Electronic structure, hyperfine interactions and disordering effects in iron nitride Fe₄N

A.N. Timoshevskii, V.A. Timoshevskii, B.Z. Yanchitsky and V.A. Yavna

(1) Institute of Magnetism, 36-b Vernadskii St., 252680 Kiev, Ukraine
(2) Rostov State University of Transport, Narodnogo Opolcheniya 2, Rostov-on-Don, 344038 Russia

Abstract

Iron nitride Fe₄N is studied by full-potential LAPW method. Structure parameters, electronic and magnetic properties as well as hyperfine interaction parameters are obtained. We observe perfect agreement with experimental results. Hypothetical Fe₄N structure was also calculated to study the influence of disordering effects on parameters of Mössbauer spectra. We performed detailed analysis of EFG formation on Fe nuclei including magnetization effects. We show that the formation of N-Fe-N local configuration is energetically favourable in nitrogen austenites.

1 Introduction

Face centered cubic (fcc) iron-based alloys are widely used for developing of stainless austenitic steels especially for using in critical temperature ranges, aggressive environment and other severe external conditions. Doping of these steels with light interstitial impurities (C,N) influence mechanics and kinetics of structure phase transitions in Fe-based alloys. Distribution of carbon and nitrogen atoms in solid solutions influence electrical and mechanical properties of alloys. Nitrogen doping enables to solve the problem of the strengthening of stainless steels.

Investigation of the influence of nitrogen on physical properties of multicomponent systems is a complicated problem. The solution of this problem should be made in several stages. On the first stage it seems important to study electronic structure of iron nitride Fe₄N, because binary γ-FeNx alloy can be modeled by non-stoichiometric nitride γ-Fe₄N₁₋ₓ.

There are a lot of experimental data about atomic and electronic structure of Fe₄N. We believe that Mössbauer spectroscopy gives most interesting information about impurity distribution, electronic structure and magnetic interactions in alloys. Studying of hyperfine structure of the energy spectra of nuclei is a powerful tool for investigation of interactions of atomic nucleus with local electric and magnetic fields. These interactions cause shifts and splittings of nuclear energy levels and enable us to obtain information about symmetry of charge distribution around the nucleus, about electronic configurations of atoms and ions, as well as about peculiarities of atomic structure of solids.

A number of experimental papers show substantial differences in Mössbauer spectra of binary Fe-N and Fe-C alloys. These differences are believed to be connected
with different C and N distribution in Fe fcc alloys [1]. In this paper we present calculation results of hyperfine interaction parameters for iron nitride Fe₄N as well as for hypothetical Fe₄N structure with another distribution of nitrogen atoms. This allows us to determine changes in Mössbauer spectra caused by redistribution on nitrogen atoms.

2 Calculation details

WIEN97 programme package [2], employing Full-potential Linearized Augmented Plane Wave (FLAPW) method was used for calculations. As far as FLAPW is an all-electron method (unlike pseudopotential methods), it allows to perform calculations of hyperfine interaction parameters from first principles. Obtained theoretical parameters of interaction of a nucleus with electric and magnetic fields can be successfully compared with parameters of experimental Mössbauer spectra.

Generalized gradient approximation (GGA) according to Perdew-Burke-Ernzerhof [3] model was used for exchange-correlation potential. The radii of atomic spheres were chosen as 1.9 a.u. and 1.68 a.u for Fe and N atoms respectively. The accuracy of calculation results depends on several basic parameters: number of \( K \)-points in Brillouin zone, number of \( LM \)-components and Fourier coefficients in charge density and potential decomposition and number of plane waves in interstitial region. The choice of the values of these parameters was based on convergence condition. Convergence tests gave the value \( R_{\text{min}} \times K_{\text{max}} = 8.8 \), which corresponds to 205 plane waves per atom in the basis set. Inside atomic spheres the wave function was decomposed up to \( l_{\text{max}} = 12 \). Charge density and potential was decomposed inside atomic spheres using lattice harmonics basis up to \( L_{\text{max}} = 6 \). In the interstitial region Fourier expansion was used with 850 coefficients. Calculations were performed for 3000 K-points in the Brillouin zone (84 K-points in the irreducible part). The values of all parameters ensure accuracy of 0.1 mRy in total energy of the system. Due to ferromagnetic nature of iron nitride all calculations were performed using spin-polarized approximation.

3 Atomic structure

The unit cell of iron nitride Fe₄N is a unit cell of \( \gamma \)-Fe with a nitrogen atom introduced in the centre of the cube (figure 1a). The structure has two symmetry types of Fe atoms: Fe₂ type forms octahedron around impurity atom and has two impurity atoms in the first coordination sphere located at 180°; Fe₀ type is located in the corners of the cell and has no impurity atoms in the first coordination sphere.

