Short-term mobility 2008: report

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This document is a scientific report about the research conducted by the author at the *Institute of Physics, Polish Academy of Sciences* (IFPAN) in Warsaw in the framework of the *Short-term mobility 2008 programme* provided by the *Consiglio Nazionale delle Ricerche* (grant N.0002372). The electronic structure of a new diluted magnetic semiconductor, $Ga_{1-x}Fe_xN$, has been studied by means of the density functional theory, using the `quantum-ESPRESSO` code. The structural relaxation of the hexagonal ϵ-Fe_3N phase has been the preliminar result of this work that is still in progress in the calculation of substitutional and interstitial Fe defects in GaN.

1 Introduction

Nowdays, the interest in diluted magnetic semiconductors (DMS) is growing due to the possible application of these materials in the field of spin-electronics [1]. To address this challenge, it is necessary to realize DMS that mantain the ferromagnetic state largely beyond room temperature. Good candidates are wide gap systems (in particular, oxides and nitrides) from which is in theory possible to obtain Curie temperatures greater than 300 K [2, 3].

(Ga,Fe)N epitaxial thin layers are being intensively studied because of their unique magnetic properties: their Curie temperature lies above room temperature even for a relatively low Fe content (few per cent), and diluted GaN:Fe layers have been proven to be an ideal workbench to study the value of the exchange integrals (giving the magnitude of the exchange interactions responsible for the magnetic response) in transition-metal doped semiconductors [4]. However, the nature of the ferromagnetic ordering of the Fe spins needs further investigations.

As a result of a collaboration with the Linz University[1] a comprehensive electrical, structural, magnetic and optical characterization of these materials has been conducted [5], identifying the probable reason for the mentioned magnetic response, namely depending on the

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fabrication parameters: the presence of incoherent ferromagnetic Fe-rich nanocrystals of a crystallographic phase other than the matrix (like Fe nitrides) embedded in the paramagnetic host lattice or spinodal decomposition leading to the formation of coherent Fe-rich regions in the GaN lattice.

Now, in order to obtain a reliable control on the system by relating the growth conditions to the magnetic and structural properties, further high-resolution investigations involving synchrotron radiation have been started. In particular, extended x-ray absorption fine structure (EXAFS) [6] experiments has been conducted by the author at the GILDA Italian beamline at the European Synchrotron Radiation Facility (ESRF) in Grenoble. EXAFS has been proven to be an ideal technique to study the local structure of dopants in semiconductors and interesting results have been obtained recently on DMS by the GILDA group [7, 8].

To support experimental EXAFS results and properly understand the physics behind this system, theoretical simulations of the electronic structure and structural relaxation of Fe impurities and precipitates in GaN are needed. To fulfill this task, the method of density functional theory (DFT) [9, 10] has been choosen. In fact, since its introduction in the 1960s, DFT has evolved into a powerful tool that is widely used in condensed matter theory and computational materials for the calculation of electronic, magnetic, and structural properties of solids. The method has been remarkably successful in predicting, reproducing, and/or explaining a wide variety of materials phenomena. In particular, this method has been successfully applied to III-V DMS [11].

For these reasons, a collaboration with the Institute of Physics, Polish Academy of Sciences (IFPAN) in Warsaw has been started[2] and a short-term research period has been spent by the author at IFPAN in order to work on DFT simulations in direct collaboration with this group. In particular, the work has been focused on the use of the `quantum-ESPRESSO` *ab-initio* DFT software [12] to calculate the relaxed atomic structures for the phases found experimentally in the studied samples. A complete study, from the structural relaxation to the calculation of the density of states (DOS) and magnetization, has been conducted on the ϵ-Fe_3N crystalline phase, that is the most probable precipitation found experimentally.

In addition, starting from lattice parameter found by x-ray diffraction experiments, a relaxation procedure has been applied on the GaN host crystal and on this result have been built 72-atoms supercells in order to continue this research simulating Fe impurities in Ga at substitutional and interstitial sites. This additional part is still work-in-progress due to huge computing load generated by such calculations.

