

Local coordination influence on the magnetic properties of iron nitride

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2000 J. Phys.: Condens. Matter 12 9061

(<http://iopscience.iop.org/0953-8984/12/42/311>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.221

The article was downloaded on 16/05/2010 at 06:55

Please note that [terms and conditions apply](#).

Local coordination influence on the magnetic properties of iron nitride

W H Xie, D S Xue and F S Li

Ministry of Education Key Laboratory of Magnetism and Magnetic Material,
Lanzhou University, 730000, People's Republic of China

Received 4 August 2000

Abstract. The electronic structure and magnetic properties of cubic iron nitrides FeN with NaCl- and ZnS-type structures have been calculated by employing a first-principle full-potential linearized muffin-tin orbital method. The results show that the local Fe–N octahedral coordination with a centred nitrogen atom is an advantageous one with which to exhibit a large exchange splitting. Meanwhile, the local Fe–N tetrahedral coordination produces a non-magnetic phase, the ZnS-type structure. A super-exchange interaction can reasonably explain the magnetism of the FeN nitrides. In comparison with other Fe–N compounds, we find a linear dependence of the magnetic moment of iron atoms with the volume, which corresponds to the octahedral coordination. Furthermore, a magnetic moment instability is presented in the NaCl-type structure.

1. Introduction

In the last century, the iron nitrides have been extensively investigated, because of their high potential in technological applications and great value in basic research [1, 2]. For α'' -Fe₁₆N₂, γ' -Fe₄N, ε -Fe₃N and ζ -Fe₂N, the magnetic properties decrease with increasing nitrogen content [1]. However, new iron nitrides (with NaCl- and ZnS-type structure), found in the γ''' -FeN_x ($x = 0.63$ – 0.65) and γ'' -FeN_x ($x = 0.91$) films [3, 4], show quite different properties. For instance, γ''' -FeN_x ($x = 0.63$ – 0.65) have a very large hyperfine field (50 T). These properties fascinate researchers.

With the x-ray diffraction and Mössbauer experiments [3–5], the crystal and magnetic structures were assumed. The lattice constants of NaCl- and ZnS-type nitrides are 4.5 and 4.33 Å, respectively. From the field dependent Mössbauer spectrum [5], the NaCl-type nitride was supposed to be an antiferromagnet, while the ZnS-type nitride is a non-magnetic compound.

The electronic structure of FeN has been calculated with the linearized augmented-plane-wave (LAPW) and the linearized muffin-tin orbital (LMTO) methods [6–10]. All the results indicate that ZnS-type nitride has a non-magnetic ground state. However, for the NaCl-type structure, someone has proposed that it has a ferromagnetic (FM) ground state [6–8] and others have proposed that it has an antiferromagnetic (AFM) ground state [9, 10]. The difference between the total energy of the AFM and FM states is very small [10].

Generally, the nitrogen atom in the iron nitrides is regarded as an interstitial atom [1]. The effects of N are: (i) to change the spd hybridization of atoms; (ii) to extend the lattice; (iii) and to change the symmetry of the iron sites. Such a thought has been applied to explain interstitial compounds in detail. However, the discussion is quite complex with the three effects for the

different iron nitrides. In this paper we compare the electronic structure difference of the ZnS- and NaCl-type nitrides and discuss how the different Fe–N coordination dominates the magnetic properties. Moreover, with the results of other iron nitrides, the details of the local Fe–N octahedral coordination on the magnetic properties are discussed.

In the next section a brief description of computational techniques is given. The calculated results and a detailed discussion are presented in section 3. Finally, some concluding remarks are summarized in section 4.

2. Computational details

Although the FeN structures can only be found in films, the electronic structure calculations for bulk FeN can provide an insight into the electronic and magnetic properties exhibited in the FeN films. In the calculation, the experimental lattice constant of the FeN nitrides was used to obtain the density of states (DOS). The AFM structure of the NaCl-type nitride was considered.

