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Effect of Gadolinium rare-earth element on $Nd_2Fe_{14}B$ permanent magnet

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Abstract. Neodymium-based permanent magnets ($Nd_2Fe_{14}B$) are the potential permanent magnets for use in various applications due to their high magnetic field strength and resistance to demagnetisation. These magnets have various applications in highly efficient energy conversion machines and devices such as wind turbines and electric vehicles due to their exceptional magnetic properties. However, they suffer low operating temperatures below 585 K. In this study, we investigate the effect of Gadolinium (Gd) rare earth element on the $Nd_2Fe_{14}B$ magnets. The structural, electronic, mechanical and vibrational properties of the magnets are calculated using the ab initio density functional theory approach. Heats of formation were used to investigate the thermodynamical stability of the magnets, where $NdGdFe_{14}B$ magnets are found to be thermodynamically stable. Moreover, the calculated elastic properties satisfy the tetragonal stability condition which alludes to the stability of $NdGdFe_{14}B$ magnets which is in agreement with the calculated eigenvalues. Furthermore, using the spin-polarized only we calculated the total magnetic moment of the $NdGdFe_{14}B$ magnet (59.92 μ_b), which is larger compared to that of $Nd_2Fe_{14}B$ magnets. Partial substitution of Nd with Gd improves the stability and the magnetic properties of $Nd_2Fe_{14}B$ permanent magnets.

1 Introduction

Permanent magnet (PM) is a material whose magnetism is derived from the intrinsic structure of the magnet [1]. Rare earth magnets (RE) are strong permanent magnets made from rare earth elements. However, REs are extremely brittle and highly susceptible to corrosion; they are usually plated or coated to prevent corrosion [2]. There are two kinds of well-known rare earth magnets namely samarium cobalt ($SmCo_5$) magnets and neodymium (NdFeB) magnets, with $SmCo_5$ magnets being 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]. 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. In addition, experimental studies show that the highest magnetic properties were obtained at the highest milling time,

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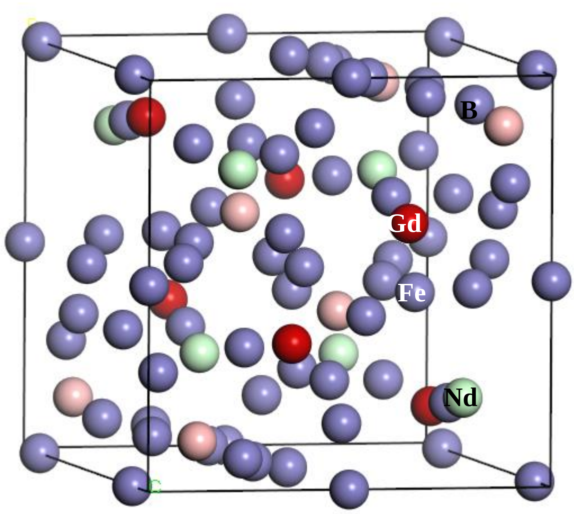
suggesting that milling time increases the value of the magnetic properties. To obtain high magnetic properties in neodymium magnets, small crystal sizes are required [6].
It was reported that neodymium magnets possess high magnetic field strength and resistance to demagnetisation. However, they suffer extremely due to low operating temperatures known as Curie temperature (Tc) below 585 K [2]. Moreover, with increasing temperature, the anisotropy field suffers a significant decrease [7, 2]. Poorly malleable, Gadolinium is a ductile rare earth element that also has a high melting temperature. It undergoes a ferromagnetic–paramagnetic transition at 293.4 K. In addition, the Gadolinium-based magnet ($Gd_2Fe_{14}B$) has the highest Curie temperature of the $R_2Fe_{14}B$ compounds [2]. The anisotropy of $Gd_2Fe_{14}B$ is relatively strong, with no contribution from the 4f orbital momentum expected [8].

