

Electronic structure and pressure dependence of magnetic properties of Fe/N/Fe multi-layers

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Abstract The electronic structure and magnetic properties of the Fe/N/Fe multi-layers were obtained by means of self-consistent band structure calculations employing the Linear Muffin-Tin Orbital method (LMTO). Calculations were carried out for several lattice parameters in order to obtain ground-state properties such as equilibrium lattice parameters and the critical pressure of these multi-layers. The analysis of the density of states at equilibrium volume gives a good understanding of the electronic and magnetic properties of these multi-layers, showing remarkable differences from the bulk properties of iron-based nitrides. Ferromagnetic calculations show that the Fe/N/Fe multi-layers, at equilibrium volume, have a ferrimagnetic order of $1.45 \mu_B$ and $-0.22 \mu_B$ as the magnetic moments at the two non-equivalent iron sites. At nitrogen sites a moment magnetic of $-0.16 \mu_B$ was found, which is opposite to the very small values found in bulk iron nitrides. The magnetic moment and hyperfine field (the Fermi Contact) show a strong dependence with the lattice spacing with a collapse of the magnetic moments at certain critical lattice spacing.

Introduction

Nowadays there is a great deal of interest in the study of the electronic structure and magnetic properties of multi-layers. These new materials consist of a periodic structure of alternating layers of different materials. Due to their potential technological applications, these materials have been intensively investigated by recently developed sophisticated synthesis and characterization techniques [1–13]. These experimental works have shown that this class of new materials presents magnetic anisotropy, which may be useful for technological applications such as recording media with high-density storage. Furthermore, some theoretical studies on multi-layers [14–22] using the local spin density have shown that a good description of the electronic and magnetic properties of multi-layers and thin films can be reached through this approximation. On the other hand, the research of new materials has also stimulated experimental and theoretical studies of iron-based nitrides. Iron nitrides are very important mainly because high-nitrogen steel presents good mechanical and corrosion resistance and also because they are hard materials to make wear-resistance materials [23–37]. Magnetic iron nitrides such as γ' -Fe₄N and α'' -Fe₁₆N₂ are characterized by their high-saturation and low coercivity and many works are devoted to enhancing the magnetic qualities of the perovskite nitride, γ' -Fe₄N, as coercive field by metallic substitution [23–33]. In this sense these two fields of research were put close together with experimental works on iron-nitride multi-layers where structural and magnetic properties of these materials were investigated [7–13]. But clearly there is no a large amount of experimental or theoretical works dealing with Fe–N

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multi-layers. This work is an effort to clearly understand the influence of nitrogen in iron multi-layers as well as to make a comparison with the bulk properties of iron-based nitrides in their electronic and magnetic features. Then, in order to give some contribution in this field we have considered an ABA stacking with tetragonal symmetry, with symmetry operations $R4Z$, MX , I . The calculations were done with a structural model where these multi-layers grow with an ABA stacking of closed packing planes (Fig. 1a) and the resulting crystal structure has tetragonal symmetry with $c/a = 2\sqrt{2}$ with four atoms in the unit cell. As shown in Fig. 1a, the iron atoms positions are at: Fe1 $\rightarrow (0,0,0)$, Fe2 $\rightarrow (0.5,0.5,0.70)$ and Fe2 $\rightarrow (0.5,0.5,2.12)$; nitrogen atoms are at the $(0,0,1.41)$ positions. In this structure two iron sites (Fe2) have the same neighborhood, which implies that they are equivalent sites. In Fig. 1b we show the crystal structure of bulk γ' -Fe₄N where are shown the FeI atoms positions, FeII atoms positions (three equivalent sites) and N atoms positions.

