

The influence of Holmium substitution on the magnetic and mechanical properties of Nd₂Fe₁₄B: a first principle study

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Abstract. In this study, the ab initio density functional theory (DFT) approach is used to investigate the effect of Holmium (Ho) on the magnetic and mechanical properties of Nd₂Fe₁₄B magnets. Neodymium-based permanent magnets (Nd₂Fe₁₄B) are the potential permanent magnets to be used in various applications such as wind turbines and electric vehicles. These magnets possess high magnetic field strength and resistance to demagnetization. However, they suffer from low operating temperatures below 585 K. Substitution of Nd with Ho enhances the magnetic strength of the Nd₂Fe₁₄B permanent magnet. NdHoFe₁₄B magnets are found to be thermodynamically stable due to negative heats of formation, which is in good agreement with the calculated density of states. Partial substitution of Nd with Ho improves the stability and the magnetic strength of Nd₂Fe₁₄B permanent magnets. The findings will provide insight into the future development of permanent magnetic compounds with good magnetic strength.

1 Introduction

Rare earth magnets (RE) are strong permanent magnets (PM) made from rare earth elements [1]. They produce a significantly stronger magnetic field than alnico and ferrite magnets, generating a magnetic field greater than 1.4 T [2]. Samarium cobalt (SmCo₅) and neodymium (Nd₂Fe₁₄B) magnets are the two well-known forms of rare earth magnets. SmCo₅ rare earth magnets are less frequent owing to their higher cost and lower magnetic field [3]. The strongest rare earth magnets are NdFeB sintered magnets, which have the highest energy product of any commercial PM material [4, 5]. It was reported that neodymium magnets possess high magnetic field strength and resistance to demagnetisation. These magnets have various applications in high-efficiency power conversion machines and devices such as wind turbines and electric vehicles due to their exceptional magnetic properties, since they operate at high temperatures. In addition, experimental studies show that the high milling time leads to high magnetic properties of Nd₂Fe₁₄B. Small crystal sizes are required to obtain high magnetic properties in neodymium magnets [6].

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$\text{Nd}_2\text{Fe}_{14}\text{B}$ permanent magnets have a low operating temperature of 585 K which is known as Curie temperature [2]. In addition, $\text{Nd}_2\text{Fe}_{14}\text{B}$ permanent magnet display poor mechanical properties, vibrational properties and brittle behaviour. When the temperature increases, the anisotropy field decreases [2, 7]. The Curie temperature of the $\text{Ho}_2\text{Fe}_{14}\text{B}$ permanent magnet is reported to be 576 K and possesses a large density with a value of 8.05 Mg/m³ compared to $\text{Nd}_2\text{Fe}_{14}\text{B}$ [2]. Holmium (Ho) is a ductile rare earth element which possesses a high melting temperature of 1747 K. Nd substitution with other rare earth elements is considered to enhance the stability and operating temperature of $\text{Nd}_2\text{Fe}_{14}\text{B}$ magnets [8].

In this study, we investigate the effect of Ho on the $\text{Nd}_2\text{Fe}_{14}\text{B}$ permanent magnet employing the first principle density functional theory (DFT) based. We observe that the substitution of Nd with Ho is found to improve the stability and magnetic properties of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ permanent magnets.

2 Methodology

The calculations were performed with ab initio density functional theory [9] formalism as implemented in the Vienna Ab initio Simulation Package (VASP) [10] with the Projector Augmented Wave (PAW) [11]. An energy Cut-off of 400 eV was sufficient to converge the total energy of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ and $\text{NdHoFe}_{14}\text{B}$ tetragonal magnets. The generalized gradient approximation by Perdew, Burke and Enzerhof (GGA-PBEsol) [12] was chosen for the exchange-correlation functional. The appropriate k-points mesh according to Monkhorst and Pack [13] of $6 \times 6 \times 3$ was used. A tetragonal $\text{Nd}_2\text{Fe}_{14}\text{B}$ and $\text{NdHoFe}_{14}\text{B}$ structures with 68 atoms were used. Full geometry optimization (GO) has been performed to relax the atoms in the structure. Lattice parameters, heats of formation, electronic density of states, elastic constants and magnetic moments were calculated using the VASP code.

3 Results and discussion

3.1 Structural and thermodynamic properties

Table 1 presents the lattice parameters, heats of formation and magnetic moments of $\text{Nd}_2\text{Fe}_{14}\text{B}$ and $\text{NdHoFe}_{14}\text{B}$ permanent magnets. The magnets are tetragonal structures consisting of a unit cell with 68 atoms and a space group of P42/mnm. The lattice parameters of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ permanent magnet are calculated where the a parameter was found to be 8.249 Å and the c parameter to be 12.12 Å [20]. These findings are in good agreement with the experimental values to within 7 %. Calculated lattice parameters of $\text{NdHoFe}_{14}\text{B}$ magnets are shown in Table 1, where a parameter is found to have a value of 8.887 Å and a c parameter has a value of 12.342 Å. It is interesting to note that the partial substitution of Nd with Ho increases the lattice parameter of the permanent magnet. This is due to the large atomic radius of Ho rare earth element.