In this work, we study the effect of Gd on $Nd_2Fe_{14}B$ magnets using density functional theory (DFT) techniques. The stability and magnetic properties of $Nd_{2-x}RE_xFe_{14}B$ alloys were studied using the lattice parameters, heats of formation, elastic properties and magnetic moment. NdGdFe14B magnets are thermodynamically stable. The elastic properties were calculated to study the mechanical stability of $NdGdFe_{14}B$ magnets. Partial substitution of Nd with Gd was found to improve the stability and magnetic properties of $Nd_2Fe_{14}B$ permanent magnets.

2 Methodology

The calculations were carried out using *ab initio* density functional theory (DFT) [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 tetragonal $Nd_2Fe_{14}B$ magnets. For the exchange-correlation functional, the generalized gradient approximation of Perdew, Burke and Enzerhof (GGA-PBE) sol [12] was chosen. The suitable k-points mesh according to Monkhorst and Pack [13] of 6×6×3 was used. A tetragonal $Nd_2Fe_{14}B$ structure with 68 atoms was used (Fig. 1).



Atom	Site
Nd1	4g
Gd1	4f
Fe1	4e
Fe2	4c
Fe3	8j1
Fe4	8j2
Fe5	16k1
Fe6	16k2
B1	4g

Fig. 1. The atomic arrangement unit cell of $NdGdFe_{14}B$ system with a space group $P4_2/mnm$.

3 Results and Discussion

3.1 Structural and thermodynamic Properties

The lattice parameters and heats of formation for the tetragonal $Nd_{2-x}RE_xFe_{14}B$ alloys are studied as shown in Table 1. The magnet is a tetragonal structure composed of 68 atoms unit cell and a space group of $P4_2/mnm$ where atoms are arranged in an eight-layer structure, 56-Fe, 7-Nd, 4-B and 1-Gd atoms. The *a* parameter of $Nd_2Fe_{14}B$ was observed to be 8.249 Å whereas the *c* parameter is 12.12 Å. The calculated lattice parameters of $NdGdFe_{14}B$ magnets are also calculated as shown in table 1, *a* parameter is found to be 8.293 Å and *c* to be 11.472 Å. It is interesting to note that the calculated *a* parameter increased whereas the c parameter decreased when Nd is substituted by Gd. This is due to the Gd element having a smaller atomic radius of 1.8 Å as compared to that of the Nd element (2.29 Å). Heats of formation are used to predict the stability of alloys. The equation for determining the heats of formation (ΔH_f) is given by [14]:

$$\Delta H_f = E_c - \sum_i x_i E_i \qquad (1)$$

where E_c is the calculated total energy of the compound, E_i is the calculated total energy of element *i* in the compound. The thermodynamic stability of these systems is calculated using the heats of formation (ΔH_f). For a structure to be stable, the heats of formation value must be negative; otherwise, a positive value indicates instability. The heats of formation for the $Nd_2Fe_{14}B$ phase were found to be -6.499 eV/atom, which alludes to the thermodynamic stability of the magnet. In addition, the heats of formation of $NdGdFe_{14}B$ magnets are addressed in Table 1, where the calculated negative ΔH_f of -6.26 eV/atom, suggesting that the magnet is thermodynamically stable.

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

Structure	Lattice parameter (Å)		ΔH_f (eV/atoms)
	Calculated	Experimental[2]	
$Nd_2Fe_{14}B$	*a* = 8.25 *b* = 8.25 *c* = 12.12	*a* = 8.82 *b* = 8.82 *c* = 12.25	-6.49
$NdGdFe_{14}B$	*a* = 8.29 *b* = 8.29 *c* = 11.47		-6.26

3.2 Elastic Properties

The elastic constants, anisotropic ratios, Pugh's ratio and magnetic moment of $Nd_{2-x}RE_xFe_{14}B$ alloys are listed in Table 2. We follow the stability criteria for each lattice to describe the mechanical stability of the ternary $Nd_2Fe_{14}B$ system, $C_{11} > |C_{12}|, C_{44} > 0, C_{66} > 0 \; and \; C_{11} + C_{12} - \frac{2C_{13}^2}{C_{33}} > 0$. C_{11} (472.474 GPa) is found to be greater than the absolute value of C_{12} (250.56 GPa) and, C_{44} and C_{66} are both greater than zero with values of 110.36 GPa and 61.82 GPa, respectively. In addition, two elastic constants are negative, namely C_{13} and C_{33} with values of -1412.67 and -2594.39, respectively. The calculated elastic shear modulus was found to be positive (C' = 110.96). This suggests that $Nd_2Fe_{14}B$ satisfy tetragonal mechanical stability criteria. In addition, the elastic properties calculated for

