magnetic structures of the three iron nitrides, $\varepsilon\text{-Fe}_3\text{N}$, $\alpha''\text{-Fe}_{16}\text{N}_2$ and $\gamma'\text{-Fe}_4\text{N}$. In Landau's theory, the so-called second-order phase transition is used to denote such a transition that has an order parameter which changes continuously at the transition point.²³ As is well known, Landau's theory is itself phenomenological, but it can provide the necessary conditions for second-order phase transitions. This theory has been applied to a great variety of transitions, and proved to be correct in physics until now.²⁴ In particular, it has been used to predict the existence of many new possible second-order phase transitions for concrete materials, which are successfully verified further by experiments. The fundamental characteristic of Landau's theory is that it can establish the relationship between the order parameters and the changes in symmetry. From this relationship, one can discuss how the symmetry changes at the transition point. Since the paramagnetic-ferromagnetic transition is typical of second order, we intend to use Landau's theory to analyze all the paramagnetic-ferromagnetic transitions present possibly in the three iron nitrides of $\varepsilon\text{-Fe}_3\text{N}$, $\alpha''\text{-Fe}_{16}\text{N}_2$ and $\gamma'\text{-Fe}_4\text{N}$ in this letter. Especially, we shall investigate, in detail, the symmetry changes occurring in those three materials by the technique of group representation.

The rest of this letter is organized as follows. At first, we introduce the three requirements as well as the five criteria for the second-order phase transitions in Landau's theory. Then, we shall discuss the magnetic structures of the three iron nitrides, respectively, by using these requirements and criteria. The theoretical results will be compared with the experiments. At last, we shall end up this letter with a summary.

According to Landau's theory, a second-order phase transition must satisfy the following three requirements.^{23,24}

- (i) For every crystal, there is a unique thermodynamic potential, Φ , that can describe both phases of the crystal, below and above the transition point, T_c . The potential Φ should be invariant under all the symmetry operations of the high-temperature phase, i.e. high-symmetry phase.
- (ii) For every second-order phase transition, there is an order parameter, η . The order parameter is zero above T_c , and nonzero below T_c . In particular, it must change continuously at the transition point. The order parameter η will evolve with temperature according to an irreducible representation of the group of the high-symmetry phase, but not according to the identity representation.
- (iii) The thermodynamic potential can be expanded into a power series of the order parameter,

$$\Phi(P, T, \eta) = \Phi_0(P, T) + A(P, T)\eta^2 + B(P, T)\eta^3 + \dots \quad (1)$$

where P and T are the pressure and temperature of the system, respectively, and, $\Phi_0(P, T)$, $A(P, T)$ and $B(P, T)$ denote the expanding coefficients, which are functions of the pressure and temperature. Mathematically, the η is proportional to the coefficients of the basis functions corresponding to the irreducible representation. Physically, the thermodynamic potential must be minimized with respect to the variation of the order parameter.

In order to reduce the amount of work necessary if one intends to apply the assumptions (i)–(iii) to the second-order phase transition in a crystal, and to decide what symmetry may appear below the transition point, Birman²⁵ introduced five group-theoretical selection rules. To explain these selection rules for the case of paramagnetic-ferromagnetic transitions considered here, some

terminologies are needed. We shall use θ and \mathbf{G}_0 to denote the operation of time inversion and the point group of a crystal structure, respectively. The grey point group corresponding to \mathbf{G}_0 will be denoted by $\mathbf{G}_0 + \theta\mathbf{G}_0$. Mathematically, \mathbf{G}_0 is the unitary subgroup of $\mathbf{G}_0 + \theta\mathbf{G}_0$. Physically, the group $\mathbf{G}_0 + \theta\mathbf{G}_0$ stands for the symmetry of the high-temperature paramagnetic phase. The symmetry of the low-temperature ferromagnetic phase will be denoted by $\mathbf{G}_1 + \theta(\mathbf{G}_2 - \mathbf{G}_1)$ where \mathbf{G}_2 is one subgroup of \mathbf{G}_0 , and \mathbf{G}_1 is the halving subgroup of \mathbf{G}_2 . Suppose that there is a transition from $\mathbf{G}_0 + \theta\mathbf{G}_0$ to $\mathbf{G}_1 + \theta(\mathbf{G}_2 - \mathbf{G}_1)$. The order parameter realizing this transition should belong to an irreducible representation of \mathbf{G}_0 , this irreducible representation will be denoted by D . Then, the five group-theoretical selection rules can be written as follows,^{24,25}