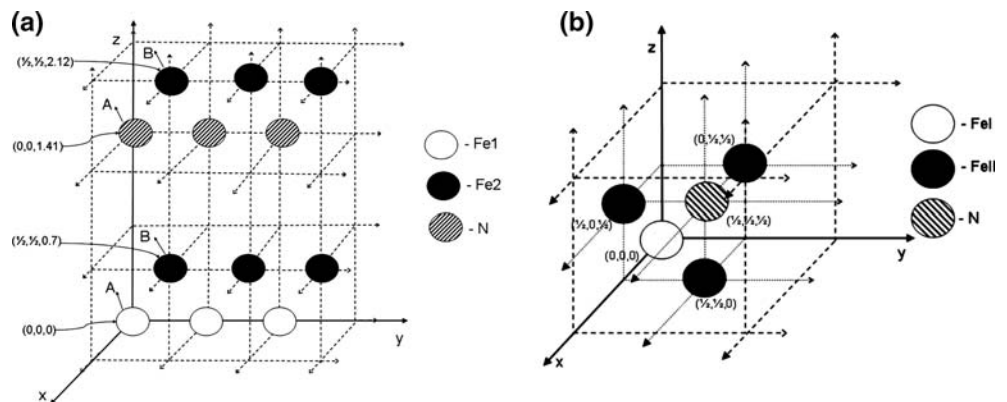
In this work the Linear Muffin-Tin Orbital (LMTO) method in the atomic spheres approximation (ASA) [38, 39] was employed and spin-polarized LMTO calculations were performed using the Vosko–Wilk–Nusair parameterization for the exchange-correlation energy of the electron gas [40]. Hedin–Lundqvist [41] parameterization was used in paramagnetic calculations. The present LMTO calculations were made without spin-orbit interaction but included combined correction terms and the solutions of the Schrödinger equation used s , p , d and f LMTO basis functions for iron atoms and s , p and d basis functions for nitrogen atoms. The radius of the Wigner–Seitz sphere around each atom was obtained using $\frac{4}{3}\pi \sum S_i^3 = \text{volume of unit cell}$. We choose the spheres around Fe1 and Fe2 atoms with the same volume while for the nitrogen we take $S_N = 0.60S_{Fe}$ since the ratio between the atomic radii of nitrogen and iron is around 60%. This choice

gives small interstitial volume and the resultant overlap between atomic spheres is $0.01a$ for Fe1 and Fe2 spheres (where a is the lattice parameter) and there is no overlap between Fe2 and N spheres and Fe1 and N spheres. The one-electron potentials were self-consistently converged for 1330 \mathbf{k} -points and 1500 points in the energy window were used to calculate the density of states. The self-consistent cycles were carried out until energy convergence on a scale better than 0.5 mRy was achieved. In the next section, the main results obtained in this work are discussed.

Results and discussion

In order to study the electronic structure and magnetic properties of Fe/N/Fe multi-layers we carried out calculations for several lattice parameters, which allow us to obtain the equilibrium volume. In our calculations we simplify the matters and do not consider structural anisotropy and therefore relaxations of the Fe–N distance was not taken into account, that is in order to optimise simultaneously c and a we must to perform a multi-variable relaxation varying the in plane lattice parameter a , the Fe–Fe distance and the Fe–N distance. This is a more difficult approach and it is beyond the scope of the present calculations. In Fig. 2 it is shown the calculated total energy as function of the lattice parameter for both non-magnetic (NM) and ferromagnetic (FM) states. As it can be seen, there is a good stability of the ferromagnetic state relative to the non-magnetic state. The energy difference between them at equilibrium lattice spacing is 6.5 mRy per atom. We comment on this difference in the discussion of the magnetic behavior under pressure. The equilibrium lattice parameters calculated by fitting the calculated total energy data point to a fourth degree polynomial are 4.587 a.u. (atomic units) and 4.474 a.u. for ferromagnetic and non-magnetic states

Fig. 1 (a) The Fe/N/Fe multi-layer structure showing the ABA planes and the iron and nitrogen positions in the unit cell. (b) Perovskite structure of Fe₄N (nitrogen at the center of the cube)



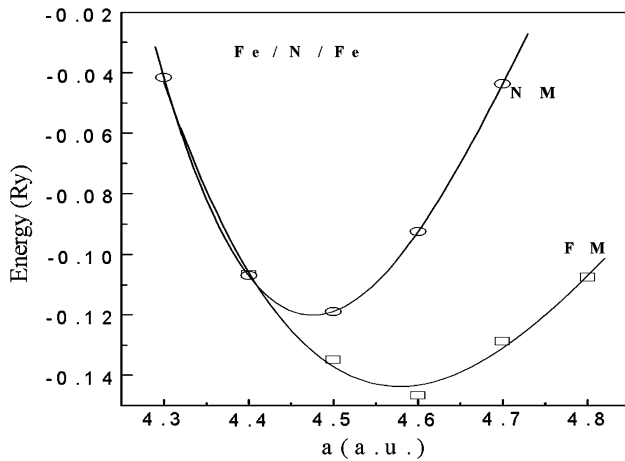


Fig. 2 Total energy curves (relative energies) versus lattice spacing (in atomic units) for ferromagnetic (FM) and non-magnetic (NM) states for Fe/N/Fe multi-layers