A self-consistent full-potential linear muffin-tin orbitals (FP-LMTO) method [11] is applied to the FeN compounds with the NaCl- and ZnS-type structures. Detailed descriptions of the LMTO method can be found elsewhere [12]. A 3κ -spd LMTO basis is set with the one-centre expansions inside the MT spheres performed up to $l_{max} = 6$. In the interstitial region, the s-, p- and d-basis functions are expanded in plane waves up to 14.7, 19.7, 28.4 Ry (168, 258, 410 plane waves), respectively. The charge density and potential are represented by spherical harmonics up to $l_{max} = 6$ inside the MT spheres and by plane waves with 185.07 Ry energy cutoff (6566 plane waves) in the interstitial region. The 3p states for Fe are treated as semicore states and calculated in separated energy windows with the approximation of neglecting hybridization with valence states. For the exchange-correlation potential, its local part is taken to be the Vosko–Wilk–Nusair formula [13] with the recently developed generalized-gradient approximation (GGA) by Perdew *et al* [14]. The k -space integration over the Brillouin zone (BZ) is performed over the (12, 12, 12) grid by means of the improved tetrahedron method. This corresponds to 136 k points in the irreducible part of BZ. The self-consistency is achieved if the total energy discrepancy between two consequent iterations is less than 10^{-6} Ry.

3. Results and discussion

3.1. The electronic structure and magnetic interaction of FeN

There are two kinds of local Fe–N coordinations in the iron nitrides. They are octahedral Fe₆N and tetrahedral Fe₄N coordination. In the equiatomic FeN compounds, the coordinations correspond to the NaCl- and ZnS-type structures, respectively (figure 1).

The orbital-projected DOS of the NaCl- and ZnS-type nitrides are given in figure 2. It is found that there is a large spin-splitting for the NaCl-type structure (figure 2(a)). A $3.5 \mu_B$ magnetic moment is obtained. On the contrary, the ZnS-type nitride does not show any magnetic energy splitting (figure 2(b)), which agrees with the observation of the experiment at 4.2 K [5].

Some bonding characters of the Fe–N interactions can be seen from the DOS. In comparison with the wide DOS peaks of the 3d electron of γ -Fe [7], all the peaks of the 3d electron for the FeN structures are very narrow. The difference indicates that there is a strong local state character in the FeN structures. In the lower energy region, the ZnS-type structure has two separate DOS peaks, which are mainly composed of the nitrogen 2p and iron 3d electrons. However, these peaks are severely expanded to overlap for the NaCl-type

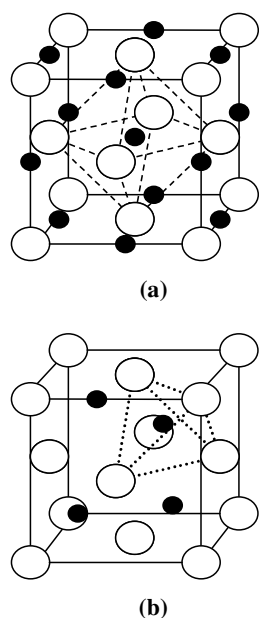


Figure 1. The crystal structure of the: (a) NaCl-type and (b) ZnS-type nitrides. The dashed and dotted lines show the local Fe–N octahedral and tetrahedral coordinations, respectively.

structure. This indicates that the ZnS structure should have a stronger Fe–N bond interaction. Near the Fermi energy, the familiar cubic crystal splitting pattern is observed for both FeN structures. From these characters, FeN is more like ionic compounds.

Obviously, such a discrepancy of the electronic structure originates from the difference of the local Fe–N coordination. As a consequence, the Fe–N octahedral coordination corresponds to a magnetic order structure and the tetrahedral coordination corresponds to a non-magnetic state. From the super-exchange theory we know that the octahedral coordination is of more advantage to the spin-splitting than the tetrahedral coordination. Therefore, in the FeN structure, the magnetic interaction seems like the super-exchange interaction.

