Effect of Co addition on the structural, electronic and magnetic properties of $Fe_{16}N_2$ employing first principles approach

R Modiba*[1]and P E Ngoepe[2]

[1] Materials Modelling Centre, University of Limpopo, Private Bag X1106, Sovenga, South Africa
[2] Materials Science and Manufacturing, CSIR, PO Box 395, Pretoria, 0001, South Africa

Email: *Rmahlangu1@csir.co.za

Abstract. Improvements in energy efficiency and reduction of greenhouse gas emissions have been some of the central topics in recent years in environment and climate change. The advantages of using permanent magnets in many different types of electromagnetic drive and static magnetic field applications are compelling. Seemingly, demand is bound to increase substantially in coming years. There are significant challenges associated with coming up with new alloys or composite materials that can be used for bulk permanent magnets with an energy product in excess of 460 kJ m^{-3}. In this study, first-principles approach employing the density of states within the generalized gradient approximation is employed. The structural, electronic and magnetic properties of $Fe_{16-x}N_2Co$ for the development of permanent magnets are investigated. Firstly, geometry optimization was performed to reach the equilibrium state of the structures and the results compared well with the available experimental results. Interestingly, the density of states at the Fermi level decreases suggesting the stability of $Fe_{16}N_2$ with Co addition.

1. Introduction

Improvements in energy efficiency and reduction of greenhouse gas emissions have been some of the central topics in recent years in environment and climate change [1]. The advantages of using permanent magnets in many different types of electromagnetic drive and static magnetic field applications are compelling. It seems demand is bound to increase substantially in coming years. There are significant challenges associated with coming up with new alloys or composite materials that can be used for bulk permanent magnets with an energy product in excess of 460 kJ m^{-3}.

The large quantity of permanent magnets needed in contemporary technology, especially with the increased interest in alternative energy sources, transmission and conversions, also causes ecological concerns and economic problems, that have been discussed in detail by Alonso et al [2]. A complete and direct (one-by-one) replacement of all critical and rare elements in permanent magnets by other more readily available elements without decreasing product performance, raising the price or both, has limitations [3]. However, the substitution of rare earths and other critical materials appears to be a feasible solution.

It is of great importance for the theoretical search for hard-magnetic materials to gain detailed insight into the most relevant physical mechanisms, which determine the intrinsic properties of the hard-

magnetic materials [4]. In almost all modern hard-magnetic materials, the intrinsic material parameters are achieved as desired [5, 6] by combining transitional metals and rare earth elements in particular proportions. This results in a large class of possible chemical compositions and crystal structures. It is therefore well established that combining these two types of elements one can get materials with both high magnetic anisotropy and high Curie temperature [4]. In this study, electronic and magnetic properties of $(Fe_{16-x}Co_x)N_2$ (x = 0, 2, 4) for the development of permanent magnets are investigated using the first principle approach.

2. Methodology

The calculations were carried out using *ab initio* density functional theory (DFT) [7, 8] formalism as implemented in Cambridge *ab initio* simulation total energy package (CASTEP) [9] with the projector-augmented wave (PAW) [10]. An energy cutoff of 520 eV and 4x4x4 *k*-points were used, as they were sufficient to converge the total energy of the structures. For the exchange-correlation functional, the generalized gradient approximation of Perdew and Wang (GGA-PBE) [11] was chosen. The Brillouin zone integrations were performed for suitably large sets of *k*-points according to Monkhorst and Pack [12]. The convergence criteria for structure optimization and energy calculation were set to fine quality with the tolerance for the stress concentration factor (SCF), energy, maximum force and maximum displacement set to 1.0×10^{-5} eV/atom, 0.03 eV/ Å, 0.001 Å; respectively. Spin polarization was included using the formal spin as initial in the calculations to correctly account for its magnetic properties owing to the great effect of Fe, N and Co on magnetic systems. All the calculation were performed at 0 K.

3. Results and discussion

3.1. Structural and magnetic properties of $Fe_{16-x}Co_xN_2$

In this section the structural and magnetic properties of the $Fe_{16-x}Co_xN_2$ (x = 0, 2 and 4) are discussed. In Figure 1, the structures of the $Fe_{16-x}Co_xN_2$ wherein in (a) the pure $Fe_{16}N_2$ and (b) doped $Fe_{14}Co_2N_2$ are shown . We studied the tetragonal $F_{16}N_2$ with a space group of I4/MMM with 18 of atoms. The structure was optimized and Fe substituted with Co resulting in $Fe_{14}Co_2N_2$ and $Fe_{12}Co_4N_2$.