respectively. In general, for substituted iron nitrides, LMTO band structure calculations give equilibrium lattice constants that compare well with the experiment. For example, our earlier LMTO result for the equilibrium lattice spacing of the Fe_4N is 7.086 a.u. [30] and the experimental value is 7.170 a.u., the difference being in general less than 1% between experiment and theory [30]. The inter-atomic distances between Fe1 and Fe2 atoms and Fe2 and N atoms in ferromagnetic Fe/N/Fe multi-layers are less than the bulk iron-nitride Fe_4N . Therefore we can expect that atomic interaction between iron-iron sites and iron-nitrogen sites in this tetragonal structure will produce new magnetic features, as we shall see below.

Table 1 shows some theoretical parameters obtained for Fe/N/Fe multi-layers with spin-polarization, at equilibrium volume. There are three different magnetic sites in the unit cell: Fe1, Fe2 and N. The

main contribution for the magnetic moment formation comes from d electrons for the iron sites and from p electrons for the nitrogen sites. The magnetic moment at Fe1 ($-0.22 \mu_B$) and N ($-0.16 \mu_B$) sites are small and opposite to the magnetic moment at the two equivalents Fe2 sites ($1.45 \mu_B$) giving a ferrimagnetic order of $2.52 \mu_B$ as the magnetic moment per unit cell. This is a weak magnetism, hence relating to the high magnetic qualities of the iron nitrides such as the perovskite nitride, γ' - Fe_4N , which has magnetic moment of $9.40 \mu_B$ per formula unit [25], Fe/N/Fe multi-layers show a weak magnetism. The perovskite nitride γ' - Fe_4N has ferromagnetic order with two different iron sites, that is FeI and FeII sites, (see Fig. 1b) with experimental local magnetic moments of $3.00 \mu_B$ and $2.00 \mu_B$ respectively and our previous LMTO calculations on Fe_4N [25] gives $3.09 \mu_B$ and $2.11 \mu_B$ at FeI and FeII sites and a small magnetic moment at N sites of $0.05 \mu_B$. This shows that a transition occurs in the ferromagnetic order with the crystallographic transformation on going from the cubic symmetry of Fe_4N to the tetragonal symmetry of the Fe/N/Fe multi-layers. The Fe/N/Fe multi-layers show also small local magnetic moment at Fe2 sites relative to the local magnetic moment at Fe sites in substituted iron nitrides such as the CoFe_3N ($2.07 \mu_B$), PdFe_3N ($1.97 \mu_B$), NiFe_3N ($2.16 \mu_B$), AgFe_3N ($1.98 \mu_B$) and SnFe_3N ($1.99 \mu_B$) and is of the order of the value for the ZnFe_3N nitride ($1.21 \mu_B$), which shows a weak magnetism [31] (in parentheses are shown the magnetic moments at Fe sites in those nitrides). Comparing also the magnetism of Fe/N/Fe multi-layers with other iron-based new materials such as Fe/Pd monolayers or 2Fe/Pd or Fe/2Pd bilayers, (from where we found high magnetic moments at Fe sites with values of 2.87 , 2.70 and $2.97 \mu_B$ respectively [17, 20]), makes it clear that Fe/N/

Table 1 Calculated spin-polarized parameters for Fe/N/Fe multi-layers using the self-consistent potentials at equilibrium volume

