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**Structures, stability, magnetic moments and growth strategies of the Fe_nN ($n=1-7$)
clusters: all-electron density functional theory calculations**

Zhi Li ^{a,*}, Zhen Zhao ^b

^a **School of Materials and Metallurgy, University of Science and Technology
Liaoning, Anshan, 114051, People's Republic of China**

^b **School of Chemistry and Life Science, Anshan Normal University, Anshan,
114007, People's Republic of China**

^c **School of Science, University of Science and Technology Liaoning, Anshan,
114051, People's Republic of China**

**Correspondence information: Zhi Li, School of Materials and Metallurgy,
University of Science and Technology Liaoning, Anshan, People's Republic of
China, Qianshan Road No.185, E-mail:lizhi81723700@163.com**

Structures, stability, magnetic moments and growth strategies of the Fe_nN ($n=1-7$) clusters: all-electron density functional theory calculations[☆]

Zhi Li^{a,*}, Zhen Zhao^b

^a*School of Materials and Metallurgy, University of Science and Technology Liaoning, Anshan 114051, PR China*

^b*School of Chemistry and Life Science, Anshan Normal University, Anshan 114007, PR China*

ABSTRACT

The geometries, electronic properties, magnetic moments and growth strategies of the Fe_nN ($n = 1-7$) clusters are investigated using all-electron density functional theory. The results show that N doping significantly distorts the Fe_n clusters. Fe_4N and Fe_6N clusters are more stable structures than other considered Fe_nN clusters. Local peaks of HOMO-LUMO gap curve are found at $n = 3, 7$, implying that the chemical stability of the Fe_3N and Fe_7N clusters is higher. Fe_2N , Fe_4N and Fe_6N clusters have larger magnetic moments compared to other considered Fe_nN ($n = 1-7$) clusters. It can be seen that the Fe_5 clusters are easier to adsorb a Fe atom while the Fe_4 clusters are easier to adsorb a N atom. The considered Fe_mN clusters prefer to adsorb a Fe atom and larger Fe_mN clusters are easier to grow.

Keywords: Magnetic Materials; Density Functional Theory Calculations; Magnetic Moments; Growth Strategies

* Corresponding author. School of Materials and Metallurgy, University of Science and Technology Liaoning, Anshan 114051, PR China. Tel.: +86 0412 5929563.
E-mail address: Lizhi81723700@163.com (Z.Li).

1. Introduction

The initial interest in iron nitride came from the steel industry to improve the abrasion strength of steels [1,2]. In particular, the magnetic properties of iron nitrides, especially due to their high saturation magnetization (σ_s) and low coercivity, have received more attention [1,2]. Subsequently, iron nitrides were applied to electromagnets, ferrofluids and catalysts [1,3]. Iron nitrides exhibited ample phase structures, including the most common stoichiometric phases FeN, γ' -Fe₄N, ϵ -Fe₃N and ζ -Fe₂N and Fe₁₆N₂ [4,5]. The particles on the Fe-N film surfaces were the spherical shapes and appear as clusters consisting of several crystallites [2]. Initially, observed small cubed particle complied with granular and columnar growth direction [2,6].

To improve the performances of the Fe-N films or nanoparticles, various techniques including colloidal chemistry, inert gas condensation, laser deposition, mechanical attrition, and electrodeposition methods have been fabricated to control the growth mechanism of iron-nitride nanoclusters or nanoparticles [7]. Because of Fe-N nanoparticles usually have higher nitriding ratio, we selected the N atoms as an impurity and investigated the geometries, stability, magnetic moments, and growth strategies of the Fe_nN (n = 1-7) clusters using all-electron density functional theory (DFT).