- (A) \mathbf{G}_1 is a subgroup of \mathbf{G}_0 .
- (B) The symmetrized cube of D can not contain the identity representation Γ_1^+ of \mathbf{G}_0 , i.e.

$$([D]^3|\Gamma_1^+(\mathbf{G}_0)) = 0. \quad (2)$$

- (C) The antisymmetrized square of D can not contain the representation of a polar vector, i.e.

$$(\{D\}^2|\mathbf{V}(\mathbf{G}_0)) = 0. \quad (3)$$

where $\mathbf{V}(\mathbf{G}_0)$ is the vector representation of \mathbf{G}_0 .

- (D) D of \mathbf{G}_0 must subduce into Γ_1^+ of \mathbf{G}_1 .
 - (D.1) If an acceptable D is one-dimensional, or if D of \mathbf{G}_0 subduces into only a multiple of Γ_1^+ of \mathbf{G}_1 , then an acceptable \mathbf{G}_1 is normal to \mathbf{G}_0 .
 - (D.2) Chain-subduction criterion
 - If $\mathbf{G}_0, \mathbf{G}_1, \mathbf{G}_1', D$ of \mathbf{G}_0 subduces into Γ_1^+ of \mathbf{G}_1 once, and D of \mathbf{G}_0 subduces into Γ_1^+ of \mathbf{G}_1' also once, then the transition $\mathbf{G}_0 \rightarrow \mathbf{G}_1'$ is eliminated.
- (E) D of \mathbf{G}_0 corresponds to a physical tensor field.

As has already been pointed out by Cracknell *et al.*,²⁴ the conditions (A), (B), (C), and (E) are the corollaries of Landau's theory, but the condition (D) is in contradiction to the latter because (D.2) violates the minimal condition. Consequently, we shall not verify the condition (D) in the following. Instead, we shall perform the minimization procedure, according to the Ref. 24.

Now, we would apply the three requirements and the four criteria, (A), (B), (C), and (E), to analyze the magnetic structures of the iron nitrides of $\varepsilon\text{-Fe}_3\text{N}$, $\alpha''\text{-Fe}_{16}\text{N}_2$ and $\gamma'\text{-Fe}_4\text{N}$. Above all, it should be pointed out that the condition (B) is automatically satisfied in the case of paramagnetic-ferromagnetic transitions, as has been demonstrated in Ref. 24. Therefore, we shall not discuss it any more. Below, we shall first employ the condition (E) to choose the irreducible representations of \mathbf{G}_0 of the high-symmetry group, and then use the condition (C) to eliminate some of those irreducible representations. Afterwards, we can construct the invariants and the thermodynamic potential from the rest irreducible representations obtained by the conditions (E) and (C). Through the solutions of the minimization of the thermodynamic potential, the unitary subgroups \mathbf{G}_1 of the ferromagnetic point groups are determined completely. Clearly, \mathbf{G}_1 fulfills the condition (A). To sum up, only the two group conditions, (C) and (E), and the minimal condition need further verifications. In the following, we shall deal with the three iron nitrides, respectively, according to this procedure.