2 Report

The calculations have been performed with `quantum-ESPRESSO` [12] within the local spin density approximation (LSDA). Ultrasoft pseudopotentials has been used[3], which enables a relatively low plane wave cutoff of 35 Ry. To take into account the effects of the electron

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[3] Fe, Ga and N Vanderbilt ultrasoft pseudopotentials with Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional have been taken from the Quantum-ESPRESSO distribution.

self-interaction, the LDA+U scheme has been also tested with different U values but results obtained within LSDA and LDA+U schemes have been found similiar.

In order to proceed at the structural relaxation of ϵ-Fe_3N, a detailed literature research has been conducted. First studies on the nitridization process of Fe were from Jack [13], confirming the existence of this hexagonal phase (Fig. 1(a)). Jacobs [14] shows a detailed structure of ϵ-Fe_3N and it is the best source to start the calculation. The space group is P6322 (No. 182) with the unit cell composed of 6 Fe atoms in the Wickoff site 6g [(x, 0, 0); (0, x, 0); (-x, -x, 0); (-x, 0, 1/2); (0, -x, 1/2); (x, x, 1/2)] where $x = 0.333$ and 2 N in site 2c [(1/3, 2/3, 1/4); (2/3, 1/3, 3/4)], that is, iron atoms show the motif of a slightly distorted hexagonal close packing (hcp) structure and nitrogen atoms occupy only corner-sharing octahedra, as shown in Fig. 1(b). Lattice parameter are $a = 4.7209(6)$ Å, $c = 4.4188(9)$ Å.

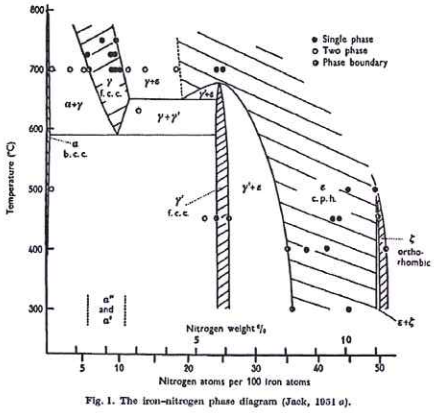


Fig. 1. The iron-nitrogen phase diagram (Jack, 1951 a).

(a) The iron-nitrogen phase diagram from [13].

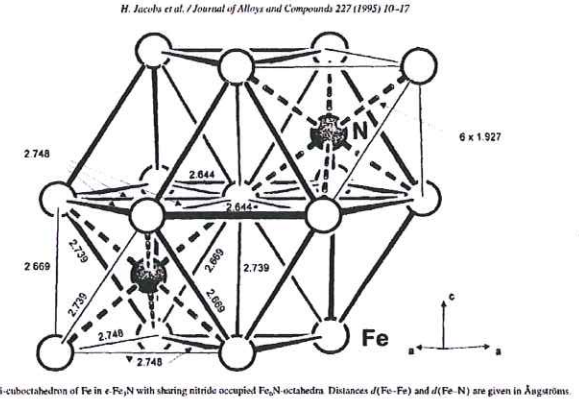
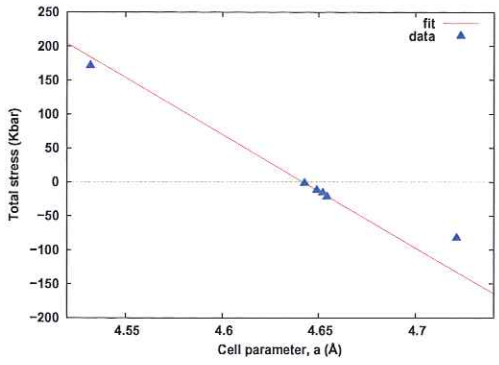


