

First principles calculations of the magnetic properties of Fe–N systems

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We report the results of the first principles calculations performed in order to investigate the electronic and magnetic properties of the Fe–N systems and to clarify the origin of giant magnetic moments in Fe–N systems. After geometrical optimization, the densities of states have been evaluated with atom resolved band populations and magnetic moments. By

examining Fe–N bond lengths in the Fe–N systems, it was found that there is a linear relationship between Fe–N bond lengths and atomic magnetic moments. Our results demonstrate that the existence of N atoms can affect charge transfer between the 4s, 4p and 3d bands of Fe atoms and is responsible for the change in magnetic moments.

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1 Introduction Fe–N systems have been of great importance in the field of magnetism and magnetic materials since the early 1970's, when Kim and Takahashi found giant magnetic moments in evaporated Fe₁₆N₂ polycrystalline films [1]. However, some details of their experiments have remained unclear. Investigation of this phenomenon regained momentum in the early 1990's, prompted by a report by Komuro et al. [2] showing that the J_s value of Fe₁₆N₂ thin films to be about 2.8–3.0 T, corresponding to an average magnetic moment of 3.1–3.3 μ_B per Fe atom. These are regarded as giant values, exceeding the Slater–Pauling curves [3].

Extensive work [4–13] has carried out to clarify the origin of giant magnetic moments. Mössbauer spectra revealed a single hyperfine field of 330 kOe for Fe₁₆N₂ [4]. The g -factor for Fe₁₆N₂ has been accurately measured to be 2.17 by ferromagnetic resonance, indicating that the magnetic moment originates mainly from spin [5]. However, the origin and properties of giant magnetic moments [6] remains still unclear. The magnetic moments of Fe₁₆N₂ in N implanted Fe layers were determined to be 15% larger than those of pure α -Fe [7]. Zhou et al. reported that Fe–N phases in sputtered films do not follow Jack's crystal structure [8].

Theoretical calculations have been performed to explain the giant magnetic moment observed in Fe₁₆N₂, in-

cluding linear muffin-tin orbital (LMTO), atomic sphere approximation (ASA), local spin density approximation (LSDA), linear augmented plane wave (LAPW) and linear combination of atom orbitals (LCAO) calculations [9–13]. It is generally believed that Fe III atoms located at 4d sites (most distant from N atoms) have a very large magnetic moment, while Fe I and Fe II atoms located at 4e and 8h sites (next to N atoms) have normal magnetic moments. The primary role of N atoms is to expand the Fe lattice, leading to the enhancement of magnetic moments.

However, most calculations reported an average magnetic moment of 2.3–2.6 μ_B , much less than the experimental values of 3.0–3.5 μ_B . Modified calculations considering the orbit contributions and self-interaction correction (SIC) do not resolve this discrepancy [10, 11]. Lai and Zheng factored the on-site Coulomb interaction into their calculations and used the generalized gradient approximation (GGA) to improve the accuracy of LSDA. With these modifications, their calculations revealed a giant magnetic moment [12].

In order to further investigate the nature of giant magnetic moments, other Fe–N compounds were studied. Kong et al. investigated N-neighbor influence on the electronic structure and magnetic properties of Fe in different Fe₄N structures and found that the number of N neighbors affects the magnetic moment of Fe [14]. Zhou et al. [15]

calculated the coupling between the Fe and N atoms in γ -Fe₄N and found that the N 2p electrons are coupled strongly with Fe II 4s electron and determine the main feature of spatial electronic distribution. Sifkovits et al. [16] studied the relationship between magnetic properties and chemical bonding of Fe_xN (where $x = 4, 3, 2, 1$) by calculation of the DOS and distribution of charge and spin, and found that the half filled minority spin forms bond with the neighbors and strongly effect the magnetic properties. Recently, Navio et al. [17] studied the electronic structure of ultra thin γ -Fe₄N (100) films epitaxially grown on Cu(100) and calculated the charge transfer, chemical bonding and magnetic properties by first principle calculations.

Although the giant magnetic moment was found in Fe₁₆N₂ thirty years ago, it remains under debate both experimentally and theoretically. What is the role of N induced volume expansion or charge transfer? Recently, we have studied the volume effect, distortion effect, and N neighbor effect in Fe₁₆N₂ [18]. In this paper, we present the results of theoretical calculations on the electronic and magnetic properties of Fe₁₆N₂, Fe₄N and Fe₄N II.

2 Calculation methods Density function theory has become an effective way to computation solid-state systems, recently. By only caring about the density of electrons, computation time can be greatly reduced and it is possible to treat a large system within affordable effort. Among the approaches employing density functional theory, the CASTEP code in Material Studio software package from Accelrys adopt plane wave basis-set, pseudo potential and fast Fourier transform to boost the computation, and computation time is much reduced [19].