It is well known that the magnetic moment of the 3d electrons has a strong shielding effect on the probability of the 4s electron appearing at the iron nuclear site, and the fewer the s electrons at the nuclear site the larger the isomer shift. From the DOS, we know that the spin polarization in the NaCl-type nitride is larger than that in the ZnS-type nitride. So, it results in a larger isomer shift of NaCl-type FeN than that of ZnS-type FeN, which is in agreement with the experimental results [4, 5].

Thus, it can be considered that the Fe_6N local octahedral coordination corresponds to a larger isomer shift and the Fe_4N four-ligand corresponds to a smaller isomer shift. From the latter point of view, the isomer shifts of γ' - Fe_4N , ε - Fe_3N , ζ - Fe_2N and NaCl-type FeN are larger than that of ZnS-type FeN. This agrees with the experimental results [4]. As the number of 4s electrons also has a strong effect on the isomer shift, more details should be considered if we want to obtain quantitative results.

3.2. The influence of local Fe–N coordination on magnetic properties

In the iron nitrides, because the octahedra has larger interstitial space than tetrahedra, the nitrogen atoms tend to locate at the octahedral interstitial sites. In order to investigate the

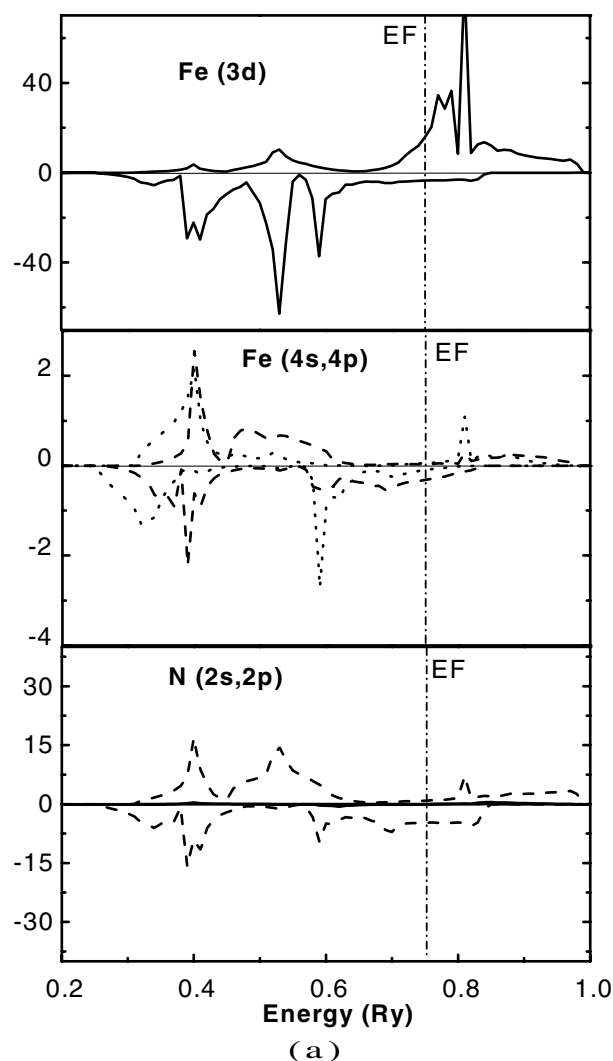


Figure 2. The orbital-projected density of states of: (a) NaCl-type; and (b) ZnS-type nitrides. The d, p and s states are presented by full, broken and dotted curves, respectively.

effect of the local Fe–N coordination on the magnetic properties, it is necessary to explore other iron nitrides besides the equiatomic FeN.

