Study on the oscillatory behaviour of the lattice parameter in ternary iron–nitrogen compounds

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ARTICLE INFO

ABSTRACT

The structural properties of the XFe$_3$N (X=Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn) cubic ternary iron based nitrides as well as the preferential occupation site of X in the structure were studied using Full Potential Linearized Augmented Plane Wave method, within the Density Functional Theory formalism, Wien2k code, the exchange-correlation potential described with the Perdew–Burke–Ernzerhof expression, based in the Local Spin Density Approximation and Generalized Gradient Approximation. According the calculations, the Sc, Co, Ni, Cu and Zn, atoms preferred the corner sites of the cubes, while Ti, V, Cr and Mn occupy the centre of the faces of the equilibrium structures. The equilibrium structure lattice parameters have an oscillatory behaviour with the atomic number of X, with decreasing amplitude as the atomic number of X increases. This trend do not correlated with the atomic radii of X.

1. Introduction

The γ'-Fe$_4$N nitride has been investigated in the last years due of their promising technological applications as a high density magnetic recording material [1,2]. Many experimental (using Mössbauer spectroscopy, magnetic, X-ray and neutron diffraction techniques [3–8]) and theoretical (mainly using the Density Functional Theory with different self-consistent methods [9–12]) studies have been performed. The compound has an anti-perovskita structure (space group Pm-3m(2 2 1)) where the Fe atoms occupy the corners (FeI) and the centre of the face (FeII), while the N ones are placed at the centre of the cube; 1a, 3c and 1b Wyckoff positions [8], respectively. In order to improve the structural and magnetic properties of γ'-Fe$_4$N, many theoretical and experimental researches have been reported on the ternary nitrides of the XFe$_3$N-type, replacing an Fe atom by X=Ti [13], V [14], Cr [13], Mn [15–19], Fe [5–12,20,21], Co [13,22–24], Ni [4,24–32], Cu[33] or Zn[34]. In the case of the theoretical studies, it has been generally assumed that X atoms substitute Fe atoms in the 1a position [13–17,22–24,32–34]. In this work, we investigate on the preferential occupancy site of the X atom replacing the Fe ones in the structure of the XFe$_3$N (X=Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn) ternary iron based nitrides and about the evolution of the equilibrium lattice parameters with X.

2. Calculations

In order to get the ternary compound XFe$_3$N, an iron atom is replaced by an X one either in 1a position or in the 3c position, given rise to the structures with space group Pm-3m or P4mmm, respectively (see Fig. 1).

The calculations were performed using Full Potential Linearized Augmented Plane Wave (FP-LAPW) method, within the Density Functional Theory formalism [35,36], Wien 2k code [37]. The exchange-correlation potential was described using the Perdew–Burke–Ernzerhof [38] expression, based in the Local
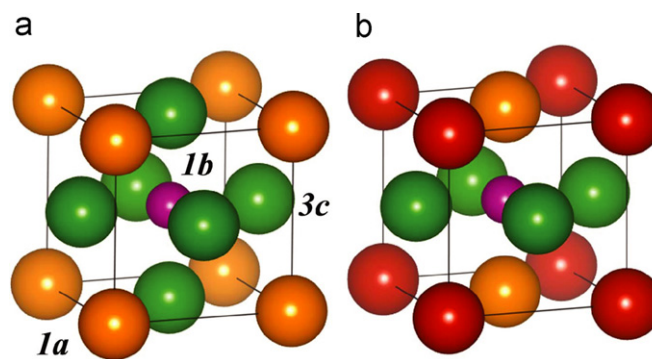

Fig. 1. The crystal lattice structure of ternary compound XFe$_3$N with space group: (a) Pm-3m and (b) P4mmm.

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Spin Density Approximation (LSDA) and Generalized Gradient Approximation (GGA) [35,36]. In all calculations, the muffin-tin radius of 2.39, 1.79 and 1.59 Bohr for X, Fe and N atoms were used, respectively; and the parameter $R_{MT}K_{max}$ was keep equal to 8. The irreducible wedge of the Brilloiun zone was described with 286 k-points. Furthermore, in all calculations were considered relativistic effects and spin polarization. The parameter of convergence of charge was 10^{-5} a. u.