In the electronic minimization process, the system was treated as metallic and the Pulay type density mixing scheme was employed. The cut-off of energy was 330.0 eV. The Perdew Burke Ernzerhof function has been used to take into account the exchange correlation effect. Monkhorst–Pack type k -points were used with a grid of size $8 \times 8 \times 8$ and 56 k -points in the irreducible first Brillouin zone.

Geometry optimizations were performed before property calculations. The convergence of the optimization was based on the energy changes, maximum displacements and forces. Band population analysis was performed for each atom, with a cut-off distance of 0.3 nm. Band structures and density of states of the Fe–N systems were analyzed after geometrical optimization. Band population and magnetic moment are calculated by evaluate the Mulliken charge and spin. The volume effect, distortion effect, and N neighbour effect in Fe₁₆N₂ can be seen elsewhere [18].

3 Results and discussion Fe₄N is a stable Fe–N phase, which is often found in Fe–N systems. Its structure is an N atom added to the center of a face center cubic (fcc) unit cell of Fe, as shown in Fig. 1(a). There are two kinds of Fe atoms: Fe atom at the apex of cell (called Fe I) and Fe atom located at the face center (called Fe II). Fe I is

not directly connected to N, while Fe II is directly connected to N. Fe₄N II is a hypothetical structure of Fe₄N, shown in Fig. 1(b). Its unit cell is a double celled Fe₄N with one cell moved by $0.5(\mathbf{a} + \mathbf{b})$. The overall structure is by a double-layered structure: all-Fe layers and mixed Fe–N layers. The Fe I atoms in the all-Fe layer have only one N nearest neighbor, while Fe II in the mixed layer are nearest neighbored by two N atoms. Fe₁₆N₂ can be described as a $2 \times 2 \times 2$ supercell of α -Fe doped with two N atoms, as seen in Fig. 1(c). There are three kinds of Fe atoms: Fe I is the atoms in the up and down corners of the octahedron surrounding the N atom, and Fe II is the atoms in the horizontal directions of the N atoms, Fe III is the Fe atoms not in the direct contact with the N atoms. These three structures are used to study the effect of N neighbors on the magnetic properties of Fe atoms.

In our calculations, a conventional unit cell was used in the calculation of Fe₄N. In the case of Fe₄N II, a primitive unit cell was constructed out of the conventional cell. The Monkhorst–Pack grids are $10 \times 10 \times 10$ and $10 \times 10 \times 13$. The k -points in the irreducible first Brillouin zone for Fe₄N and Fe₄N II are 35 and 36, respectively. The lattice constant of Fe₄N was optimized to be 0.3771 nm, which is slightly smaller than the experimental value. The lattice constants of Fe₄N II were optimized to be $a = 0.3752$ nm and $c = 0.7375$ nm, indicating tetragonal.

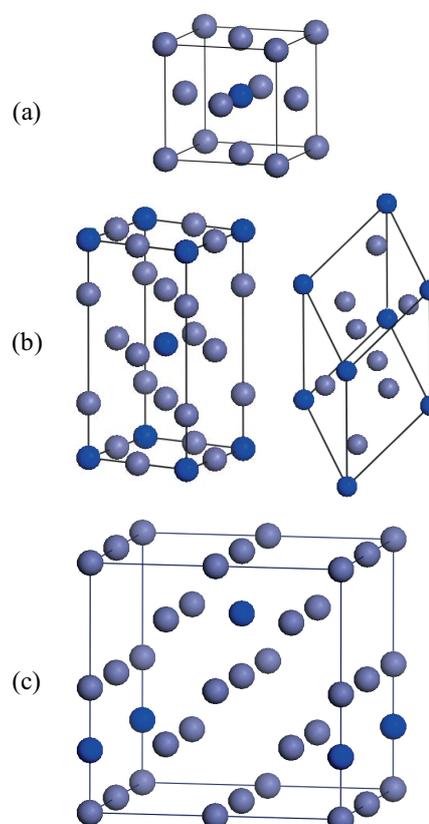


Figure 1 (online colour at: www.pss-b.com) (a) Unit cell of Fe₄N and (b) a hypothetical Fe₄N II phase, (c) Fe₁₆N₂.