	Fe 1			Fe2			N		
	\uparrow	\downarrow	$\uparrow - \downarrow$	\uparrow	\downarrow	$\uparrow - \downarrow$	\uparrow	\downarrow	$\uparrow - \downarrow$
n_s	0.3219	0.3291	-0.0072	0.3269	0.3167	0.0102	0.9019	0.8928	0.0091
n_p	0.3679	0.3833	-0.0154	0.3682	0.3398	0.0284	1.3587	1.5298	-0.1711
n_d	3.1110	3.3261	-0.2151	4.0584	1.6500	1.4084	0.0149	0.0125	0.0024
n_f	0.0647	0.0457	-0.0190	0.0561	0.0530	0.0031			
N	3.8655	4.0842	-0.2187	4.8096	3.3595	1.4501	2.2755	2.4351	-0.1596
$N(E_F)$	24.8331	9.0820		8.4078	16.0578		2.4392	4.0983	
$N_T(E_F)$	33.9151			24.4656			6.5375		
$N_c(E_F)$	64.9182								
γ	11.2236								
E_F	0.74651								
ΔQ	-0.0469			0.1674			-0.2878		

Here, n is in electrons/spin; N in states/atom spin Ry; N_T in states/atom Ry; N_C in states/unit cell Ry; γ in mJ/mol K^2 ; E_F in Ry and ΔQ in electrons

Fe multi-layers do not present great deal of technological interest in the sense of new magnetic materials as a man-made material in developing, for example, magnetic recording heads. That is, the Fe/N/Fe multi-layer is a poor magnetic material as is the case of ZnFe_3N nitride [31].

The anti-ferromagnetic coupling between atomic $2p$ moment and atomic $3d$ and $2s$ moments give $-0.16 \mu_B$ for the net magnetic moment at N sites shown in Table 1. This is an appreciable value when compared with the small values for the magnetic moment at N sites found for all the above mentioned iron-nitrides, which have magnetic moment at N sites of the order of $0.05 \mu_B$ or less. The net magnetic moment at N sites comes from the strong interactions between N atoms and Fe2 atoms and, as it can be seen in Table 1, the charge transfer from N sites to two equivalent Fe2 sites is much greater than the charge transfer from Fe1 sites to Fe2 sites. The short magnetic moment per cell comes from the new electronic structure of these multi-layers and is mainly due to the strong interactions between Fe2–N. As we will see in the following (in the discussion of the density of states), there are no appreciable interactions between Fe1 sites and N sites. Also in Table 1 we provide the calculated linear coefficient of specific heat (γ) which increases relatively to the iron-based nitrides, reflecting a high density of states at the Fermi level $N(E_F)$. This high value for $N(E_F)$ has the largest contribution from spin-up d -electrons for Fe1 sites and from spin-down d -electrons for Fe2 sites and the

small contribution of N sites comes from spin-down p -electrons.

Some aspects of the electronic interaction between Fe1–N, Fe2–N and Fe1–Fe2 sites of modeled Fe/N/Fe multi-layers are reflected in local density of states. Therefore, to investigate the trends of the chemical bonds in these multi-layers we have calculated the l -projected density of states (DOS). Figure 3 shows the DOS for s -, p -, and d -electrons for both spin directions, at Fe2 sites. The density of states at Fe2 sites show a structure in the low energy region -0.5 Ry to -0.20 Ry for s , p and, although very small, for d states. These bonding states reflect clearly the interactions between nitrogen s and p states and iron (Fe2) s , p and d states. This can be seen in Fig. 4 where this structure appears for s -DOS at N sites in the same energy region, which also indicates, as expected, the more localized character of s states at nitrogen sites. The interaction between p states of Fe2 sites and p states of N sites makes it clear through the appearance of bonding states in the range 0.35 Ry to 0.40 Ry at Fe2 (Fig. 3b) sites, which is the region of the strong peaks in p -DOS at N sites (Fig. 4b). The DOS in Fig. 4 makes clear the hybridized character of N states. There is a mixing between s and p states, and the d -DOS (Fig. 4) however weak, shows an extension towards s and p states. The hybridization of s , p and d states at N sites for Fe/N/Fe multi-layers was found also at N sites of bulk Fe_4N [25] and other substituted iron-based nitrides [26–33]. This can give some support to the assumption of an octahedral hybridization of nitrogen orbital, in the

Fig. 3 The s , p and d -projected densities of states for spin-up and spin-down electrons at Fe2 sites for Fe/N/Fe multi-layers. E_F is the Fermi energy