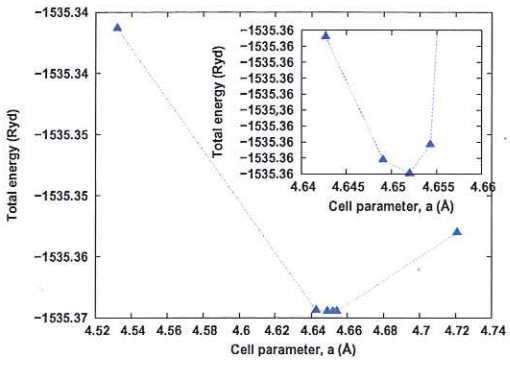
Fig. 7. Anti-cuboctahedron of Fe in ϵ-Fe_3N with sharing nitride occupied Fe_6N-octahedra. Distances d(Fe–Fe) and d(Fe–N) are given in Ångströms.

(b) Unit cell of ϵ-Fe_3N from [14].

Figure 1: Some extracts from literature on iron nitrides.



(a) Fit of the stress.



(b) Total energy (minimum zoomed in the inset).

Figure 2: Convergence study on the cell parameters (example of the a parameter).

The first step of the structural relaxation, where all atoms in the unit cells are allowed to relax, has been a convergence study on the Bruillouin zone summations performed using the

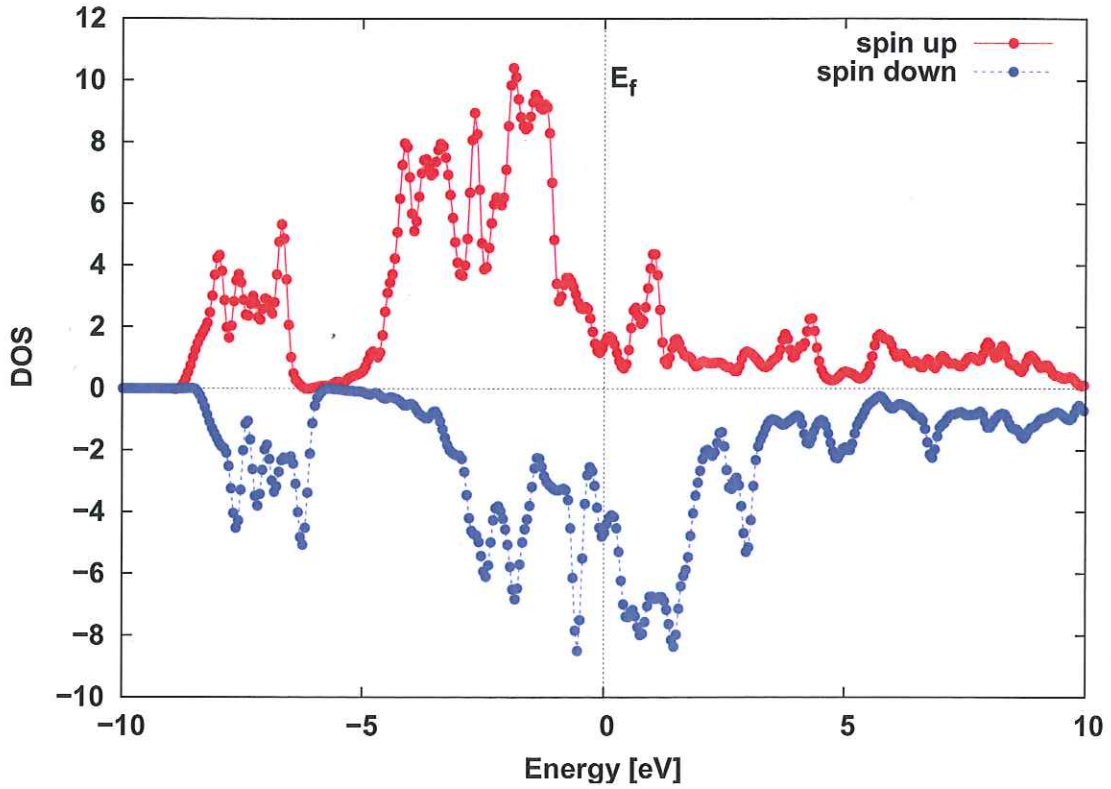


Figure 3: ϵ-Fe_3N total DOS for the two spin configurations.