γ' -Fe₄N, which is very similar to the NaCl-type nitride, has a face-centred cubic lattice and one nitrogen atom fill into one of the four octahedral sites. The face-centred-site and corner-site iron atoms have large magnetic moment about 2.0 and 3.0 μ_B , respectively [1]. ε -Fe₃N which has a hexagonal lattice and nitrogen atoms located on octahedral interstitial sites, shows a magnetic moment about 1.9 μ_B [1]. It is found that the magnetic moments of Fe in the Fe₆N octahedra for NaCl-type FeN, ε -Fe₃N and γ' -Fe₄N are proportional to the octahedral volume (figure 3). In other words, in the iron nitrides that have perfect octahedral configuration, the magnetic moment of Fe μ_{Fe} satisfies

$$\mu_{Fe} = A \times V (\mu_B)$$

where V represents the volume of the octahedra, and the constant A is about 0.033 μ_B a.u.⁻³.

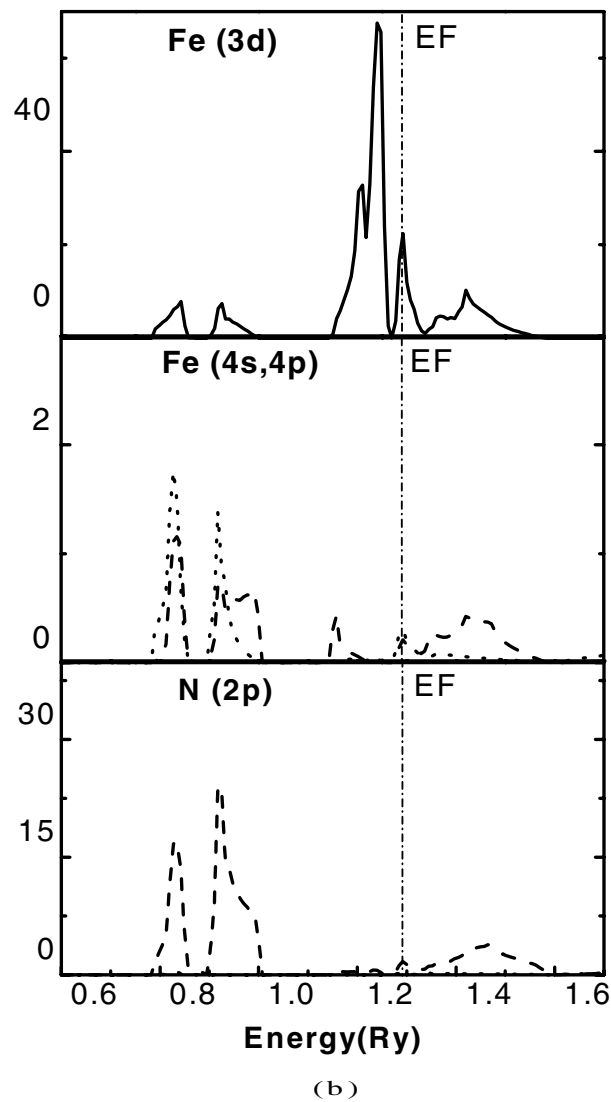


Figure 2. (Continued)

It is known that α'' -Fe₁₆N₂ and ζ -Fe₂N have a distorted octahedral coordination [1]. α'' -Fe₁₆N₂ forms a body-centred cubic structure with three different iron sites. Along the z -axis direction the octahedral coordination is compressed, and two inequivalent iron sites 8h and 4e are produced. If we consider that the iron atoms on 8h sites maintain the octahedral sites, their magnetic moment should be close to the linear dependence (in figure 3). The magnetic moment of iron atoms on 4e sites is smaller than that of the 8h sites, because of the compression in the z -direction. This can be qualitatively explained by the decrease in magnetic moment with the volume discussed below. For ζ -Fe₂N, which is a distorted hexagonal lattice, the shear distortion from octahedra to tetrahedra is so strong that magnetism decreases severely. It should be mentioned that the influence of distortion on the magnetism should be investigated in the future.