(a) $\varepsilon\text{-Fe}_3\text{N}$

As shown in Fig. 1, the crystal structure of $\varepsilon\text{-Fe}_3\text{N}$ is hexagonal. Its point group is 622,²⁶ i.e. $\mathbf{G}_0 = 622$. Correspondingly, the grey point group of the paramagnetic phase of $\varepsilon\text{-Fe}_3\text{N}$ is 6221', i.e. $\mathbf{G}_0 + \theta\mathbf{G}_0 = 6221'$. Among the six single-valued irreducible representations of 622, there are only two representations that can satisfy the condition (E),²⁷ they are Γ_2 and Γ_5 . In other words, the basis vectors of Γ_2 and Γ_5 can be constructed of axial vectors.^{24,27} As shown by the Ref. 28, Γ_2 satisfies the condition (C) whereas Γ_5 violates it. As a result, only Γ_2 can be used to construct the invariants and the thermodynamic potential. The matrices of Γ_2 are listed in the Table 2.2 of Ref. 29, they are one-dimensional. Here, we shall choose the c-axis as the z-axis. Under this condition, the

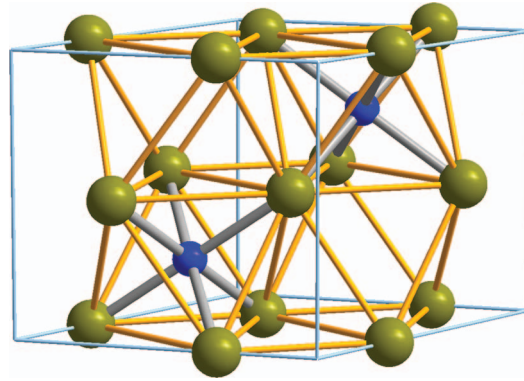


FIG. 1. Crystal structure of ϵ -Fe₃N. Large dark yellow spheres: Fe atoms; small blue spheres: N atoms.

z -component of spin, S_z , is the irreducible basis of Γ_2 .²⁷ The magnetization M can thus be written as

$$M = cS_z \quad (4)$$

where c is a coefficient. This coefficient must be determined by minimizing the thermodynamic potential Φ , and Φ can be constructed from the invariants. For the one-dimensional case considered here, there can only exist two invariants,

$$S_z^2, \quad S_z^4 \quad (5)$$

From them, the potential Φ can be expressed as follows,

$$\Phi = \Phi_0 + Ac^2 + Bc^4 \quad (6)$$

where A and B are two real coefficients. Obviously, there are only two solutions for the c ,

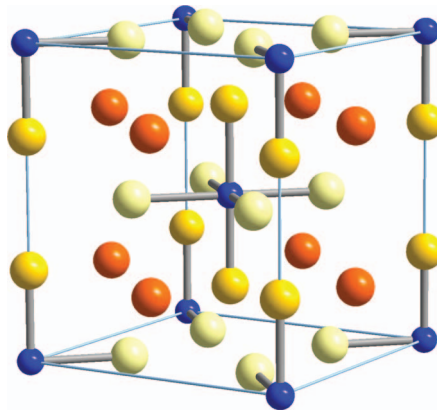
- (i) c is equal to zero.
- (ii) $c^2 = -A/B$.

Clearly, the magnetization M corresponding to the first solution is identically zero, and it is thus nothing to do with the ferromagnetism. As to the second solution, its corresponding magnetization M is nonzero, and so it stands for a ferromagnetic phase. Through substituting the second solution into the representation Γ_2 in the Table 2.2 of Ref. 29, all the invariant operations in 622 (G_0) can be found to form exactly the point group 6, which is G_1 of the ferromagnetic phase. In addition, all the invariant operations that consist of $\theta(G_2 - G_1)$ can also be obtained by the substitution of the second solution into the representation Γ_2 , and then G_2 can be determined to be just 622, i.e. $G_2 = G_0 = 622$. Therefore, the magnetic point group of the ferromagnetic phase should be 62'2', i.e., $G_1 + \theta(G_2 - G_1) = 62'2'$. As a result, the transition from 6221' ($G_0 + \theta G_0$) to 62'2' ($G_1 + \theta(G_2 - G_1)$) fulfills all the conditions of Landau's theory. Now, $M = \pm\sqrt{-A/B}S_z$, so there can exist only one direction of magnetization in the system, i.e. [0001], or equivalently the c -axis of the hexagonal structure. Thus far, the possible magnetic structure of ϵ -Fe₃N has been determined theoretically: Its magnetization must be parallel to the c -axis of the hexagonal structure.