3. Results and discussion

In order to obtain the equilibrium structure, the total energy vs. lattice parameter curves were obtained for the XFe$_3$N ternary nitrides, calculated assuming both Pm-3m and P4mmm structures. These curves, presented in Fig. 2, were fitted using the Birch-Murnaghan's state equation [39] to determine the energy minima and the equilibrium lattice parameters.
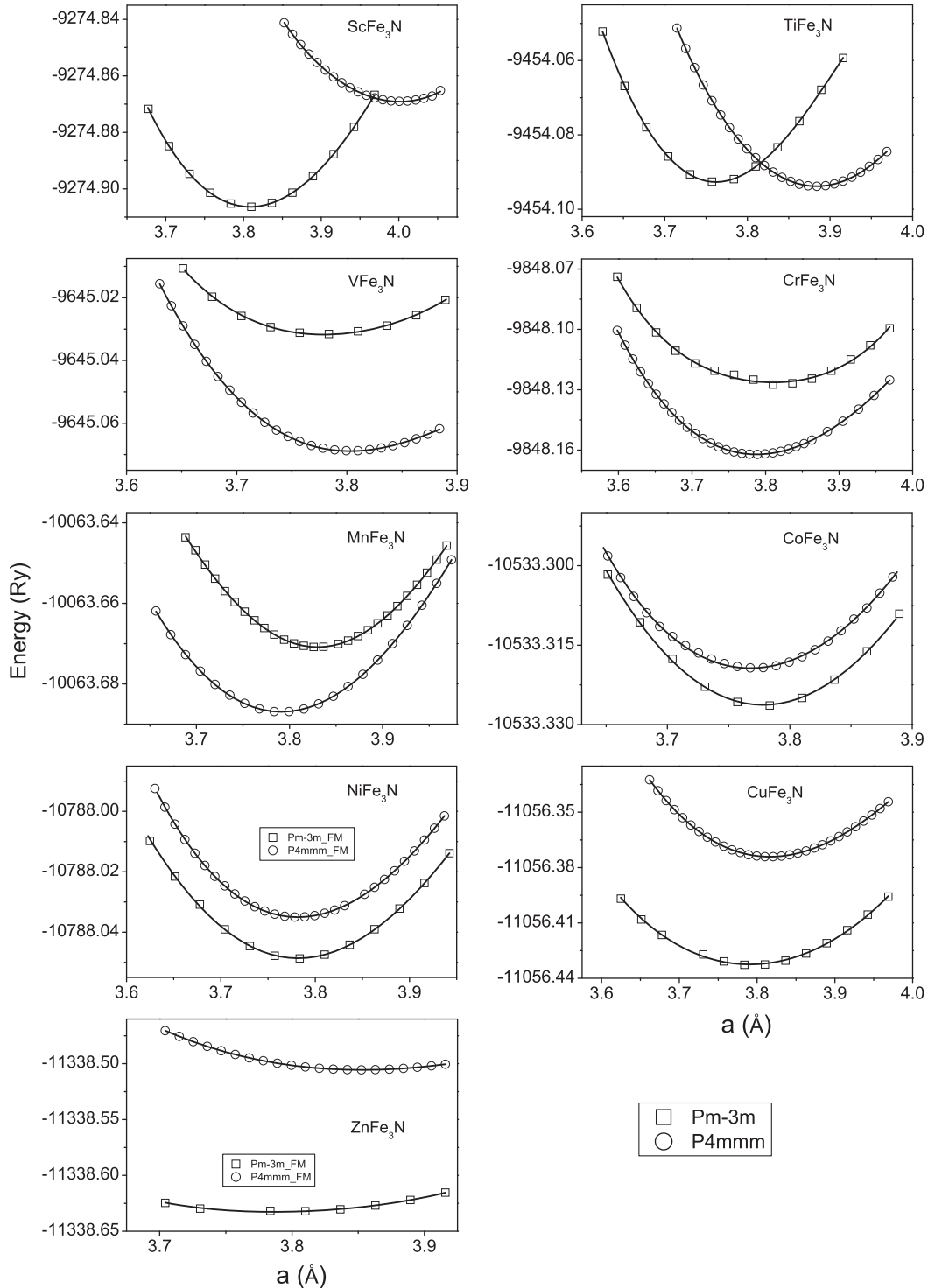

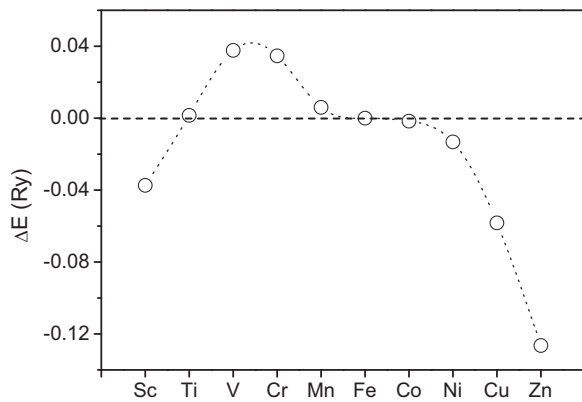**Fig. 2.** Energy vs. lattice parameter curves.