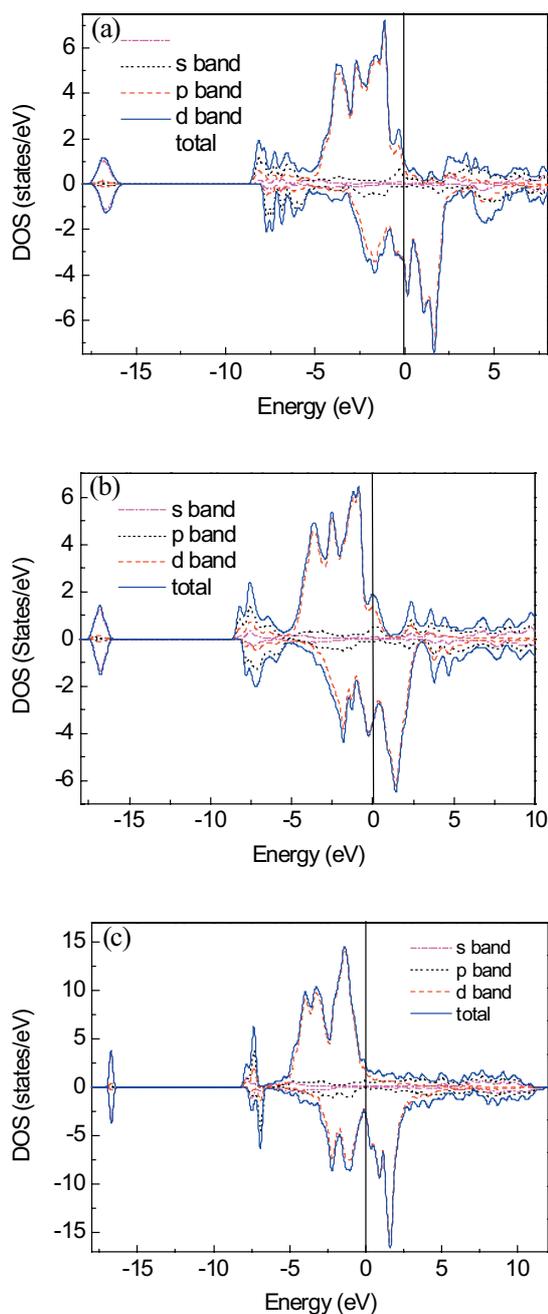


Figure 2 (online colour at: www.pss-b.com) Density of states of (a) Fe_4N , (b) $\text{Fe}_4\text{N II}$ and (c) Fe_{16}N_2 .

The electronic structure and magnetic properties were calculated after geometrical optimization. Figure 2 shows the density of states for the two phases of Fe_4N [Fig. 2(a) and 2(b)], and the density of state of Fe_{16}N_2 is as shown in Fig. 2(c). The DOS structures of Fe_4N are similar to that of Fe_{16}N_2 . The main difference is that the Fermi level lies on the d-band peaks of the minor spins, and that the density of states at Fermi level is larger in Fe_4N . Table 1 lists the band populations and magnetic moments of atoms. Different types of Fe atoms have different band occupations and

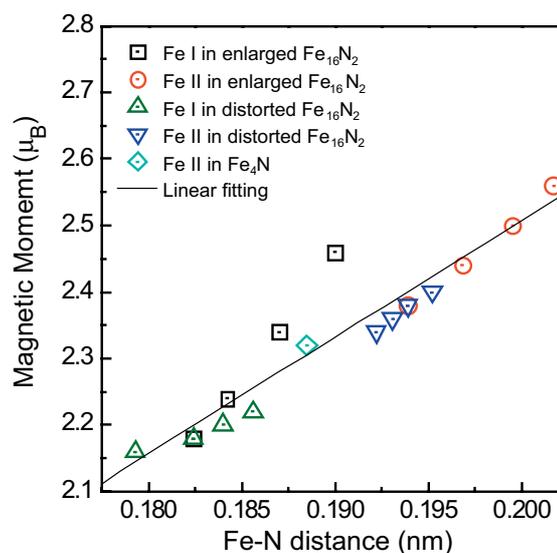


Figure 3 (online colour at: www.pss-b.com) Atomic magnetic moments of Fe atoms in the Fe–N systems as a function of the Fe–N distance.

magnetic moments. The total cell moment was $9.938\mu_B$ and $8.895\mu_B$ for Fe_4N and $\text{Fe}_4\text{N II}$, respectively, while total energy was -3737.27 eV and -3737.23 eV, respectively. The hypothetical phase had a small magnetic moment and was unfavourable in terms of energy.