2. Computational details

We considered that N atoms should interact with the iron clusters on the surface of iron nitride thin film, so in order to obtain the initial structures of the Fe_nN clusters, we placed a N atom on each possible site of various iron nano-clusters studied previously [8,9]. All the hypothetical initial structures must be geometric optimized [10]. Our

calculations were performed using the spin polarized DFT implemented in the DMol³ package [11,12] within the generalized gradient approximation (GGA) using BLYP functional [13,14]. The double numerical polarization (DNP) basis set [11] was chosen. All of these have been applied in previous calculations [10,15]. Mülliken population analysis was adopted to obtain the atomic charges of the clusters [16,17]. In the geometry optimization process, the energy gradient and atomic displacement converged to within 1×10^{-5} Hartree/Bohr and 5×10^{-3} Å, respectively. Corresponding to a total energy convergence of 1×10^{-5} Hartree, the charge density in the self-consistent iterations converged to within 1×10^{-6} e/Å³. All the vibration frequencies of the considered Fe_{n+1} and Fe_nN are positive, no virtual frequencies are obtained by the DFT calculations.

The average binding energy $E_b(n)$ is defined as [10]

$$E_b(n) = [nE(Fe) + E(N) - E(Fe_nN)]/(n+1) \quad (1)$$

where n is the number of Fe atoms. $E(Fe)$ and $E(N)$ are the single atom energies of the Fe and N atoms, respectively. $E(Fe_nN)$ is the total energy of the lowest-energy structure of the corresponding Fe_nN cluster.

The relative stability of the Fe_nN clusters can be better understood by calculating the second derivative of the binding energies $\Delta^2 E$ [18]

$$\Delta^2 E_n = E_{n+1} + E_{n-1} - 2E_n \quad (2)$$

where E_{n+1} , E_{n-1} and E_n represent the binding energies of Fe_{n+1}N, Fe_{n-1}N and Fe_nN clusters, respectively. As for the second derivative of the binding energies $\Delta^2 E$ of Fe_{n+1} clusters, E_{n+1} , E_{n-1} and E_n represent the binding energies of Fe_{n+2}, Fe_n and Fe_{n+1} clusters, respectively.

The adsorption energy is defined as [19]:

$$E_{ads} = E_{Fe_n N} - E_{Fe_n} - E_N \quad (3)$$

$$E_{ads'} = E_{Fe_{n+1}} - E_{Fe_n} - E_{Fe} \quad (4)$$

where $E_{Fe_n N}$, E_{Fe_n} , E_N , $E_{Fe_{n+1}}$ and E_{Fe} are the spin-polarized total energies of the lowest-energy structures of the $Fe_n N$, Fe_n , N , Fe_{n+1} and Fe clusters, respectively.

To understand the growth strategies of $Fe_n N$ clusters, in this study only two cluster aggregation models are considered for the lowest-energy structures of $Fe_n N$ ($n=1-7$) clusters, that is, $Fe_m N + Fe_{n-m} \rightarrow Fe_n N$. The reaction energy ΔE is defined as [20]

$$\Delta E = (E_m + E_{n-m} - E_n) / n \quad (5)$$

where E_m , E_{n-m} and E_n represent the binding energies of $Fe_m N$, Fe_{n-m} and $Fe_n N$, respectively.

To confirm the accuracy of approaches used, the dissociation energy of $Fe-N$ was calculated. Our result ($D_e=4.02$ eV) is in excellent agreement with spectroscopy/mass spectrometry experimental value ($D_e=3.94$ eV [21]) and PBE functional calculation value ($D_e=4.05$ eV [19]). Therefore, the BLYP scheme is reliable and it is accurate enough to describe the $Fe-N$ systems.

3. Results and discussion

3.1. Structures

The lowest-energy structures of the pure Fe_{n+1} clusters and some typical stable isomers of each $Fe_n N$ cluster are shown in Fig.1. (Gray ball represents Fe atom and blue ball represents N atom.) Comparing the $Fe_n N$ ($n=1-7$) structures with the lowest-energy structures of Fe_{n+1} clusters, which can be found that N doping significantly distorts the Fe_n clusters. Such as the planar C_{2h} Fe_4 cluster [9] transforms to the

triangular bipyramid (C_{3v}) Fe_3N structure. The supposed hexagonal bipyramid (C_{6v}) Fe_7N structure ultimately changed to C_{2v} Fe_7N isomer with two diagonal Fe atoms elongated in the hexagon.