$NdGdFe_{14}B$ magnets are also shown in Table 2. C_{11} (382.08 GPa) is much more than the absolute value of C_{12} (142.82 GPa), whereas C_{44}, C_{66} and C' are all greater than zero, with values of 113.30 GPa, 117.25 GPa, and 119.63 GPa, respectively. These suggest that the $NdGdFe_{14}B$ magnet is mechanical stable since the calculated elastic constants meet the tetragonal stability criterion. The anisotropy factor *(A)* is equal to 1 for an isotropic material, while the deviation of the A values from unity indicates the degree of elastic anisotropy [15]. Elastic anisotropy for non-cubic is given by A_1, A_2 and A_3. A_1 and A_2 of $Nd_2Fe_{14}B$ are less than unity with A values of 0.56 and 0.31, respectively, while A_3 (1.79) is greater than one, indicating that the material is anisotropic. In addition, the predicted A-ratios for the $NdGdFe_{14}B$ magnet indicate that the material exhibits isotropic behaviour as the calculated A_1, A_2, and A_3 are closer to unity at values of 0.98, 0.94, and 0.97, respectively.

Table 2. Elastic constants, anisotropy, Pugh's ratio and magnetic moment of $Nd_2Fe_{14}B$ and $NdGdFe_{14}B$ permanent magnets.

Properties	$Nd_2Fe_{14}B$	$NdGdFe_{14}B$
C_{11}	472.47	382.08
C_{12}	250.56	142.82
C_{13}	-1412.67	141.31
C_{16}	449.37	-5.73
C_{33}	-2594.39	332.59
C_{44}	110.36	113.30
C_{66}	61.82	117.25
C'	110.96	119.63
$A_1 = 2C_{66}/(C_{11}-C_{12})$	0.56	0.98
$A_2 = 2C_{66}/(C_{11}-C_{12})$	0.31	0.94
$A_3 = 2C_{44}/(C_{11}+C_{33}-2C_{13})$	1.79	0.97
B/G	-14.42	1.91
Magnetic Moment	35.63	59.92

The ratio of bulk to shear modulus is known as Pugh's ratio (B/G), can be used as a measure to determine the brittle and ductile nature of the material [16]. $Nd_2Fe_{14}B$ meets the conditions for brittleness since the B/G values are less than 1.75. The $NdGdFe_{14}B$ magnets have calculated Pughs ratios greater than 1.75 with a value of 1.91. These findings suggest that the $NdGdFe_{14}B$ magnet is ductile. The magnetic moment of $Nd_2Fe_{14}B$ and $NdGdFe_{14}B$ structures was calculated as shown in Table 2. The calculated magnetic moment was 35.63 μ_B which is comparable to the experimental values of 35.0 μ_B/f.u or 37.1 μ_B/f.u [2, 17]. These findings are in good agreement with previous theoretical and experimental data. Furthermore, the magnetic moment of the $NdGdFe_{14}B$ magnet is 59.92 μ_B which suggests that Gd has a great effect on the magnetic properties of the $Nd_2Fe_{14}B$ magnet. Replacing Nd with Gd strengthens the magnetic moments of $Nd_2Fe_{14}B$ permanent magnets.

Table 3 below shows the calculated eigenvalues of $Nd_2Fe_{14}B$ permanent magnets. Materials with negative eigenvalues are mechanically unstable, while materials with positive eigenvalues are considered to be stable [18]. We have found two negative Eigenvalues, -1012.67 and -3534.49. This is due to negative elastic constants, C_{13} and C_{33}. Therefore, the negative eigenvalues reveal that the $Nd_2Fe_{14}B$ magnet is mechanically unstable. The eigenvalues of the $NdGdFe_{14}B$ magnets are all positive, indicating that the material is mechanically stable. The results show that replacing Nd with Gd improves the mechanical stability of the magnet.