The Fe I atoms in Fe_4N have a similar arrangement as the Fe III atoms in Fe_{16}N_2 : neither of them is connected directly to N atoms [18]. The d-band occupation of each atom is low, and the magnetic moment is as high as $2.96\mu_B$. The Fe II atoms in Fe_4N have two nearest neighbor N atoms, so their s- and p-band occupations are small, but their d-band was not affected [18]. The magnetic moments of Fe I and Fe II in Fe_4N are similar (see Table 1). Therefore, Fe atoms not directly connected to N atoms are very likely to have giant magnetic moments. For the hypothetical $\text{Fe}_4\text{N II}$ phase, both types of Fe atoms are directly connected to N atoms. Fe I has only one N nearest neighbor while Fe II has two. The Fe II atoms have less 4s and 4p electrons and more 3d electron than Fe I, leading to a smaller atomic magnetic moment for Fe II.

Atomic Fe has an electronic configuration of $4s^2 3d^6$ and an atomic magnetic moment of $4\mu_B$. However, due to the broadening of 4s and 4p bands in the periodic structure, 4s and 4p band populations decreased while the 3d band population increased, resulting in a small magnetic moment. For example, for Fe atoms in α -Fe, the most common Fe phase, the 4s and 4p band occupation number was very small like as 0.57 and 0.55, respectively. Alternatively, the 3d band occupation was raised to 6.88, yielding an atomic moment of only $2.2\mu_B$ [18]. In Fe_{16}N_2 , the Fe I and Fe II atoms, which are directly connected to N atoms, lost their outer shell electron (4s and 4p) to N. However, their 3d electrons remained almost unchanged, such that the atomic magnetic moment was similar to that of α -Fe [18].

Table 1 Atomic band population and magnetic properties of the Fe–N system.

phases	atoms	s electrons	p electrons	d electrons	total	moment (μ_B)
Fe ₄ N	N	1.67	4.07	0.00	5.75	–0.04
	Fe I	0.46	0.70	6.74	7.90	2.96
	Fe II	0.35	0.59	6.85	7.79	2.32
Fe ₄ N (II)	N	1.68	4.03	0.00	5.71	–0.04
	Fe I	0.41	0.61	6.82	7.85	2.50
	Fe II	0.34	0.54	6.91	7.80	1.96
Fe ₁₆ N ₂ [18]	N	1.69	4.01	0.00	5.70	–0.06
	Fe I	0.46	0.60	6.86	7.92	2.18
	Fe II	0.44	0.60	6.86	7.90	2.38
	Fe III	0.50	0.67	6.77	7.94	2.84

On the other hand, the Fe III atoms, which are not directly connected to N atoms, have high 4s and 4p band occupations and low 3d occupation leading to a giant magnetic moment. This can be attributed to the electron transfer among the bands. As more spaces are vacated, the 4s and 4p electrons of Fe atoms, which are not directly connected to N atoms, have more space to occupy. The increase in the occupation number gives rise to the decrease in its 3d band occupation, providing a giant magnetic moment. The electron occupations and magnetic properties are similar to those of Fe₁₆N₂ (see Table 1).

Figure 3 shows the variation of the magnetic moments of Fe atoms directly connected to N as a function of Fe–N distance for Fe₁₆N₂ and Fe₄N. The magnetic moment of Fe atoms were found to increase with Fe–N distances. The existence of N atoms can affect the charge transfer between the 4s, 4p and 3d bands of Fe atoms and is responsible to the change of magnetic moments. The linear relationship is likely to be reasonable not only for different Fe atoms in the same unit cell, but also for the same Fe atoms with different lattice constants, such as the enlarged unit cell and the distorted unit cells. The giant magnetic moments are due to only Fe atoms, which are not directly connected to N, like the Fe III in Fe₁₆N₂ [18] and Fe I in Fe₄N.

4 Conclusions *Ab initio* calculations were performed to investigate the electronic structures and magnetic properties of Fe–N systems. Our results show that only Fe III, Fe atoms not directly connected to N atoms, possess the giant magnetic moment of approximately 2.84 μ_B . However, Fe I and Fe II atoms, which are directly connected to N atoms, were found to show normal magnetic moments.

Atom resolved band population analysis on Fe I and Fe II revealed that the s and p electron-rich N atoms affect mainly the 4s and 4p outer shell electrons, but do not change the 3d band. For Fe III atoms, the 4s and 4p electron populations increased, while the 3d electron population decreased, leading to giant atomic magnetic moments [18]. The calculated results of electron occupations and magnetic properties on Fe₄N are similar to those of Fe₁₆N₂.

We also found that as the unit cell volume increases, the atomic magnetic moment increases, particularly like Fe I and Fe II atoms, directly connected to N atoms. Distorted unit cells with different a/c ratios at constant unit cell volumes do not provide giant magnetic moments. Although the magnetic moments of individual Fe atoms change as Fe–N length changes, the overall unit cell magnetic moment is not sensitive to the distortion. Our results demonstrate that as unit cell volume increases, 4s band population decreases and that the 4p band population increases, giving rise to the increase in the magnetic moment.

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