In Ref. 30, the ASW calculations of band structure have been already performed on ϵ -Fe₃N, the magnitude of magnetic moment is obtained. Regrettably, the easy axis of the ϵ -Fe₃N can not be given by the method of Ref. 30 because it do not include the spin-orbit coupling. As pointed out by Siberchicot *et al.*,¹³ the easy axis can be determined only after taking into account the spin-orbit coupling. After taking into account the spin-orbit coupling, Ref. 13 obtains the magnetocrystalline anisotropy energies, and thus it proves that the magnetization of ϵ -Fe₃N should be along the c -axis. Experimentally, Robbins and White¹¹ reported that the magnetization of ϵ -Fe₃N is parallel to the c -axis, by means of neutron diffraction. These results are in good agreement with our theoretical analysis. On the contrary, the magnetization of ϵ -Fe₃N is found to be perpendicular to the c -axis, by M-H curves in Ref. 8 and TOF neutron diffraction in Ref. 10. Evidently, they are directly in contradiction to Landau's theory. That may be due to the situation that the materials used in the

TABLE I. The comparisons between the results from other literatures and our theoretical analysis of the magnetic structure of ε -Fe₃N.

ε -Fe ₃ N	
The experimental and theoretical results from other literatures	Whether be consistent with our theoretical results by the Landau theory
Siberchicot <i>et al.</i> , ¹³ by the calculations of magnetocrystalline anisotropy energies.	Yes
Robbins and White, ¹¹ by neutron diffraction.	Yes
Yamaguchi <i>et al.</i> , ⁸ by magnetization measurement.	No
Leineweber <i>et al.</i> , ¹⁰ by TOF neutron diffraction.	No

FIG. 2. Crystal structure of α'' -Fe₁₆N₂. Large light yellow, gold, and orange spheres: three types of Fe atoms, respectively; small blue spheres: N atoms.

experiments of Refs. 8 and 10 are not single crystal with good quality. The above experimental and theoretical results are all summarized in Table I and compared with our result. So far, the debates on the easy axis of ε -Fe₃N have been concluded completely.

(b) α'' -Fe₁₆N₂

As shown in Fig. 2, the crystal structure of α'' -Fe₁₆N₂ is tetragonal. Its point group is 4/mmm,²⁶ i.e. $G_0 = 4/mmm$. Correspondingly, the grey point group of the paramagnetic phase of α'' -Fe₁₆N₂ is 4/mmm1', i.e. $G_0 + \theta G_0 = 4/mmm1'$. Among the ten single-valued irreducible representations of 4/mmm, there are merely two representations that can satisfy the condition (E),²⁷ they are Γ_2^+ and Γ_5^+ . Both of them can be demonstrated to satisfy the condition (C).²⁸ And then, Γ_2^+ and Γ_5^+ could be considered as the candidates for a paramagnetic-ferromagnetic transition. The matrices of Γ_2^+ and Γ_5^+ are listed in Tables 2.2 and 2.3 of Ref. 29.

For the one-dimensional representation Γ_2^+ , the situation is the same as Γ_2 of ε -Fe₃N. There exists only one possible direction of magnetization in the system, and this direction must be along [001], i.e. the c-axis of the tetragonal structure.