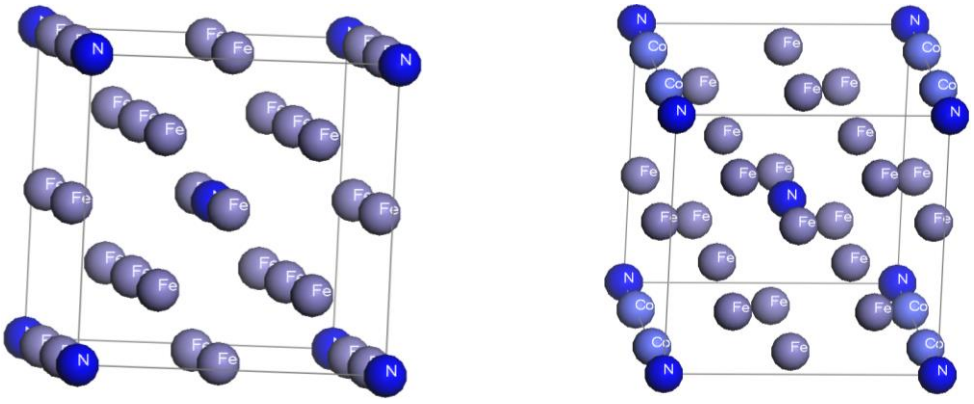

Figure 1. The structures of (a) Pure $Fe_{16}N_2$ and (b) doped $Fe_{14}Co_2N_2$ wherein the dark blue represents N, purple Fe and light blue Co atoms.

In Table 1, the structural and magnetic properties of the $Fe_{16-x}Co_xN_2$ structures are shown wherein all the structures were subjected to full geometry optimization. The c/a ratio of $Fe_{14}Co_2N_2$ was found to be smaller than that of $F_{16}N_2$ and $F_{12}Co_4N_2$. The magnetic moment of both Fe1and Fe2 for the $Fe_{14}Co_2N_2$ is found to be smaller than that of $Fe_{12}Co_4N_2$ whereas Fe3 and Fe4 are larger. The total magnetic of $Fe_{14}Co_2N_2$ was also found to be larger than that of the other two structures and is predicted as the metallic magnet whereas the other structures as half-metallic ferromagnetic.

3.2. Density of states

In Figure 2, the graph of total density of states (tDOS) for the $Fe_{16-x}Co_xN_2$ structures is shown. We observe the exchange splitting of spin-up and spin-down separated by Fermi level (E_f). The tDOS were found to be similar in shape to the $Fe_{16}N_2$ except that when Co is added there is a shift of peaks observed. The $Fe_{14}Co_2N_2$ was found to have the highest peak at E_f as compared to the other structures. The peak above the E_f is seen to be shifting to the right towards the E_f which behaves like a metal as predicted by the magnetic properties. The same behaviour is observed with $Fe_{12}Co_4N_2$ which has a higher peak as compared to the pure $Fe_{16}N_2$. On the spin down curves, the E_f hits the $Fe_{16}N_2$ at the pseudo and shifts to the lower energy with an increase in Co content.

Table 1: Lattice parameters (Å) and magnetic moment Bohr magnetons (μB) of $Fe_{16-x}Co_xN_2$

Structure	a	c	c/a	Atom	Magnetic moments	Total
$Fe_{16}N_2$	5.633	6.222	1.10	Fe1	2.311	18.7546
				Fe2	2.096	
				Fe3	2.799	
				N	-0.054	
$Fe_{14}Co_2N_2$	5.656	6.207	1.09	Fe1	2.789	36.019
				Co	1.284	
				Fe2	2.015	
				Fe3	2.288	
				Fe4	2.423	
				N	-0.056	
				N2	-0.057	
$Fe_{12}Co_4N_2$	5.616	6.241	1.11	Fe1	2.908	34.922
				Fe2	1.887	
				Fe3	2.25	
				Co	1.583	
				Fe4	2.286	
				N	-0.019	
				N2	-0.04	