Table 3. Eigenvalues of $Nd_2Fe_{14}B$ and $NdGdFe_{14}B$ permanent magnets.

$Nd_2Fe_{14}B$	$NdGdFe_{14}B$
-1012.67	238.17
1671.11	650.49
-3534.49	207.03
473.33	453.30
473.33	453.30
1529.71	470.22

3.3 Density of states (DOS)

In order to correlate the structural and mechanical stability of the $Nd_{2-x}RE_xFe_{14}B$ alloys, we compare their total density of states (tDOS) plots in Figure 2. 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 $Nd_2Fe_{14}B$ magnet shows the highest density of states at E_f, confirming that it is the least stable structure, while $NdGdFe_{14}B$ is the most stable magnet due to the lowest density of states at E_f.

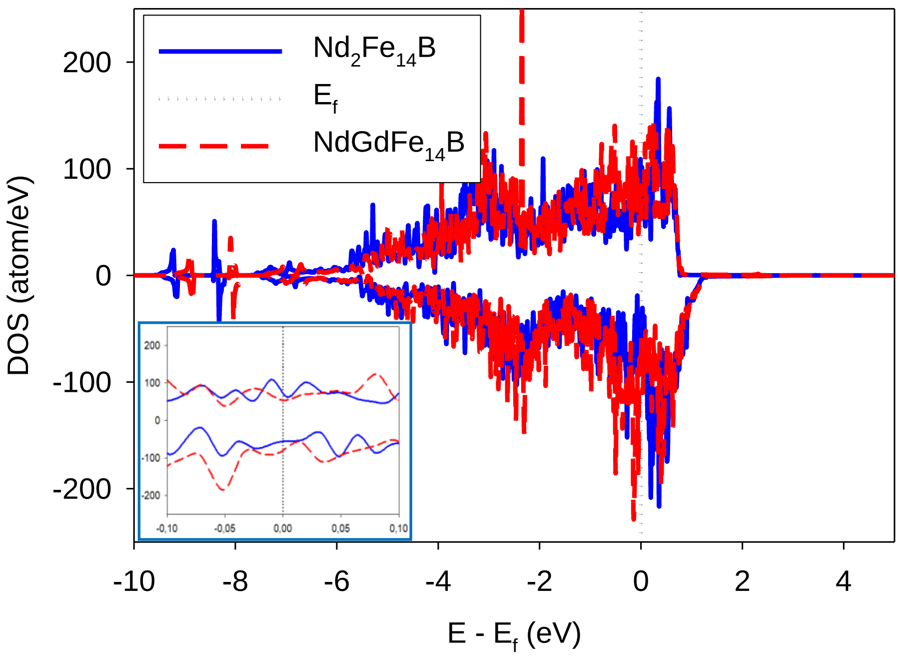


Fig. 2. Total density of states for $Nd_2Fe_{14}B$ and $NdGdFe_{14}B$ permanent magnets.

4 Conclusion

In this study, the structural, mechanical and magnetic properties of $Nd_{2-x}RE_xFe_{14}B$ alloys were investigated using the ab initio density functional theory technique. It was found that the lattice parameters for $Nd_2Fe_{14}B$ structures agree well with the experimental findings and the substitution of Nd by Gd has a slight influence on the lattice parameters. In addition, the heats of formation were found to be negative for both $Nd_2Fe_{14}B$ and $NdGdFe_{14}B$, indicating that the magnets are thermodynamically stable. It is interesting to note that all elastic constants of $Nd_2Fe_{14}B$ magnets meet tetragonal stability criteria. However, the eigenvalues indicate that the magnet is mechanically unstable. Furthermore, the calculated elastic properties for $NdGdFe_{14}B$ magnets meet the tetragonal stability criterion, this relates to the mechanical stability of the material, as the calculated eigenvalues are all positive. The Gd substitution enhances the mechanical stability of $Nd_2Fe_{14}B$ magnets. Replacing Nd with Gd improves the magnetic moment of $Nd_2Fe_{14}B$ from 35.63 B to 59.92 B. Partial substitution of Nd with Gd was found to improve the stability and magnetic properties of $Nd_2Fe_{14}B$ permanent magnets.

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