Monkhorst-Pack k-points grid in the folded Bruillouin zone. Convergent results have been found for a $12 \times 12 \times 8$ k-grid. Subsequently a convergence study on the cell parameters has been taken into account in order to minimize the total energy of the system. The optimal value found at the zero value of the linear fit of the total stress (Fig. 2(a)) that corresponds to the minimum of the total energy (Fig. 2(b)) is $a = 4.65$ Å, that is $\approx 2\%$ contraction of the experimental value, a typical effect of the LSDA approximation. Furthermore, the relaxation properly reproduce the experimental value of x that is a 0.009 contraction from the 1/3 ideal value of x for Fe in hcp.

Once reached the structural minimization to respect the total energy, has been possible to extract informations on the magnetization that results of 2.2 μ_B/atom, in accord with experimental value as found from neutron diffraction at 4.2 K [15]. Finally, the total DOS has been calculated as shown in Fig. 3 and, calculating also the band structure, there is a clear evidence of the metallic behaviour of this system.

Following the same structural relaxation procedure used for ϵ-Fe_3N, the minimum of total energy for GaN has been found as a function of crystal cell parameters (Fig. 4). The minimized results are $a = 3.267$ Å and $c = 5.227$ Å. With these relaxed values a 72-atoms supercells, that is a $3 \times 3 \times 2$ GaN unit cells, have been built in order to proceed at Fe defects calculations. For the substitutional defect, one Ga atom has been substituted by Fe at (0,0,0) position in the unit cell. Furthermore, two types of interstitials defects have been taken into account: tetrahedral

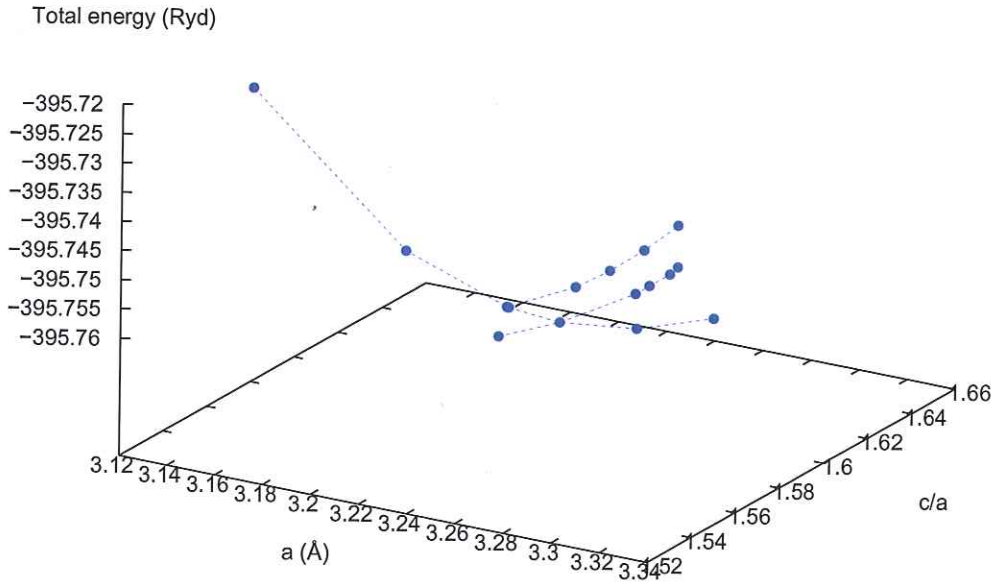


Figure 4: Structural relaxation of GaN crystal: convergence study on cell parameters, a and c.

interstitial - Fe at (0, 0, u/2) position in the unit cell - and octrahedral interstitial - Fe at (2/3 1/3 u/2) in the unit cell - where $u = 0.382$ is the relaxed value. Calculations on these defects have been started at IFPAN computing center and a complete analysis of the electronic structure results is still in progress.

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