As for the representation Γ_5^+ , it is two-dimensional. Here, we shall choose a- and b-axis as the x- and y-axis, respectively. Under this choice, the x- and y-component of spin, S_x and S_y , are the irreducible basis of Γ_5^+ .²⁷ The magnetization M can thus be written as

$$M = c_x S_x + c_y S_y \quad (7)$$

where c_x and c_y are the expansion coefficients, which can be fixed by minimizing the thermodynamic potential. In this case, there are only three invariants,

$$S_x^2 + S_y^2, \quad S_x^4 + S_y^4, \quad S_x^2 S_y^2. \quad (8)$$

With them, the potential Φ can be constructed as follows,

$$\Phi = \Phi_0 + A(c_x^2 + c_y^2) + B(c_x^4 + c_y^4) + C(c_x^2 c_y^2) \quad (9)$$

where A , B , and C are real coefficients. There are two nontrivial solutions of the minimum problem:

- (i) One of the coefficients c_i is equal to zero,
- (ii) $c_x^2 = c_y^2 = -A/(2B + C)$.

It is not difficult to find that \mathbf{G}_1 are the same for both of the solutions, and it is $2/m$, i.e. $\mathbf{G}_1 = 2/m$. The same situation also holds for \mathbf{G}_2 , which is shown to be mmm for both the solutions, i.e. $\mathbf{G}_2 = mmm$. Therefore, the magnetic point group of the ferromagnetic phase, $\mathbf{G}_1 + \theta(\mathbf{G}_2 - \mathbf{G}_1)$, should be $m'm'm$, i.e. $\mathbf{G}_1 + \theta(\mathbf{G}_2 - \mathbf{G}_1) = m'm'm$. As a result, the transition from $4/mmm1'$ ($\mathbf{G}_0 + \theta\mathbf{G}_0$) to $m'm'm$ ($\mathbf{G}_1 + \theta(\mathbf{G}_2 - \mathbf{G}_1)$) fulfills all the conditions of Landau's theory. Now, the two results for Γ_5^+ can be listed as follows.

- (1) The magnetization $M = c_x S_x$ or $M = c_y S_y$ for the first solution. If $M = c_x S_x$, the corresponding direction of magnetization is $[100]$. And If $M = c_y S_y$, the corresponding direction of magnetization will be $[010]$. Physically, the both are equivalent.
- (2) The magnetization $M = \pm\sqrt{-A/(2B + C)}S_x \pm \sqrt{-A/(2B + C)}S_y$ for the second solution. The corresponding directions of magnetization are $[110]$, $[1\bar{1}0]$, $[\bar{1}10]$, $[\bar{1}\bar{1}0]$, respectively. Physically, all of them are equivalent.

So there are only two nonequivalent directions for the magnetization: $[100]$, and $[110]$, i.e. the a -axis, and the bottom face diagonal direction of the tetragonal structure.

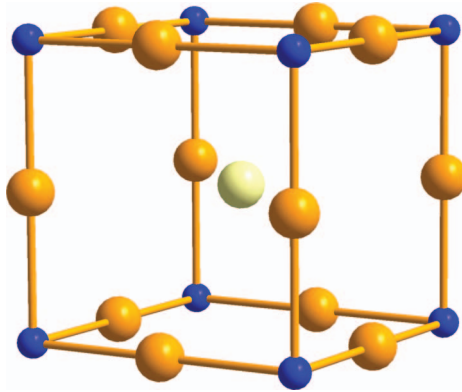
In conclusion, the possible magnetic structures of α'' -Fe₁₆N₂ have been clarified by Landau's theory. There are totally three nonequivalent directions for the magnetization of α'' -Fe₁₆N₂: the c -axis, the a -axis, and the bottom face diagonal direction of the tetragonal structure.