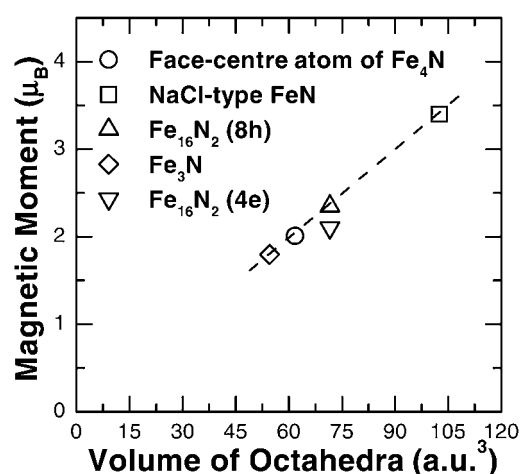


Figure 3. The M - V proportional relation in the iron nitrides. The calculated moments of Fe_{16}N_2 and Fe_3N are adopted [1].

It is also noted that in the rare-earth iron nitrides the nitrogen atoms tend to locate on the octahedral interstitial sites so that the magnetic properties are improved. As a result, in the interstitial iron nitride, the improvement of magnetic properties seems to originate from the local Fe-N octahedral coordination.

3.3. The volume effect of local Fe-N coordination

From the above we know that the octahedral Fe-N coordination has a positive effect on the magnetic properties, and the dependence of the magnetic moment on the octahedral volume is linear for the perfect octahedra in different iron nitrides with the equilibrium lattice. In order to study the effect of the local Fe-N coordination, it is necessary to investigate the volume dependence of the magnetic moment for each nitride. In the following, the volume dependence of the magnetic moment in the NaCl-type FeN is discussed.

In figure 4 the change of magnetic moment with the octahedral volume for the NaCl-type nitride is plotted. It is observed that the magnetic moment decreases with the volume reduction of the NaCl structure. Especially when the volume is close to 75 a.u.^{-3} , the magnetic moment of the NaCl structure declines sharply. This shows an instability of the magnetic structure. On the contrary, in both cases of small and large volume, the decrease of the magnetic moment is relatively slow with decreasing volume. This resembles the magnetic-volume instability (MVI) exhibited in Invar alloys. It is still a problem to explain such a MVI phenomenon in a NaCl-type structure.

However, γ -Fe is well known as an Invar-like alloy, and there is a similar MVI curve as shown in figure 4. A difference between the NaCl-type nitride and γ -Fe can be found. On the high-spin state, the magnetic moment of both compounds is very close, on the low-spin state the NaCl-type nitride has a moment of about $1.0 \mu_B$ while γ -Fe does not show spin polarization. This should originate from the different magnetic mechanism between γ -Fe and the NaCl-type nitride. Comparing the DOS of γ -Fe [7], the difference between γ -Fe and NaCl-type FeN can be explained. The 3d bands of γ -Fe expand to a wide band which corresponds to itinerate magnetism, on the contrary, the NaCl-type structure shows a strong Fe-N bond interaction which corresponds to a super-exchange mechanism. Such a magnetic