Heats of formation (ΔH_f) have been calculated to investigate the thermodynamic stability of permanent magnets [14]. The materials are considered to be thermodynamically stable if calculated ΔH_f is negative; otherwise, a positive value alludes to instability. We note that the calculated ΔH_f of $\text{Nd}_2\text{Fe}_{14}\text{B}$ permanent magnet is -6.499 eV/atom, suggesting that the material is thermodynamically stable. In addition, $\text{NdHoFe}_{14}\text{B}$ permanent magnet is found to be thermodynamically stable due to negative calculated ΔH_f with the value of -6.28 eV/atom.

Magnetic moments are calculated to derive the magnetic strength of the materials. The magnetic moment of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ permanent magnet is 35.63 μ_B , which is in good

agreement with previously reported values ($35.0 \mu_B$ or $37.1 \mu_B$) [2, 17]. It is interesting to note that substituting Ho for Nd increases the magnetic strength of $Nd_2Fe_{14}B$ magnets to $37.47 \mu_B$ suggesting that Ho has a great impact in enhancing the strength of the magnets.

Table 1. Lattice parameters, Heats of formation (ΔH_f) and magnetic moments of the $Nd_2Fe_{14}B$ and $NdHoFe_{14}B$ magnets.

Structure	Lattice parameter (Å)		ΔH_f (eV/atoms)	Magnetic Moments (μ_B)
	Calculated	Experimental ^[2]		
$Nd_2Fe_{14}B$	$a = 8.25$	$a = 8.82$	-6.49	35.63
	$b = 8.25$	$b = 8.82$		
	$c = 12.12$	$c = 12.25$		
$NdHoFe_{14}B$	$a = 8.89$		-6.26	37.47
	$b = 8.89$			
	$c = 12.34$			

3.2 Elastic properties

Table 2 shows the calculated elastic constants, anisotropic ratios, Pugh’s ratio and Poisson’s ratio for $Nd_2Fe_{14}B$ and $NdHoFe_{14}B$ permanent magnets. The mechanical stability of $Nd_2Fe_{14}B$ and $NdHoFe_{14}B$ permanent magnets is deduced from the elastic constants (C_{ij}) using the tetragonal stability criteria, which are as follows [ref]:

$$C_{11} > |C_{12}|, C_{44} > 0, C_{66} > 0 \text{ and } C_{11} + C_{12} - \frac{2C_{13}^2}{C_{33}} > 0. \tag{1}$$

$Nd_2Fe_{14}B$ permanent magnet is found to be mechanically stable, this is due to the calculated elastic constant which satisfies the tetragonal stability criteria. The calculated C_{44} and C_{66} are both greater than zero with values of 65.77 GPa and 119.56 GPa, respectively. Moreover, C_{11} with a value of 298.13 GPa is greater than the absolute value of C_{12} (159.30 GPa). The calculated elastic shear modulus is positive, $C' = 69.42$. For Nd substitution with Ho, C_{44} is found to be greater than zero with a value of 52.06 GPa. C_{66} (91.29 GPa) and elastic shear modulus ($C' = 59.44$) are both greater than zero. In addition, C_{11} with a value of 160.46 GPa is larger than the absolute value of C_{12} (41.59 GPa). These findings suggest that the $NdHoFe_{14}B$ magnet is mechanically stable since the magnet satisfies the tetragonal stability criterion.

Table 2 shows the anisotropy factors of $Nd_2Fe_{14}B$ and $NdHoFe_{14}B$ permanent magnets. These results indicate that the $Nd_2Fe_{14}B$ permanent magnet is anisotropic. In addition, the $NdHoFe_{14}B$ magnet is found to exhibit anisotropic behaviour since the calculated $A_1, A_2,$ and A_3 are not closer to unity. The Pugh’s ratio (B/G) is calculated to study the brittleness and ductility of the materials. The calculated B/G of the $Nd_2Fe_{14}B$ magnet is 1.13, suggesting that the magnet is brittle since the B/G ratio is less than the critical value of 1.75. Moreover, $NdHoFe_{14}B$ magnet is also brittle but the substitution of Nd with Ho improves the ductility of the $Nd_2Fe_{14}B$ magnets. If the Poisson’s ratio value is greater than 0.26, this indicates that the material is ductile; otherwise, it is a brittle material [20]. $Nd_2Fe_{14}B$ permanent magnets have the Poisson’s ratio of 0.16 which is less than the critical value of 0.26. These results suggest that $Nd_2Fe_{14}B$ magnets are brittle and in good agreement with the calculated Pugh’s ratio. Moreover, the calculated Poisson’s ratio of $NdHoFe_{14}B$ magnets is less than 0.26 with a value of 0.25, which suggests that the magnets are brittle. Substitution of Nd with Ho rare

earth element reduces the brittleness of Nd₂Fe₁₄B permanent magnets toward the ductile critical value (1.75) and this is seen from the calculated Pugh's and Poisson's ratios.