Experimentally, it is reported that the easy axes of α'' -Fe₁₆N₂ grown on InGaAs are along $[010]$ and $[100]$.¹⁴ As mentioned above, for α'' -Fe₁₆N₂, $[010]$ and $[100]$ are physically equivalent, and thus there are, in fact, only one nonequivalent easy axes of α'' -Fe₁₆N₂ grown on InGaAs, i.e. $[100]$. However, the easy axis of α'' -Fe₁₆N₂ grown on Fe is found to be along $[111]$.¹⁴ As pointed out by Sugita *et al.*, these two results are completely inconsistent and thus form a puzzle, which has not been explained yet.¹⁴ According to the present theoretical analysis, this puzzle can be interpreted as follows: The easy axes of α'' -Fe₁₆N₂ grown on InGaAs are in accordance with the above results of Landau's theory. Nevertheless, the experimental result of the easy axis of α'' -Fe₁₆N₂ grown on Fe, i.e., $[111]$, contradicts Landau's theory, directly. The cause for this incorrect experimental result may be attributed to the fact that Fe, as the substrate, is ferromagnetic, and different from InGaAs which is of non-magnetism. To be specific, there should be two primary mechanisms that the iron substrate can modify the magnetic easy axis of Fe₁₆N₂ film. First, the direct exchange interaction between the Fe ions of iron substrate and Fe₁₆N₂ film can have influence on the magnetic properties of Fe₁₆N₂ film, especially at the interface of Fe and Fe₁₆N₂. Secondly, since the resistivity of Fe₁₆N₂ is only three times as large as that for pure Fe,³¹ Fe₁₆N₂ could be considered as a conductor. Therefore, the magnetisms of Fe and Fe₁₆N₂ are both produced by itinerant electrons. These itinerant electrons move within the whole structure of the bilayer, i.e. Fe film and Fe₁₆N₂ film. As such, the magnetisms of Fe and Fe₁₆N₂ are wholly correlated, this correlation effect will make the iron substrate impose strong influence on the magnetic properties of Fe₁₆N₂ film because, in the present case, the thicknesses of the two films are in the same order of magnitude (Fe₁₆N₂ film: 100 nm; Fe film: 10–30 nm).

Besides the experiment in,¹⁴ Takahashi *et al.* drew the conclusion that $[100]$ and $[001]$ directions are the easy axes of α'' -Fe₁₆N₂ through torque measurement and ferromagnetic resonance spectrum.³² And Nakajima *et al.* have also found that the $[001]$ is the easy axis according to the quadrupole effect in their Mössbauer spectrum.³³ These experimental results agree well with our theoretical analysis. All the above experimental results of α'' -Fe₁₆N₂ are summarized and compared with our theoretical analysis in Table II. In the end, it should be noted that the third possibility of magnetization, i.e. $[110]$, has not been reported yet by the experiments, to our knowledge.

TABLE II. The comparisons between the results from other literatures and our theoretical analysis of the magnetic structure of α'' -Fe₁₆N₂.

α'' -Fe ₁₆ N ₂	
The experimental results from other literatures	Whether be consistent with our theoretical results by the Landau theory
Sugita <i>et al.</i> , ¹⁴ grown on InGaAs, by torque measurement.	Yes
Sugita <i>et al.</i> , ¹⁴ grown on Fe, by torque measurement	No
Takahashi <i>et al.</i> , ³² by torque measurement and ferromagnetic resonance spectrum.	Yes
Nakajima <i>et al.</i> , ³³ by quadrupole effect in the Mössbauer spectrum.	Yes

FIG. 3. Crystal structure of γ' -Fe₄N. Large light yellow and light orange spheres: two types of Fe atoms; small blue spheres: N atoms.(c) γ' -Fe₄N

As depicted in Fig. 3, the crystal structure of γ' -Fe₄N is cubic. Its point group is $m\bar{3}m$,²⁶ i.e. $G_0 = m\bar{3}m$. Correspondingly, the grey point group of the paramagnetic phase of γ' -Fe₄N is $m\bar{3}m1'$, i.e. $G_0 + \theta G_0 = m\bar{3}m1'$. Of the ten single-valued irreducible representations of $m\bar{3}m$, there is only one representation that can satisfy the condition (E),²⁷ it is Γ_4^+ . Furthermore, it follows from the table of Ref. 28 that Γ_4^+ fulfills the condition (C). Consequently, Γ_4^+ can be used to construct the invariants and the thermodynamic potential. The matrices of Γ_4^+ are listed in Table 2.3 of Ref. 29, they are three-dimensional. Here, we shall choose a -, b - and c -axis as the x -, y - and z -axis, respectively. With this choice, the three spin components, S_x , S_y and S_z , are the irreducible basis of Γ_4^+ . The magnetization M can thus be expanded as