In order to find the value of lattice parameter, corresponding to the minimum total energy of the system we performed calculations for five different values of lattice parameter. The results were approximated by second-order polynomial using least square fit method. Then the value of lattice parameter was obtained analytically. Calculated value of lattice parameter \( C=7.164 \) a.u. is in good agreement with experimental value \( C=7.17 \) a.u. [8]. Calculations of electronic structure and hyperfine interaction parameters were performed using obtained optimized value of lattice parameter.

Optimization procedure was also performed for another two systems: \( \gamma \)-Fe (Fe-fcc)
and hypothetical Fe₄N structure (figure 1b). Both calculations were also performed in spin-polarized approximation. Calculation of γ-Fe seems interesting because it allows us to determine the influence of introducing of nitrogen atom on electronic structure and hyperfine interaction parameters of Fe-fcc. Optimization of hypothetical Fe₄N structure (figure 1b) was performed including variation of interatomic Fe-N distance. This structure has two types of iron atoms: Fe₁ and Fe₂, having one and two N atoms in the nearest neighbourhood respectively. We found out that with this type of ordering the total energy of the structure is 18 mRy larger, than the total energy of iron nitride. This shows that the formation of Fe-N-Fe-N chains (Fe₂ configuration) without Fe-N pairs (Fe₁ configuration) is energetically favourable.

From the point of view of atomic structure of Fe-N alloys iron nitride Fe₄N is the simplest structure where Fe-N chains are combined with Fe-Fe chains. This makes possible to perform detailed analysis of the influence of nitrogen on electronic structure and hyperfine interaction parameters and to use obtained information later for analyzing more complicated Fe-N alloys. This step-by-step approach, based on application of up-to-date \textit{ab initio} calculation method, appears to be most accurate for solving the problem of the influence of impurity atoms on the properties of Fe-based alloys.

Table 1: Cell parameters (a,b,c) and magnetic moments (M) for γ-Fe, iron nitride and model Fe₄N structure. Cell parameter is presented in atomic units, magnetic moment - in Bohr magnetons.

| Structure   | a, b, c (a.u) | a, b, c (a.u) | M(\(\mu_B\)) | M(\(\mu_B\)) |
|------------|---------------|---------------|----------------|----------------|
| Fe(fcc)    | a = 6.58      | a = 6.89\(^a\) | 1.04           |                |
| Fe₄N       | a = 7.164     | a = 7.171\(^b\) |                |                |
| Fe₀        |               |               | 2.90           | 3.0\(^c\)      |
| Fe₂        |               |               | 2.31           | 2.0\(^c\)      |
| Aver./atom |               |               | 2.50           | 2.21\(^c\)     |
| Fe₄N (model)| a=7.114      | c = 14.266    |                |                |
| Fe₁        |               |               | 2.53           |                |
| Fe₂        |               |               | 1.98           |                |
| Aver./atom |               |               | 2.27           |                |

\(^a\) reference\(^b\) reference\(^c\) reference
4 Hyperfine interactions

Ferromagnetic nature of iron nitride Fe₄N makes Mössbauer spectrum of this compound much more complicated. The presence of magnetic field leads to combined magnetic and electric hyperfine interactions. The Hamiltonian of the system, including these interactions is given by

\[ \hat{H} = -\left(\vec{\mu} \times \vec{H}\right) + e \sum_{ij} Q_{ij} V_{ij}, \]  

(1)

where \( \vec{\mu} \) - magnetic moment of the nucleus, \( \vec{H} \) - magnetic field, \( Q_{ij} \) - tensor of the nuclear quadrupole moment, \( V_{ij} \) - tensor of electric field gradient (EFG). The principal EFG axis and magnetization axis may be non-collinear, which makes finding of Hamiltonian eigenvalues much more complicated. Using \( eQ/\mu H \ll 1 \) approximation and taking into account that \( I = 3/2 \) for excited state of \(^{57}\text{Fe} \) nucleus, the energy levels of the system are given by

\[ E = -g\mu_n Hm_I + (-1)^{m_I+1/2} \frac{eQV_{zz}3\cos^2 \theta - 1}{2} \left( 1 + \frac{\eta^2}{3} \right)^{1/2}, \]  

(2)

\[ m_I = -I, -I + 1, \ldots, I - 1, I \]

In this expression \( m_I \) - magnetic quantum number, \( V_{zz} \) - the principal component of EFG tensor, \( \eta \) - asymmetry parameter, \( \theta \) - angle between the principal axis of EFG tensor and the direction of magnetic field \( \vec{H} \).