Table 2. Elastic constants, anisotropy, Pugh's ratio and Poisson's ratio of Nd₂Fe₁₄B and NdHoFe₁₄B permanent magnets.

Properties	Nd ₂ Fe ₁₄ B	NdHoFe ₁₄ B
C_{11}	298.13	160.46
C_{12}	159.30	41.59
C_{13}	65.59	37.34
C_{33}	94.12	163.66
C_{44}	65.77	52.06
C_{66}	119.56	91.29
C'	69.42	59.44
A_1	1.72	1.54
A_2	0.50	0.42
A_3	0.55	0.57
B/G	1.13	1.64
σ	0.16	0.25

3.3 Density of states

To correlate the structural and mechanical stability of the Nd_{2-x}RE_xFe₁₄B alloys, we compare their total density of states (tDOS) as shown in Figure 1. It has been reported that the DOS of structures of the same composition can be used to study the stability trend related to their behaviour at the E_f (Fermi level). The structure with the highest and lowest density of states at E_f is considered to be the least and most stable, respectively [19]. The total density of states for NdHoFe₁₄B magnets is shown in Figure 1. Between 0 and -5 eV, the highly localized peaks were found to be confined. There are two peaks in the valence band at approximately -7.5 eV and -8.5 eV and one peak in the conduction band at 2 eV. Furthermore, a dominant peak at -3 eV is found in the valence band. It was found that the NdHoFe₁₄B magnet has the lowest states at the E_f as compared to other magnets which suggests that the magnet is the most stable. In addition, there is a considerable difference in the spin-up and spin-down tDOS which account for net magnetic moments hence Nd₂Fe₁₄B and NdHoFe₁₄B magnets are ferromagnetic.

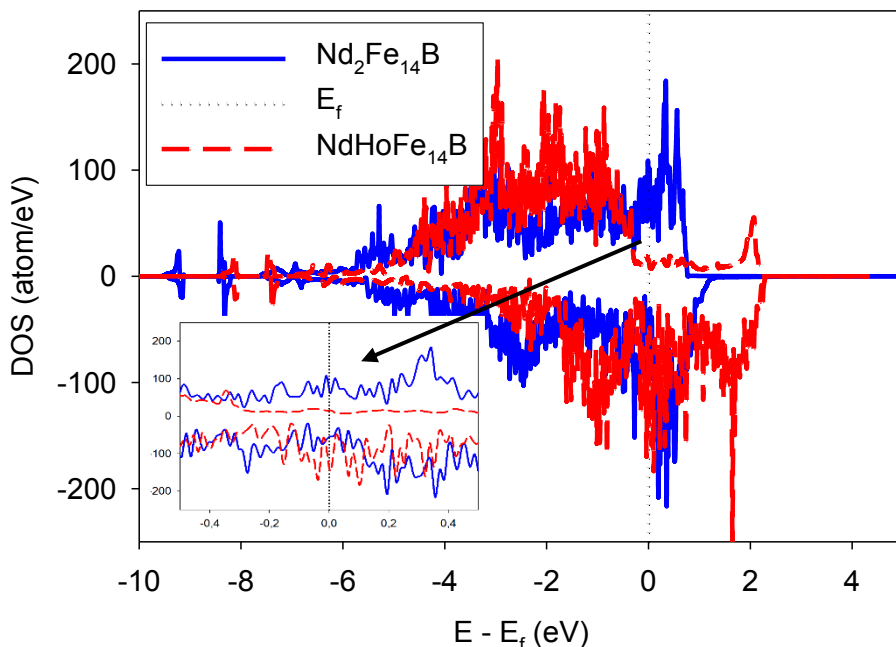


Fig. 1. Total density of states for $\text{Nd}_2\text{Fe}_{14}\text{B}$ and $\text{NdHoFe}_{14}\text{B}$ permanent magnets.

4 Conclusion

The structural, magnetic properties, mechanical and electronic properties of $\text{Nd}_2\text{Fe}_{14}\text{B}$ and $\text{NdHoFe}_{14}\text{B}$ permanent magnets were studied using the ab initio density functional theory technique. Calculated lattice parameters of $\text{Nd}_2\text{Fe}_{14}\text{B}$ permanent magnets are found to compare well with the available experimental findings. The addition of Ho shows a great effect on the calculated lattice parameters. Furthermore, the calculated heats of formation show that both $\text{Nd}_2\text{Fe}_{14}\text{B}$ and $\text{NdHoFe}_{14}\text{B}$ permanent magnets are thermodynamically stable, which is in good agreement with the calculated density of states. It is interesting to note that the substitution of Ho for Nd enhances the mechanical stability of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ permanent magnets. Doping Ho for Nd reduced the brittleness of the magnet towards the ductile critical value. Moreover, the calculated magnetic moments of the $\text{NdHoFe}_{14}\text{B}$ permanent magnets is $37.47 \mu_B$ which suggests that Ho has a great effect on the strength of the magnets. In conclusion, Ho substitution for Nd shows to improve both the stability and magnetic strength of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ permanent magnets.

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