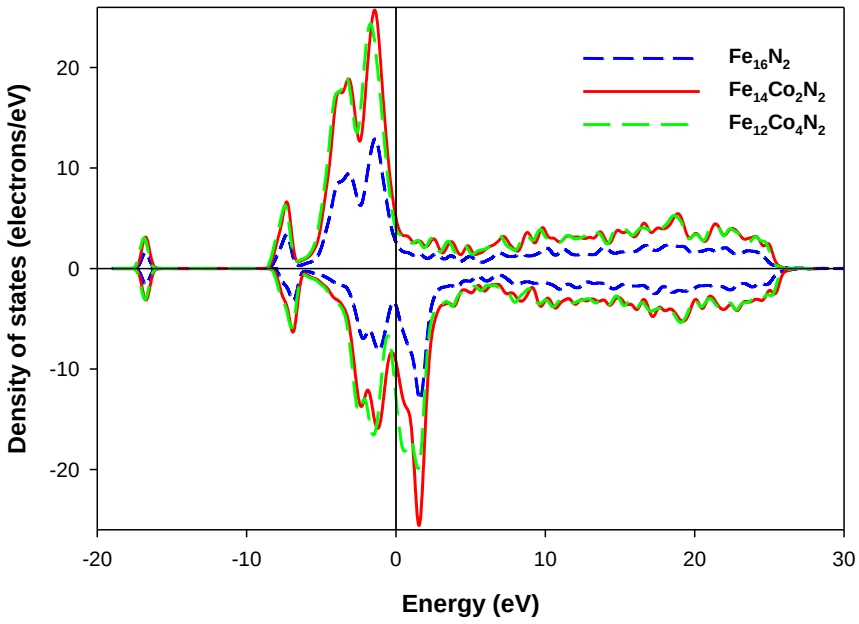

Figure 2. Comparison of the total density of states (tDOS) for the $Fe_{16-x}Co_xN_2$ (x=0, 2, 4) structures. The Fermi energy is taken as the energy zero ($E-E_f=0$).

4. Summary and Conclusions

$Fe_{16-x}Co_xN_2$ magnetic properties were investigated using ab initio techniques. The $Fe_{14}Co_2N_2$ was found to have high magnetic moment of 36 μB, which is good for strong magnets. Moreover, the structure is considered to be magnetic metallic as depicted by the tDOS at Fermi level. Both $Fe_{16}N_2$ and $Fe_{12}Co_4N_2$ were found to be half-metallic ferromagnets with the lowest total magnetic moment of the systems. This was found to be agreeing with the density of states wherein the $Fe_{14}Co_2N_2$ had the highest spin up and down tDOS; respectively. In future, the magnetic saturation and electronic transport properties of the structures will be investigated to further understand this material.

Acknowledgements

The authors acknowledge the CSIR and DSI for their financial support. The calculations were carried out using computer resources at the Materials Modelling Centre (MMC) at the University of Limpopo and the Centre for High Performance Computing (CHPC) in Cape Town.

References

[1] Ziervogel G *et. al.* 2014 *WIREs Clim. Change* **5** 605-620.
[2] Alonso E *et. al*. 2012 *Environ. Sci. Technol.* **46** 3406-3414.
[3] Graedel T E, Harper E M, Nassar N T and Reck B K 2015 *PNAS* **112** 6295-6300.
[4] Fähnle M, Hummler K, Liebs M and Beuerle T 1993 *Appl. Phys.* **A57** 67-76.
[5] Buschow K 1991 *Rep. Prog. Phys.* **54** 1123.
[6] Coey J M D 1996 *Phys. Scr.* **T66** 60-69.
[7] Hohenberg P and Kohn W 1964 *Phys. Rev.* B **136** 864-871.
[8] Kohn W and Sham L J 1965 *Phys. Rev.* A **140** 1133-1138.

[9] Clark S J et. al 2005 *Z. Kristallographie* **220** 567-570.
[10] Blöchl P E 1994 *Phys. Rev. B* **50** 17953-17979.
[11] Perdew J P, Burke K and Enzerhof M 1996 *Phys. Rev. Lett.* **77** 88-92.
[12] Monkhorst H J and Pack J D 1976 *Phys. Rev.* B **13** 5188-5192.