Fig. 3. Evolution of the difference between the minima of the energy corresponding to Pm-3mm and P4mmm structures.
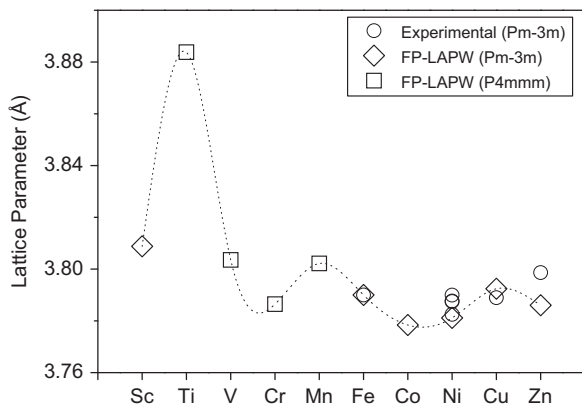

Fig. 4. Equilibrium lattice parameters.

The difference between the minima of the energy corresponding to Pm-3mm and P4mmm structures ($\Delta E = E_{\mathrm{Pm3m}} - E_{\mathrm{P4mmm}}$) are displayed in Fig. 3. These differences allow us to determine the preferential occupancy site for each X specie. For the TiFe$_3$N, VFe$_3$N, CrFe$_3$N and MnFe$_3$N nitrides the crystalline P4mmm structure is preferred, while in the cases of ScFe$_3$N, CoFe$_3$N, NiFe$_3$N, CuFe$_3$N and ZnFe$_3$N the equilibrium configurations correspond to the Pm-3m structure. In the case of the nitrides with Pm-3m equilibrium structure, the Fe–X magnetic interaction is ferromagnetic with the exception of the ScFe$_3$N which is non-magnetic, while in the other nitrides with P4mmm structure the interaction is antiferromagnetic. The resulting equilibrium lattice parameters are presented in Fig. 4. An oscillatory behaviour is observed with decreasing amplitude as the atomic number of X increases. Contrary to the claimed in some studies [28,31,40,][41], a deep analysis of the data indicates that there is no correlation between the equilibrium lattice parameter and the atomic radii of X atoms.

So, it is tempting to ascribe this trend to the magnetic interaction between the Fe and X atoms. The experimentally determined lattice parameters of FeFe$_3$N (Fe$_4$N) [7], NiFe$_3$N [25–27], CuFe$_3$N [33] and ZnFe$_3$N [34] are also included in the figure showing a good agreement between the experimental and the present values.

4. Conclusions

The structural properties of the XFe$_3$N cubic ternary iron based nitrides as well as the preferential occupation site of X in the structure have been determined using *ab-initio* methods. Two structures with space group Pm-3m or P4mmm were used to determine the preferential occupancy site of X. The equilibrium structure were determined considering the difference between the minima of the energy corresponding to Pm-3mm and P4mmm structures, permitting us to conclude that the TiFe$_3$N, VFe$_3$N, CrFe$_3$N and MnFe$_3$N nitrides the crystalline P4mmm structure is preferred (the X atom occupy the *3c* site), while in the cases of ScFe$_3$N, CoFe$_3$N, NiFe$_3$N, CuFe$_3$N and ZnFe$_3$N, the equilibrium configurations correspond to the Pm-3m structure (the X atom occupy the *1a* site). In effect, the corner of the cube is not preferred by all the X atoms, as was previously assumed. The equilibrium lattice parameters showed an oscillatory behaviour with the atomic number of X, with decreasing amplitude as the atomic number of X increases. This trend is not related with the atomic radii of X. It is important to remark that X atoms with small Z number and antiferromagnetically interacting with Fe atoms expand the cell more than the higher Z ones, trying to stabilize the lattice parameter at around 3.79 Å. Further calculations are in progress to fully understand this oscillatory behaviour.

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