$$M = c_x S_x + c_y S_y + c_z S_z \quad (10)$$

where c_x , c_y and c_z are the expansion coefficients. Now, there are three invariants,

$$S_x^2 + S_y^2 + S_z^2, \quad S_x^4 + S_y^4 + S_z^4, \quad S_x^2 S_y^2 + S_y^2 S_z^2 + S_z^2 S_x^2. \quad (11)$$

Correspondingly, the potential Φ can be constructed as follows,

$$\Phi = \Phi_0 + A(c_x^2 + c_y^2 + c_z^2) + B(c_x^4 + c_y^4 + c_z^4) + C(c_x^2 c_y^2 + c_y^2 c_z^2 + c_z^2 c_x^2) \quad (12)$$

where A , B , and C are three real coefficients. There are three nontrivial solutions of the minimum problem:

- (i) Two of the coefficients c_i is equal to zero.
- (ii) $c_i = 0$, and $c_j^2 = c_k^2 = -A/(2B + C)$, where $i \neq j$, $i \neq k$, and $j \neq k$.
- (iii) $c_x^2 = c_y^2 = c_z^2 = -A/(2B + 2C)$.

TABLE III. The comparisons between the results from other literatures and our theoretical analysis of the magnetic structure of γ' -Fe₄N.

γ' -Fe ₄ N	
The experimental results from other literatures	Whether be consistent with our theoretical results by the Landau theory
Wood <i>et al.</i> , ¹⁵ by the analysis of Mössbauer spectrum.	Yes
Gallego <i>et al.</i> , ¹⁶ by surface magneto-optic Kerr effect.	Yes
Yamaguchi <i>et al.</i> , ¹⁷ by magnetization curves.	Yes
Lololee <i>et al.</i> , ¹⁸ by magnetization measurement.	Yes
Nikolaev <i>et al.</i> , ¹⁹ by magnetization measurement.	Yes
Atiq <i>et al.</i> , ²⁰ by angle-dependent magnetization measurement.	Yes
Xiang <i>et al.</i> , ²¹ by magnetization measurement.	Yes
Costa-Krämer <i>et al.</i> , ²² by magnetization measurement.	Yes
Ecija <i>et al.</i> , ³⁴ by Kerr magnetization measurement.	Yes

Corresponding to these three solutions, \mathbf{G}_1 is found to be 4/m, or 2/m, or $\bar{3}$ ($\mathbf{G}_1 = 4/m$, or $\mathbf{G}_1 = 2/m$, or $\mathbf{G}_1 = \bar{3}$), and \mathbf{G}_2 is determined to be 4/mmm, or mmm, or $\bar{3}$ m ($\mathbf{G}_2 = 4/mmm$, or $\mathbf{G}_2 = mmm$, or $\mathbf{G}_2 = \bar{3} m$). Therefore, the magnetic point group of the ferromagnetic phase $\mathbf{G}_1 + \theta(\mathbf{G}_2 - \mathbf{G}_1)$ should be 4/mm'm', or m'm'm', or $\bar{3} m'$, i.e. $\mathbf{G}_1 + \theta(\mathbf{G}_2 - \mathbf{G}_1) = 4/mm'm'$, or $\mathbf{G}_1 + \theta(\mathbf{G}_2 - \mathbf{G}_1) = m'm'm'$, or $\mathbf{G}_1 + \theta(\mathbf{G}_2 - \mathbf{G}_1) = \bar{3} m'$. As a result, the transition from m3m1' to 4/mm'm', or m'm'm', or $\bar{3} m'$ fulfills all the conditions of Landau's theory. Now, the total results can be listed as follows.