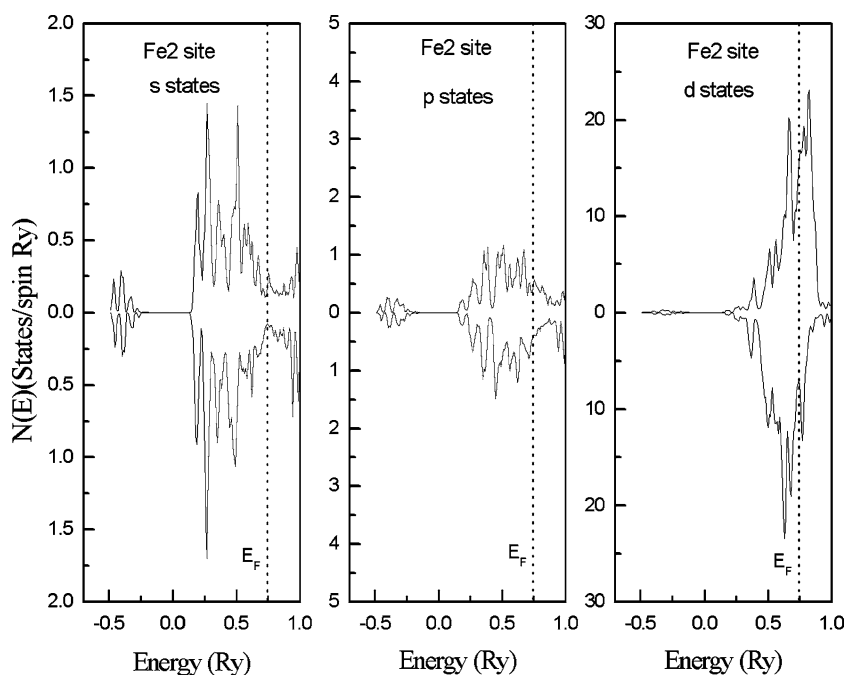
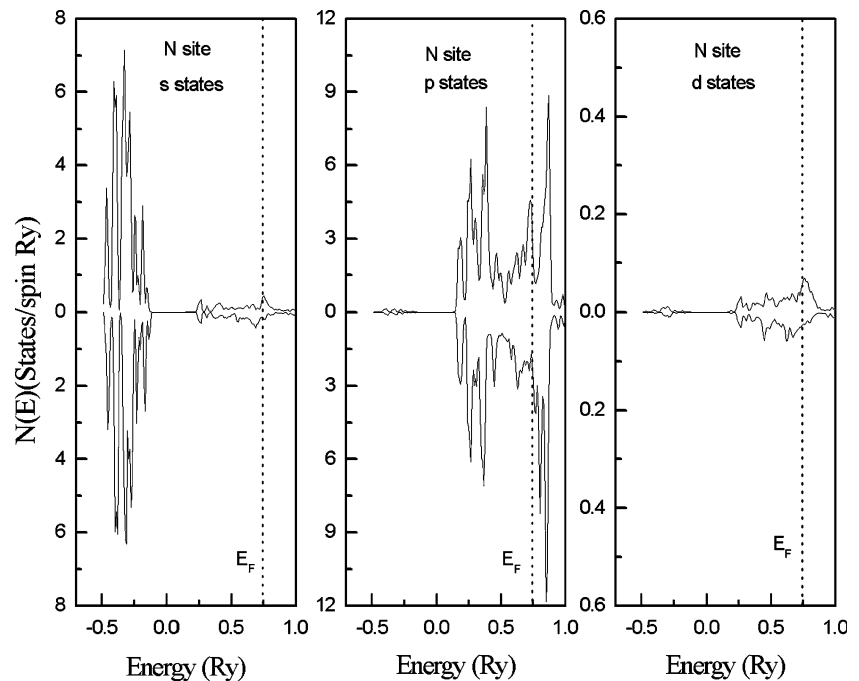