The presence of magnetic field reduces the symmetry of the system. In iron nitride Fe atoms, located in the centre of the cube faces are now divided into two types: Fe₂, for which principal EFG axis is parallel to magnetic field, and Fe’₂, for which this axis is perpendicular to magnetic field (figure 1a). Mössbauer spectra of these two types of Fe atoms will have different quadrupole splitting. So, due to magnetic field, we have three different types of iron atoms in iron nitride structure. The total Mössbauer spectrum of this compound will consist of eighteen peaks. Twelve of these peaks, which belong to Fe₂ and Fe’₂ atoms, will have different shifts due to different quadrupole interactions. The ratio of the number of these atomic types in iron nitride unit cell is Fe₀:Fe₂:Fe’₂=1:1:2, which leads to the same ratio of intensities of respective Mössbauer peaks. All described features of the spectrum are totally approved by experimental data [12].

Quadrupole splitting, expressed in \( \text{mm/s} \), is given by

\[ \Delta_v[\text{mm/s}] = 0.5205 \times Q[\text{b}]V_{zz}[10^{21}v/m^2] \frac{3\cos^2 \theta - 1}{2} \left( 1 + \frac{\eta^2}{3} \right)^{1/2}, \]  

(3)

In our calculations we used the value of nuclear quadrupole moment \( Q^{^{57}\text{Fe}} = 0.16 \text{b} \). This value was determined by Dufek, Blaha and Schwarz [3] by comparing experimental quadrupole splitting and theoretical EFG values, calculated by FLAPW method, for fourteen different Fe compounds.

For temperatures above the Curie point \( (T_c) \) the system becomes paramagnetic, and Fe₀ atoms will not contribute to Mössbauer spectrum. Fe₂ and Fe’₂ atomic types
Table 2: Contributions to $V_{zz}(10^{21} v/m^2)$ from inside the spheres and from interstitial region. Theoretical and experimental values of quadrupole splitting (QS)(mm/s) for Fe atoms with different angle $\theta$ between $\vec{H}$ and principal EFG axis.

| System | Atom | Valence EFG | Lattice EFG | Total EFG | $\eta$ | $\theta^o$ | QS theory | QS expt. [12] |
|--------|------|--------------|-------------|-----------|------|-----------|-----------|--------------|
| Nitride | Fe$_2$ | -3.369 | +0.382 | -2.987 | 0 | 0$^o$ | -0.25 | -0.26 ± 0.02 |
| Model  | Fe$_1$ | -0.34 | +0.14 | -0.20 | 0 | 90$^o$ | 0.12 | 0.12 ± 0.02 |
|        | Fe$_2$ | -2.41 | +0.62 | -1.79 | 0.76 | 0$^o$ | 0.01 | 0.08 |
|        | Fe$_2'$ | -2.41 | +0.62 | -1.79 | 0.76 | 90$^o$ | 0.16 | 0.33 |

become totally identical, and Mössbauer spectrum in this case is a doublet with quadrupole splitting

$$\Delta_v [mm/s] = 1.041 \times Q[b]V_{zz}[10^{21} v/m^2] \left( 1 + \frac{\eta^2}{3} \right)^{1/2}.$$ (4)

In this paper electric field gradient was calculated according to method, developed by Blaha et al [10]. According to this approach EFG is calculated on ab-initio basis directly from electronic density distribution. We obtain EFG contributions from charge density inside atomic spheres (valence EFG) and outside the spheres (lattice EFG). Valence EFG is calculated as an integral of the value $\rho_{LM}(r)/r$ over the atomic sphere [11]. The values $\rho_{LM}$ originate from two radial wave functions with $l$ and $l'$:

$$\rho_{LM}(r) = \sum_{E<E_F} \sum_{l,m} \sum_{l',m'} R_{lm}(r) R_{l'm'}(r) G_{LM}^{Mm'm'},$$ (5)

where $R_{lm}(r)$ - LAPW radial wave functions, $G_{LM}^{Mm'm'}$ - Gaunt integrals.

Table 2 presents calculated principal values of EFG tensor and obtained according to (3) values of quadrupole splitting (QS) for Fe$_2$ and Fe$_2'$ atoms. The table shows that our results are in perfect agreement with experimental data, obtained by Focx et al [12] for the sample at T=4K. Excellent agreement with experiment also shows that chosen direction of magnetic axis (001) is a direction of real magnetic field in iron nitride Fe$_4$N.