[Table 1](#) lists the point group symmetries, average binding energies E_b (in eV). It can be seen that the lowest-energy structure of FeN is a linear structure (C_v). For Fe_2N , the lowest-energy structure is an isosceles triangle (C_{2v}), which is obtained by replacing one vertex of the Fe_3 cluster with a N atom. The binding energies of the other two linear structures (C_v) are 0.54 eV and 1.14 eV higher than that of the isosceles structure (C_{2v}). The lowest-energy structure of Fe_3N is a planar isomer: three Fe atoms form an isosceles triangle and the N atom caps the base resulting in the asymmetrical rhombus structure (C_{2v}). The binding energy of the three-dimensional (3D) structure (C_{3v}) is 0.08 eV higher than that of the C_{2v} structure. For Fe_4N , a C_s structure with the N atom located as one apex is the lowest-energy structure. The binding energies of the other low-lying Fe_4N isomers (C_{3v} , C_{2v} and C_{4v}) are slightly higher.

Starting from the $n = 5$, the lowest-energy structures of Fe_nN clusters convert to 3D structures. The lowest-energy structure of Fe_5N is a triangle bipyramid (C_s) with the N atom located at one side of the bipyramid. The binding energies of the other two isomers (C_s and C_{4v}) are 0.47 eV and 1.43 eV higher than that of C_s structure, respectively. For Fe_6N , the lowest-energy structure is a distorted pentagonal bipyramid (C_{2v}), which the N atom become a part of the pentagonal ring. The binding energies of the two C_1 and one C_{5v} structures in which the N atom is capped onto the Fe cages are 0.29 eV, 0.34 eV, and 1.64 eV higher than that of C_{2v} structure, respectively. For Fe_7N , the C_s structure is the lowest energy structure. The second isomer is also the C_s structure. The energy difference between them is only 0.007 eV.

3.2. Stability

The average binding energies and the second derivative of the binding energies of Fe_nN ($n = 1-7$) and Fe_{n+1} clusters are displayed in Fig. 2-3, respectively. From Fig. 2 it can be seen that the average binding energies monotonically decreased with the increasing of cluster size. The average binding energies of Fe_nN ($n = 1-7$) clusters are larger than those of Fe_{n+1} clusters. From Fig. 3 it can be demonstrated that Fe_4 clusters have much higher structural stability compared to other Fe_{n+1} clusters, while the Fe_4N and Fe_6N clusters are more stable than other considered Fe_nN clusters.

The highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) gaps of Fe_nN ($n = 1-7$) and Fe_{n+1} clusters are plotted in Fig. 4 (the HOMO states and the values of the HOMO-LUMO gaps are also listed in Table 1). In general, clusters with larger HOMO-LUMO energy gap are more stable and less chemical reactive. For Fe_{n+1} clusters, local peaks are found at 4, 7, implying that the Fe_4 and Fe_7 clusters have higher chemical stability than their neighbors, while for Fe_nN ($n = 1-7$) clusters, local peaks are found at $n = 3, 7$, which means that the Fe_3N and Fe_7N clusters have higher chemical stability than their neighbors.

Table 1 also lists the electron occupation number n_e in the HOMO states, the on-site charge Q (in e) of the N atoms. It can be seen that the loss electrons in Fe 3d and 4p orbital are more than the acquired electrons from Fe 4s orbital. The Mülliken population analysis also indicates that electrons transfer from the Fe atoms to the N atom.

3.3 Magnetic Moments

The magnetic moments of the lowest-energy Fe_n ($n = 1-8$) clusters and Fe_nN ($n = 1-7$) clusters are plotted in Fig. 5. Magnetic moments of small Fe_{n+1} clusters were previously verified about $3.0 \mu_B/\text{atom}$ by Stern-Gerlach deflection experiments [22,23]. From Fig.

5, it can be found that the doped N atoms have a significant influence on the original spin states of the underlying Fe_{n+1} clusters. The local magnetic moments of the N atoms are anti-ferromagnetic and they are less than $0.298 \mu_B$ for Fe_nN ($n = 1-7$). Consequently, the Fe sub-clusters in Fe_nN ($n = 1-7$) clusters have not exhibited different magnetic orderings. It is noted that Fe_2N , Fe_4N and Fe_6N clusters have larger magnetic moments compared to other considered Fe_nN ($n = 1-7$) clusters. It is due to the distribution of the electron spin density of Fe clusters which is influenced by N doping [24].