- (1) The magnetization $M = c_i S_i$ where $i = x$ or y or z for the first solution. The corresponding directions of magnetization are [100], [010], [001], respectively. Physically, all of them are equivalent.
- (2) The magnetization $M = \pm\sqrt{-A/(2B+C)}S_j \pm \sqrt{-A/(2B+C)}S_k$ where $j \neq k$ for the second solution. The corresponding directions of magnetization are [110], [101], [011], [$\bar{1}10$], [$\bar{1}01$], [0 $\bar{1}1$], [$\bar{1}\bar{1}0$], [$\bar{1}0\bar{1}$], [0 $\bar{1}\bar{1}$], respectively. Physically, all of them are equivalent.
- (3) The magnetization $M = \pm\sqrt{-A/(2B+2C)}S_x \pm \sqrt{-A/(2B+2C)}S_y \pm \sqrt{-A/(2B+2C)}S_z$ for the third solution. The corresponding directions of magnetization are [111], [$\bar{1}\bar{1}\bar{1}$], [$\bar{1}11$], [$\bar{1}\bar{1}1$], [$\bar{1}1\bar{1}$], [$\bar{1}\bar{1}\bar{1}$], [$\bar{1}\bar{1}1$], [$\bar{1}\bar{1}\bar{1}$], respectively. Physically, all of them are equivalent.

So there are only three nonequivalent directions of the magnetization, they are [100], [110], and [111], i.e. the axial, the face diagonal, and the body diagonal direction of the cubic structure respectively. So far, the possible magnetic structures of γ' -Fe₄N have been clarified: Its magnetization should be parallel to the axial, or the face diagonal, or the body diagonal direction of the cubic structure.

Experimentally, Wood *et al.* found that the magnetization of γ' -Fe₄N is along [100], through the detailed analysis of certain peaks in the Mössbauer spectrum.¹⁵ Afterwards, the same result has also been obtained by many other researchers through various techniques.^{16–22} Specially, Ecija *et al.* found that there is a little difference between the easy axis and [100] direction, which is only about 4°. ³⁴ These experiments are summarized in Table III, all of them confirm the first case of our theoretical analysis. And, to our knowledge, it is the only case that has already been observed in the experiments. As to the other two cases, they might be verified in the future, with the improvement of quality of crystal.

In summary, the magnetic structures of the three iron nitrides ϵ -Fe₃N, α'' -Fe₁₆N₂ and γ' -Fe₄N have been studied within the framework of Landau's theory of the second-order phase transitions. Firstly, the ferromagnetic point group of ϵ -Fe₃N is found exactly to be 62'2', which means that the corresponding magnetic structure is uniaxially anisotropic, with the easy axis being the c-axis of the hexagonal structure. This result concludes the debates on the easy axis of ϵ -Fe₃N definitely. Secondly, the ferromagnetic point group of α'' -Fe₁₆N₂ can be classified into two categories, i.e.

4/mm'm' and m'm'm. The magnetization for 4/mm'm' is along [001] direction of the tetragonal structure. As to the magnetization of m'm'm, it can take on two different orientations, one is along [100] direction of the tetragonal structure, and the other along [110]. Of the three theoretical results, only the two cases of [001] and [100] have been observed by the experiments of α'' -Fe₁₆N₂, with the third one of [110] in need of the experimental examination. In any case, there is no possibility for the magnetization along [111], which solves rigorously the puzzle why the easy axes of the samples of α'' -Fe₁₆N₂ on InGaAs and Fe are different from each other. Finally, the magnetic structure of γ' -Fe₄N is clarified to be 4/mm'm', or m'm'm, or $\bar{3}$ m', the corresponding magnetization is along [100], or [110], or [111] direction of the cubic structure, respectively. Among the three cases of [100], [110], and [111], only the first one, i.e. [100], has been discovered by the experiments. The other two are left to the future experiments.

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