Using (4) we also calculated quadrupole splitting at $T > T_c$. Our value $\Delta_v=0.50$ mm/s is also in excellent agreement with experimental data of Focx (0.50 mm/s), obtained at T=763K [12].

Table 2 also presents calculation results for model Fe$_4$N structure. Magnetization axis is assumed to be directed along one of Fe-N-Fe-N chains. Redistribution of nitrogen atoms leads to substantial changes of EFG values. The quadrupole splitting of Fe$_2$ atoms is reduced by 1/3 of the previous value when Fe$_1$ configuration appears in the structure. The same effect we observe at $T>T_c$: quadrupole splitting becomes now 0.33 mm/s. We see that quadrupole splitting is very sensitive to redistribution of impurity atoms in Fe-fcc. This fact can be used for interpretation of Mössbauer spectra of real fcc-alloys with different distribution of interstitial impurity.
5 Charge density and electric field gradient

We performed detailed analysis of EFG formation in iron nitride Fe₄N. Table 2 shows that valence component makes 90% contribution to the total value. So, we can focus on this component for understanding of EFG origin. According to our approach the valent band of the compound (Fe-3⁢s⁢3⁢p⁢3⁢d, N-2⁢s⁢2⁢p) was divided to four energy regions according to table 3. These energy intervals are formed mostly by different electronic shells of iron and nitrogen atoms. We also analyzed EFG contributions from wavefunctions of different symmetry (according to (5)) for each of energy regions.

Table 3: Principal EFG component (10²¹ v/m²) for iron nitride Fe₄N. Contributions to Vzz from different energy intervals and from radial wavefunctions of different symmetry.

| Energy region | s − d | p − p | d − d | Total |
|---------------|-------|-------|-------|-------|
| Fe-3s3p       | −0.046| +4.437| −0.001| +4.390|
| N-2s          | −0.021| −7.889| −0.364| −8.274|
| N-2p          | −0.037| −14.652| −5.680| −20.369|
| Fe-3d         | +0.092| +7.892| +13.121| +21.105|
| Valent        | −0.012| −10.212| +7.076| −3.148|

Table 4: Vzz contributions from N-2p and Fe-3d energy regions for electrons with different spin orientation.

| Energy region | Spin | s − d | p − p | d − d | Total  |
|---------------|------|-------|-------|-------|--------|
| N-2p          | up   | −0.015| −6.535| −3.021| −9.571 |
|               | down | −0.022| −8.117| −2.659| −10.798|
| Fe-3d         | up   | +0.042| +2.216| +10.190| +12.448|
|               | down | +0.050| +5.676| +2.931| +8.657 |

First of all let us analyze the electric field gradient, caused by the whole valent band (valence EFG). Table 2 shows that s − d contribution is negligibly small for all energy regions. EFG is practically formed by p − p and d − d contributions, which have different signs. We see that negative p − p contribution is dominating, although it is greatly canceled by positive d − d contribution.

The analysis of table 3 data allows us to conclude that main contribution to EFG formation is made by 2p and 2s nitrogen states, and contribution from 2p states is dominant. It should be noted that we are now talking about electrons, which have energy of nitrogen 2p states, but spatially are located in Fe₂ sphere. Substantial asymmetry of spatial distribution of these electrons (figure 2a) gives main negative contribution to total EFG. The interesting fact is that more than 70% of charge, formed by these electrons, have p−symmetry, and 30% - d−symmetry relative to the centre of Fe₂ sphere. This follows from analysis of p − p and d − d contributions for N-2p interval (table 3). The same situation is observed for 2s—electrons of nitrogen, but their total EFG contribution is 2.5 times smaller than 2p—electrons contribution. The EFG contribution of N-2s—electrons is practically caused only by electrons of p—symmetry relative to the centre of Fe₂ sphere.
Substantial negative EFG, caused by described asymmetry of nitrogen electrons, is greatly canceled by positive gradient, caused by own Fe electrons (figure 2b). These are first of all Fe-3d-electrons, which density is distributed in such a way, that greatly cancels asymmetry of 2s and 2p electrons of nitrogen. Comparative analysis of \( p\)–\( p \) and \( d\)–\( d \) contributions shows that more than 60% of asymmetrically distributed electrons of Fe-3d energy region have \( d \)–symmetry, and less than 40% \( p \)–symmetry (table 3) relative to the centre of \( Fe_2 \) sphere. Redistribution of rather localized Fe-3s3p states also gives positive EFG contribution, but this contribution is almost 5 times smaller than contribution of \( 3d \)–states.