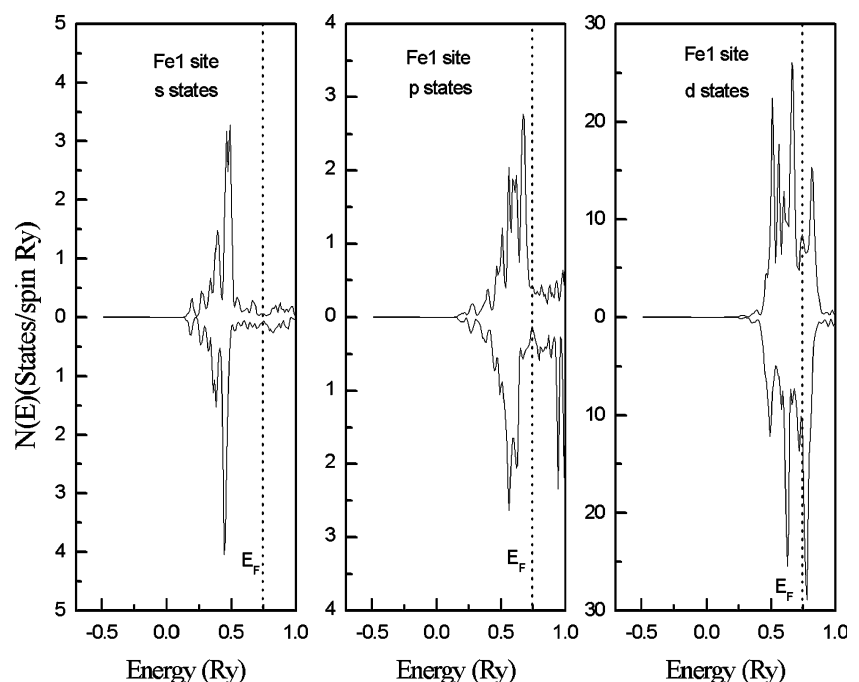
Fig. 4 The *s*, *p* and *d*-projected densities of states for spin-up and spin-down electrons at N sites for Fe/N/Fe multi-layers. E_F is the Fermi energy



sp^3d^2 states, to treat this class of compounds using the molecular orbital (MO) description. Contrary to the evident strong interaction between N layer and Fe2 layers, a weak interaction exists between the N layer and the Fe1 layer. The *l*-DOS at Fe1 sites shown in Fig. 5 make clear the absence of any evident structure that can reflect some appreciable interaction between Fe1 and N sites. The general features of the *l*-DOS at various sites were also reported earlier for

bulk iron-based nitrides [25–33] and reveal the metallic character of these Fe/N/Fe multi-layers and other iron-substituted nitrides. The formation of moments out of completely delocalised electrons for these multi-layers is explained also with the aid of *d*-DOS for Fe1 and Fe2 sites (Figs. 3c, 5c). Figure 3c shows that spin-up *d* states are fully occupied and that most spin-down *d* states are empty, hence giving the calculated magnetic moment of $1.45 \mu_B$ at Fe2 sites (Table 1). On the other

Fig. 5 The *s*, *p* and *d*-projected densities of states for spin-up and spin-down electrons at Fe1 sites for Fe/N/Fe multi-layers. E_F is the Fermi energy



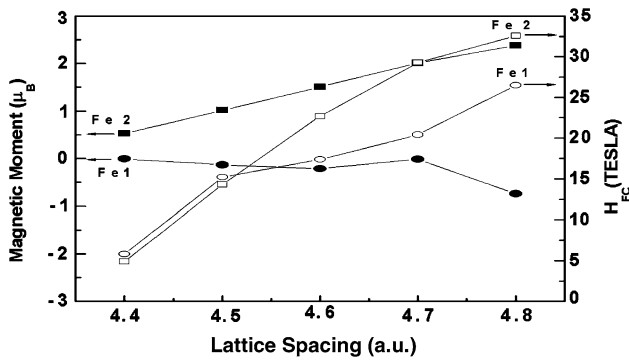


Fig. 6 The magnetic moment (in Bohr magnetons) at Fe1 (●) and Fe2 (■) sites and the absolute values of the hyperfine field (in Tesla) at Fe1 (○) and Fe2 (□) sites for Fe/N/Fe multi-layers

hand, Fig. 5c shows that spin-up *d* states are partially occupied and more of the spin-down *d* states are populated giving the net magnetic moment of $-0.22 \mu_B$ at these sites.