The average Mülliken atomic spin densities of the typical linear structures, triangular structures and bigger cluster Fe_nN clusters are shown in Fig. 6. It can be seen that the magnetic moment of Fe atom is obviously larger than that of N atom. Fe plays main role on the total magnetic moment [25]. The magnetic moments of the linear Fe_nN ($n=1-2$) clusters are found to be localized on the Fe atoms with negative contribution from N atoms, which indicate the local magnetic moments between Fe and N are antiferromagnetically coupled. From other two structures of Fe_nN clusters in Fig. 6, it can be found that the geometrical effects: the projections of Fe and N atoms on the molecular axis are responsible for the various total magnetic moments of the clusters [26], the increasing interatomic spacing enhances magnetic moments of Fe atoms and the increasing coordination number has the reverse effect as a function of the cluster size [9].

3.4 Growth Strategies

The energies of the lowest-energy Fe_n ($n = 1-7$) clusters which adsorb a Fe atom and a N atom are plotted in Fig. 7. From Fig. 7 it can be found that the considered Fe_n clusters prefer to adsorb a N atom. The Fe_4 and Fe_5 clusters are easier to adsorb a N atom than the other considered Fe_n clusters. The Fe_5 clusters are easier to adsorb a Fe

atom than the other considered Fe_n clusters.

To understand the growth strategies of the Fe_nN clusters, we observed the 28 optimized combination reactions ($\text{Fe}_m\text{N} + \text{Fe}_{n-m} \rightarrow \text{Fe}_n\text{N}$) in Table 2. The greater the difference of reaction energy, the easier reaction will occur. From Table 2, it can be seen that the considered Fe_mN clusters prefer to adsorb a Fe atom. It can be also seen that the reaction energy increases with the increasing of cluster size. It means that larger Fe_mN clusters are easier to grow.

4. Conclusions

In summary, we have calculated the structures, stability, magnetic moments and growth strategies of the Fe_nN ($n = 1-7$) clusters using all-electron DFT-GGA calculations. The results show that the N doping significantly distorts the Fe_n clusters. Fe_4N and Fe_6N clusters are more structurally stable than other considered Fe_nN clusters. Local peaks of HOMO-LUMO gap curve are found at $n = 3, 7$, implying that the chemical stability of the two clusters is higher. The local moments of the N atoms are anti-ferromagnetic with respect to those of the Fe atoms. It can be seen that the Fe_5 clusters are easier to adsorb a Fe atom while the Fe_4 clusters are easier to adsorb a N atom than the other considered iron clusters. The considered Fe_mN clusters prefer to adsorb a Fe atom and larger Fe_mN clusters are easier to grow.

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Figure Captions

Fig. 1. The pure Fe_{n+1} clusters and the lowest-energy configurations and low-lying isomers of Fe_nN ($n = 1-7$) clusters.

Table 1 The calculated results of the Fe_nN ($n = 1-7$) clusters.

Fig. 2. Size dependence of the average binding energies (E_b/atom) of the Fe_nN ($n=1-7$) and Fe_{n+1} clusters.

Fig. 3. Size dependence of the second derivative of the binding energies of the Fe_nN ($n = 1-7$) and Fe_{n+1} clusters.

Fig. 4. Size dependence of the HOMO-LUMO gaps of the Fe_nN ($n = 1-7$) and Fe_{n+1} clusters.

Fig. 5. Size dependence of the magnetic moments of the lowest-energy Fe_n ($n=1-7$) clusters.

Fig. 6. The average Mlliken atomic spin densities of the typical Fe_nN clusters.

Fig. 7. Size dependence of the adsorption energies of the lowest-energy Fe_n ($n=1-7$) clusters.

Table 2. The ΔE of $\text{Fe}_m\text{N} + \text{Fe}_{n-m} \rightarrow \text{Fe}_n\text{N}$ (Unit: eV/atom).

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Fig. 7. Size dependence of the adsorption energies of the lowest-energy Fe_n ($n=1-7$) clusters.