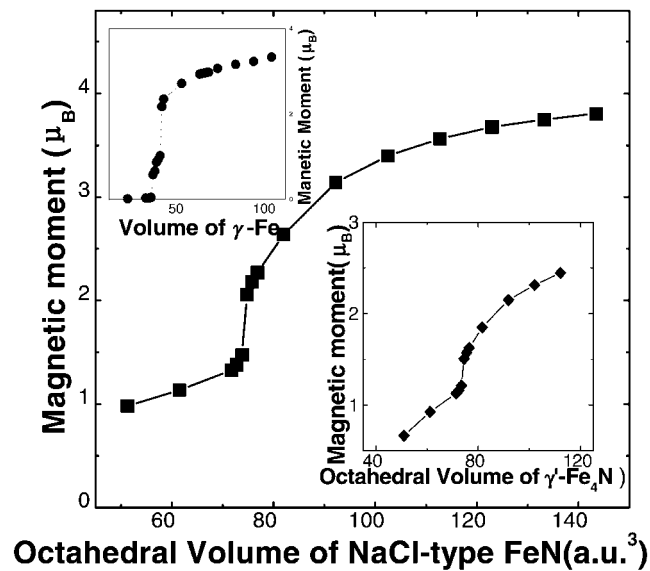


Figure 4. The volume dependence of magnetic moment in the NaCl-type nitride. The top-left inset shows the MVI curve of γ -Fe. The bottom-right inset shows the MVI curve of the face-centred-site iron of γ' -Fe₄N obtained by Mohn and Matter [15].

mechanism difference results from the appearance of Fe–N local coordination which changes the local magnetic interaction.

Considering γ' -Fe₄N, the iron atoms of the corner site and the face-centred site should have different M – V relations because they have different local coordination. The M – V curve of the corner-site iron atom should be more like that of the γ -Fe as they have similar local coordination. The magnetic moment value quickly falls from about $3.0 \mu_B$ of the high-spin value to the zero of the low-spin value [15]. Based on the same reasoning, the M – V curve of the face-centred-site iron atom should be more like that of the NaCl-type FeN [15]. Hence the similar local coordination results in the similar MVI behaviour.

4. Conclusions

In this paper, we have investigated the electronic structure and magnetic properties of FeN with NaCl- and ZnS-type structures. The FeN is more like an ionic compound and is reasonable to explain the magnetic structure of FeN by the super-exchange interaction. From the analysis, the influence of local coordination in the iron nitride has been considered. The role of Fe–N local octahedral coordination is prominent for the magnetic properties. At equilibrium volume, a proportional relation of magnetic moment with volume for perfect octahedra has been presented. Such an octahedral coordination can be used to explain the effect of interstitial nitrogen atoms in other iron nitrides. A MVI tendency is indicated for NaCl-type FeN. It is worth mentioning that from the local coordination point of view it is easier to understand the magnetic properties of Fe–N nitrides, because not only the Fe–N interaction but also the Fe–Fe interactions are involved in the local coordination structure. However, much more detailed investigation should be made in the future because of the existence of distortion in the local coordination.

Acknowledgment

The authors acknowledge the financial support of National Science Fund of China.

References

- [1] Cory J M D and Smith P A I 1999 *J. Magn. Magn. Mater.* **200** 405
- [2] Heiman N and Kazama N S 1981 *J. Appl. Phys.* **52** 3562
- [3] Suzuki K, Morita H, Kaneko T, Yoshida H and Fujimori H 1993 *J. Alloys Comp.* **201** 11
- [4] Nakagawa H, Nasu S, Fujii H, Takahashi M and Kanamaru F 1991 *Hyperf. Int.* **69** 455
- [5] Hinomura T and Nasu R 1997 *Physica B* **237-238** 557
- [6] Shimizu H, Shirai M and Suzuki N 1998 *J. Phys. Soc. Japan* **67** 922
- [7] Sifkovits M, Smolinski H, Hellwig S and Weber W 1999 *J. Magn. Magn. Mater.* **204** 191
- [8] Filippetti A and Pickett W E 1999 *Phys. Rev. B* **59** 8397
- [9] Eck B, Dronskowski R, Takahashi M and Kikkawa S 1999 *J. Mater. Chem.* **9** 1527
- [10] Kong Y 1999 *J. Phys.: Condens. Matter* **12** 4161
- [11] Savrasov S Y 1996 *Phys. Rev. B* **54** 16 470
- [12] Andersen O K 1975 *Phys. Rev. B* **12** 3060
- [13] Vosko S H, Wilk L and Nusair M 1980 *Can. J. Phys.* **58** 1200
- [14] Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865
- [15] Mohn P and Mater S F 1999 *J. Magn. Magn. Mater.* **199** 234