Total energy calculations showed that the weak ferrimagnetic order of Fe/N/Fe multi-layers has a good stability relative to the non-magnetic state (Fig. 2). Therefore, it is interesting to investigate the behavior under pressure of the weak magnetism found at the equilibrium volume. Thus, we studied the sensitivity of the magnetic moment against lattice spacing by calculating the magnetic moment for several lattice parameters, where the multi-layer structure was kept constant, simulating pressure effects. Figure 6 shows the behavior of the magnetic moment at Fe1 and Fe2 sites as a function of the lattice parameter. As it can be seen, for high volumes the absolute values of the magnetic moment at Fe1 and Fe2 sites increase but the ferrimagnetic order still remains. On the contrary, for low volumes the magnetic moments go continuously to zero. For the lattice parameter $a = 4.4$ a.u. the magnetic moments at Fe1 and N sites are zero but remain finite at Fe2 sites ($\approx 0.5 \mu_B$) which means a transition from ferrimagnetic order to a ferromagnetic order with a short net magnetic moment per unit cell ($\approx 1.0 \mu_B$). However, at lower volumes, the magnetic moment at Fe2 sites goes down to zero, which occurs for $a = 4.30$ a.u., meaning a transition from the weak ferromagnetic state to a paramagnetic state with null magnetic moment per unit cell.

Theoretical calculations using the LMTO method [26] and FPLAPW method [29] on Fe₄N have shown that the magnetic moments at the two non-equivalent iron sites go to zero for high pressure. This decrease of the magnetic moment with pressure was observed in bulk iron-based nitrides in experiments such as thermal expansion of forced magnetostriction of Fe₄N and

NiFe₃N [42] and applied pressure Mössbauer spectroscopy on Fe₄N [43, 44]. This is the first time that this behavior is observed in iron nitrides multi-layers. The usual critical pressure is defined as $P_c = -\Delta E/\Delta V$ where ΔE is the difference between non-magnetic and ferromagnetic equilibrium energies (per atom) and ΔV is the difference between non-magnetic and ferromagnetic equilibrium volumes (per atom). This definition of the critical pressure (P_c) was employed first by P. Mohn et al. in their work on magnetoelastic anomalies in Fe–Ni Invar alloys [45] and NiFe₃N nitride [46] and has been used also by us in the study of magnetic transition of inter-metallic bilayers and substituted iron nitrides [17, 20, 21, 30]. From Fig. 2 the critical pressure obtained is $P_c = 194$ kbar and this result is of the order of the experimental and theoretical values for the critical pressure of the iron-nitride Fe₄N ($P_c = 280$ kbar) and certain iron-substituted nitrides such as SnFe₃N [26], NiFe₃N and PdFe₃N [27]. These nitrides are known as having an Invar-like behavior and also present the collapse of their magnetic moment with pressure. From our results on magnetism and critical pressure it is easy to see that the same type of behavior also occurs in the case of Fe/N/Fe multi-layers so this behavior is not a specific feature of the above-mentioned bulk compounds.

The obtained magnetic transition for Fe/N/Fe multi-layers merits a further analysis. It is possible to define the type of magnetic transition based on two possible approaches for band calculations. In the fixed spin-moment procedure, as developed by Moruzzi et al. [47–49], the magnetic moment is treated as second independent parameter, at a given volume, which allows one to obtain the total energy versus moment curves ($E(M)_V$). Hence the spin-fixed moment band calculations yield both ferromagnetic and non-magnetic states simultaneously and magnetic transitions are classified from the behavior of the $E(M)_V$ curves. In the present work conventional band calculations were performed, that is, two types of calculations. First, non-magnetic calculations were performed where the numbers of spin-up and spin-down are taken as equal. Then spin-polarized calculations were performed where the magnetic moments develop freely. Therefore, these calculations result in $E(V)_{NM}$ and $E(V)_{FM}$ but not $E(M)_V$ (M as independent parameter). From the total energy of Fe/N/Fe multi-layers shown in Fig. 2, it is clear that the total energy of the system is represented by two separated but crossing branches (NM and FM states), where the overlap defines a region of co-existence, that is, at the crossing branch the moment can be zero or have a finite value without any change in the total energy of the system. Thus, the

Fe/N/Fe system present a first order transition as already discussed by Moruzzi et al. [47–49]. However, LMTO conventional band calculations present some problem on predicting the correct lattice parameter for the magnetic transition to occur. For Fe/N/Fe multi-layers, ferromagnetic calculations predicts a collapse of the magnetic moment (Fig. 6) at a very low volume ($a = 4.30$ a.u.). This result is opposite to the total energy calculations where we expected that a transition should occur around 4.4 a.u. (the crossing point of the two curves), since as seen in Fig. 1, below this lattice spacing the NM energies are lower than the FM ones. This indicates that within the local spin density approximation a ferromagnetic calculation is not capable of predicting the correct non-magnetic state. Clearly non-local effects must increase with pressure and therefore non-locality must be taken into account for a correct prediction of the NM state.