Table 1 The calculated results of the Fe_nN (n = 1-7) clusters.

n	Point group	E _b (eV)	HOMO	Gap(eV)	n _e	Q	Spin (μ _B /atom)
1	C _v	-2.22	a1.1	0.305	0.661	-0.320	-1.673
2	C _{2v}	-2.64	b2.1	0.532	0.888	-0.569	2.249
	C _v	-2.46	b1.1	0.444	0.893	-0.330	-0.986
	C _v	-2.26	a1.1	0.327	0.754	-0.347	-0.339
3	C _{2v}	-2.81	b1.1	0.550	0.926	-0.485	1.824
	C _{3v}	-2.79	e.2	0.610	0.507	-0.617	2.250
4	C _s	-2.91	e.2	0.341	0.820	-0.613	2.307
	C _{3v}	-2.88	a'.1	0.458	0.900	-0.628	2.307
	C _{2v}	-2.81	a1.1	0.531	0.847	-0.637	2.241
	C _s	-2.77	a'.1	0.099	0.622	-0.550	2.359
	C _{2v}	-2.72	b1.1	0.434	0.868	-0.670	2.572
	C _{4v}	-2.71	e.2	0.507	0.957	-0.635	2.282
5	C _s	-3.02	a'.1	0.308	0.753	-0.652	1.574
	C _s	-2.95	a'.1	0.372	0.513	-0.619	2.360
	C _{4v}	-2.79	a1.1	0.332	0.906	-0.591	-1.180
6	C _{2v}	-3.05	b1.1	0.149	0.527	-0.693	2.662
	C ₁	-3.01	a	0.543	0.876	-0.642	0.956
	C ₁	-3.00	a	0.535	0.890	-0.651	2.423
	C _{5v}	-2.82	e.2.2	0.462	0.766	-0.660	2.497
7	C _s	-3.14	a".1	0.411	0.949	-0.657	-2.598
	C _s	-3.14	a".1	0.391	0.942	-0.657	-2.596

C _s	-3.13	a".1	0.325	0.670	-0.661	2.582
C _s	-3.07	a".1	0.183	0.666	-0.672	2.552
C ₁	-3.04	a	0.397	0.763	-0.693	0.385
C _{2v}	-3.03	b2.1	0.430	0.833	-0.526	2.589
C _{2v}	-3.01	b2.1	0.330	0.788	-0.708	2.588
C _s	-3.01	a".1	0.446	0.802	-0.689	1.124
C ₁	-3.00	a	0.291	0.777	-0.687	0.384
C _s	-2.99	a'.1	0.496	0.862	-0.688	0.364

Table 2 The ΔE of $\text{Fe}_m\text{N} + \text{Fe}_{n-m} \rightarrow \text{Fe}_n\text{N}$ (Unit:eV/atom)

	m=0	m=1	m=2	m=3	m=4	m=5	m=6
n=1	2.1256						
n=2	1.6359	4.0371					
n=3	1.3433	3.1548	4.7203				
n=4	1.1368	2.6245	3.8855	5.1083			
n=5	0.9429	2.2754	3.3583	4.3844	5.4097		
n=6	0.7104	1.8960	2.9036	3.8106	4.6955	5.6057	
n=7	0.6285	1.6414	2.5611	3.4242	4.2226	5.0243	5.7763

Graphical Abstract:

Fig. 6. The average Mulliken atomic spin densities of the typical Fe_nN clusters.

The average Mulliken atomic spin densities of the typical linear structures, triangular structures and bigger cluster Fe_nN clusters are shown in Fig. 6. It can be seen that the magnetic moment of Fe atom is obviously larger than that of N atom. Fe plays main role on the total magnetic moment [25]. The magnetic moments of the linear Fe_nN ($n=1-2$) clusters are found to be localized on the Fe atoms with negative contribution from N atoms, which indicate the local magnetic moments between Fe and N are antiferromagnetically coupled. From other two structures of Fe_nN clusters in Fig. 6, it can be found that the geometrical effects: the projections of Fe and N atoms on the molecular axis are responsible for the various total magnetic moments of the clusters [26], the increasing interatomic spacing enhances magnetic moments of Fe atoms and the increasing coordination number has the reverse effect as a function of the cluster size [9].