It should be noted that quadrupole splitting was calculated using total EFG value, given in table 3, and for calculation of valence EFG contribution summation in (5) was done up to \( l_{\text{max}} = 12 \). On the other hand, for analysis of partial EFG contributions we limited the summation only up to \( l_{\text{max}} = 2 \) (due to the absence of ”chemical” \( f \)-states). This is the reason for small differences of valence EFG values in tables 2 and 3.

The values of local magnetic moments play an important role in EFG formation in iron nitride \( Fe_4N \). The calculations show that the upper edge of Fe-3d spin down states is located 2 eV above the Fermi level. Substantial difference in population of states with different spin orientation greatly influence EFG formation. Table 3 gives EFG contributions from states with different spin orientation for N-2p and Fe-3d energy regions. We notice considerable difference in EFG values, caused by spin up and down electrons of Fe-3d interval. This effect mostly influence the value of \( d\)–\( d \) contribution of this energy region. This contribution is mainly formed by density distribution of own \( 3d \)–electrons of iron. Spin up contribution is more than 3 times larger than spin down contribution for \( d\)–\( d \) component of Fe-3d–region.

The fact that spin down states are partially ”pulled” above the Fermi level considerably decreases compensating positive component, and leads to increasing of absolute value of total (negative) EFG. In the absence of this effect we would have considerably larger compensating component, which would lead to decreasing of total EFG value and, as a consequence, to decreasing of quadrupole splitting in Mössbauer spectra.

Figure 2: Charge distribution in N-2p (a) and N-2pFe3d (b) energy region for iron nitride \( Fe_4N \), \( e/(a.u.)^3 \).
6 Summary

We performed \textit{ab initio} band structure calculations of iron nitride Fe\textsubscript{4}N. All our results are in very good agreement with experimental data. Structure characteristics as well as magnetic properties are well reproduced. We also performed calculations of hypothetical Fe\textsubscript{4}N disordered structure. Comparative analysis of these two calculations showed that the formation of Fe-N pairs in Fe\textsubscript{4}N compound is energetically unfavourable.

We also calculated hyperfine interaction parameters for both Fe\textsubscript{4}N structures taking into account the presence of magnetic field. For iron nitride structure we obtained perfect agreement of quadrupole splitting values with experimental data. For disordered Fe\textsubscript{4}N structure we observe considerable decreasing of quadrupole splitting for Fe-N-Fe-N chains, and very small quadrupole splitting for Fe-N pairs.

Detailed analysis of EFG formation in iron nitride Fe\textsubscript{4}N allows us to conclude that EFG is mainly formed by space distribution of nitrogen 2\textit{s} and 2\textit{p} electrons, although it is greatly canceled by Fe3\textit{d}–electrons. Magnetization reduces this cancellation effect and increases the value of total EFG in iron nitride structure.

References

[1] V.G.Gavriljuk \textit{et al}, Acta mater 45, 225 (1997), Acta mater 47, 927 (1999)

[2] P.Blaha, K.Schwarz, and J.Luitz, WIEN97, A Full Potential Linearized Augmented Plane Wave Package for Calculating Crystal Properties (Karlheinz Schwarz, Techn. Universität Wien, Austria), 1999. ISBN 3-9501031-0-4

[3] Perdew J.P.,Burke S. and Ernzerhof M. 1996,Phys.Rev.Lett.77,3865

[4] J.Häglund, Phys. Rev. B 47, 566 (1993)

[5] D.Singh, Phys. Rev. B 43, 6388 (1994)

[6] P.Dufek, P.Blaha and K.Schwarz, Phys. Rev. Lett. 75, 3545 (1995)

[7] M.Acet, H.Zähres, E.F.Wasserman and W.Pepperhoff, Phys. Rev. B 49, 6012 (1994)

[8] H.Jacobs, D.Rechenbach and U.Zachwieja, Journal of Alloys and Compounds 227, 10 (1995)

[9] H.C.Herper, E.Hoffmann and P.Entel, Phys. Rev. B 60, 3839 (1999)

[10] P.Blaha, K.Schwarz and P.Herzig, Phys. Rev. Lett., 54, 1192 (1985)

[11] K.Schwarz, C.Ambrosch-Draxl and P.Blaha, Phys. Rev. B, 42, 2051 (1990)

[12] P.Rochegude and J.Foct, Phys. Stat. Sol. (A) 98, 51 (1986)

[13] R.Coehoorn, G.H.O.Daalderop and H.J.F.Jansen, Phys. Rev. B, 48, 3830 (1993)