The magnetic field acting on a nucleus is given as the sum of four contributions:

$$H = H_{\text{ext}} + H_{\text{FC}} + H_{\text{orb}} + H_{\text{dip}}$$

where H_{ext} is the external applied magnetic field at the nucleus, H_{FC} is the hyperfine interaction (or Fermi contact term), which comes from an unbalanced spin density of the s -electrons [50, 51],

$$H_{\text{FC}} = -\frac{8}{3}\pi\gamma_{\text{N}}\left[|\Psi_{\uparrow(0)}|^2 - |\Psi_{\downarrow(0)}|^2\right]$$

here γ_{N} is the nuclear gyromagnetic ratio and $\psi_{\uparrow\downarrow(0)}$ is the wave function at the nucleus for spin-up and spin-down s -electrons. The other two contributions for the H are the fields arising from the orbital magnetic moment (which is small for $3d$ -metals) and from the dipole interaction surrounding atoms. These contributions are often small, even in the case of ordered alloys. For example, for ordered transition metals alloys, the orbital contribution is of the order of 2.0 Tesla (which obviously must be taken into account in accurate calculations). Therefore, since our present goal is to obtain an idea about the trends of hyperfine field in Fe/N/Fe multi-layers, these contributions can be neglected.

At equilibrium volume the calculated hyperfine field H_{FC} was found as being 16.8 T and -21.0 T at Fe1 and Fe2 sites respectively of the Fe/N/Fe multi-layers. By comparison, the experimental values for the H_{FC} at the two non-equivalent iron sites of the Fe_4N nitride are -34.1 T and -21.4 T respectively and the calculated values with the LMTO method are -32.8 T and -24.4 T [25]. This reveals that on going from

cubic symmetry of bulk Fe_4N to the tetragonal symmetry of Fe/N/Fe multi-layers a drastic change occurs in the hyperfine parameters indicating its strong dependence on the local arrangement of the atoms. Our results also indicate a strong dependence of the H_{FC} at Fe1 and Fe2 sites on the lattice spacing as shown in Fig. 6. At Fe2 sites the Fig. 6 shows the absolute values of H_{FC} . As it is seen in this figure, the hyperfine field goes to zero for high pressure as it happens to the magnetic moments in accordance with the linear relationship between magnetic moment and hyperfine field. The quicker drop of H_{FC} at Fe2 sites is due to the strong interaction with nitrogen atoms as near neighbors as we have shown by the analysis of local density of states. The decreasing of H_{FC} with decreasing volume may be related to the reduction of the contribution of the s -electrons to the spin density at iron nuclei. This behavior of H_{FC} with lattice spacing is similar to that obtained in the Fe_4N case by Paduani et al. [52] employing the discrete variational method in the self-consistent charge approximation (DVM-SCC).

Conclusions

Using the LMTO method in the ASA approximation and with VWN parametrization for electron gas exchange-correlation energy, a phenomenological metallic description of the electronic structure and magnetic properties of Fe/N/Fe multi-layers was done. The calculations show that at equilibrium volumes the ferrimagnetic state is energetically favored over non-magnetic state by 6.5 mRy/atom, with 1.45, -0.22 and $-0.16 \mu_{\text{B}}$ as the magnetic moment at Fe2, Fe1 and N sites, respectively, giving a small magnetic moment per formula unit ($2.52 \mu_{\text{B}}$). This weak magnetism shown by Fe/N/Fe multi-layers, in comparison with other iron-based new materials, makes it clear that it does not offer great interest for technological applications as magnetic material. The analysis of the density of states shows that Fe2 atoms interact strongly with N atoms and no prominent interaction was found between Fe1 atoms and N atoms. The behavior of the magnetic moments with lattice spacing variations show a first order transition from ferrimagnetic state at equilibrium volume to a non-magnetic state, at low volumes. The calculated critical pressure shows that these multi-layers have an Invar-like behavior as other iron-nitrides compounds. The hyperfine field (the Fermi Contact) shows also a strong dependence with lattice spacing going to zero for small volumes.

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