First-principles study of crystalline Nd–Fe alloys

Yuta Ainai1, Yasutom Tatsuet1,2, Asako Terasawa1, and Yoshihiro Gohda1,2,1

1Department of Materials Science and Engineering, Tokyo Institute of Technology, Yokohama 226-8502, Japan
2University Center for Liberal Arts Education, Meio University, Nago 905-8585, Japan

E-mail: gohda.yab@meio.ac.jp

Received October 23, 2019; revised November 28, 2019; accepted December 16, 2019; published online January 3, 2020

Nd–Fe–B sintered magnets are used in a wide range of industry products such as wind-turbine generators and the electric-vehicle motors, due to their high maximum energy products.1–8 Nevertheless, it is problematic that the coercivity of Nd–Fe–B sintered magnets decreases significantly at high temperatures showing typically only 0.2 T at around 500 K. The key to improving the coercivity of Nd–Fe–B sintered magnets lies not only in the physical property of the main phase, Nd2Fe14B, but also in microstructures, e.g. the chemical composition, the magnetism and the thickness of subphases.9–13 In particular, among the subphases in Nd–Fe–B sintered magnets, grain-boundary (GB) phases consisting mainly of Nd and Fe have impact on achieving the high coercivity. This is attributed to the fact that the electronic states of microstructure interfaces between the main phase and GB phases are responsible for the pinning effect to prevent the magnetization reversal caused by thermal fluctuation.14,15 Recent investigations have demonstrated that doping of metallic elements such as Al, Co, Cu, and Ga greatly modifies the microstructure including the GB phase improving the coercivity.20,21 In this sense, the atomic configurations and the magnetism of the GB phase is of significant importance.

It has been reported the chemical composition, the structure, and the magnetic state of GB phases strongly depend on the surface index of the main phase grains.22–24 In particular, the GB phase facing at the (001) surface of the main phase is crystalline, containing approximately 60–70 at% of Nd and nonmagnetic at room temperature.23 Even though the structure of this crystalline Nd–Fe GB phase has been reported as the fcc type for Ga-added Nd–Fe–B permanent magnets from the nanobeam-electron-diffraction pattern and the fast-Fourier-transform pattern of the high-angle annular dark field images of scanning transmission electron microscope,24 more details of the structure are yet to be identified.

In this letter, we systematically investigate the structure for Nd–Fe alloys as fcc-type GB phases by first-principles calculations. Among the tested crystal structures of Nd0.67Fe0.33, fluorite, half-Heusler, cuprite, fcc, and quasi-sphalerite, the fluorite structure is found to be most stable. Furthermore, we find that the crystal structure of the fluorite NdFe1−x is stable for a wide composition range of approximately 0.6 < x < 1, even though the structural phase transition into another phase is expected for large x. The fluorite crystal structure for 0.67 ≤ x ≤ 1 has negligibly small distortions with the Fe-vacancy formation. For x < 0.67 having structures with the substitution of Nd at the 8c sites by Fe, the distortion of the fluorite structure becomes larger as x becomes smaller. The formation energy for this phase is always positive, which means that the separated pure phases of double hcp (dhcp) Nd and bcc Fe are more stable at the zero temperature. To stabilize the binary fluorite alloys, the entropy of mixing is necessary as the finite-temperature effect. In addition, we examine the effect of a third element for Al, Cu, and Ga with its composition y up to approximately 20 at%. We identify that the ternary Nd–Fe–Ga alloy with the fluorite structure is more stable than the corresponding Nd–Fe binary structure, where Nd–Fe–Ga can even have negative formation energies. In this case, Ga atoms preferably occupy Fe sites.

Our first-principles calculations of Nd0.67Fe1−x and Nd0.67Fe0.33−M (M = Al, Co, Cu, and Ga) alloys are based on density function theory using pseudopotentials and pseudo-atomic-orbital basis functions as implemented in the OpenMX code.25 In all calculations, the Perdew–Burke–Ernzerhof exchange-correlation functional was within the generalized-gradient approximation was used. As basis sets, s2p2d2 configurations were adopted for Nd, Fe, Al, Co, Cu, and Ga with cutoff radii of 8.0, 6.0, 7.0, 6.0, 6.0, and 7.0 Bohr, respectively. Semicore orbitals of 3s and 3p in Fe, Al, Cu, Co, and Ga as well as 5s and 5p in Nd were treated as valence electrons. An open-core pseudopotential was used for Nd atoms, where 4f electrons were treated as spin-polarized core electrons. As for convergence criteria, the maximum force on each atom and the total-energy variation are 10−3 Hartree/Bohr and 10−5 Hartree, respectively. Collinear spin structures neglecting the spin–orbit coupling of the valence electrons are considered with the energy cutoff of 500 Ry and the k-point grid of 5 × 5 × 5 for the 2 × 2 × 2 cubic unit cell. The initial spin configuration has the antiparallel structure between Nd and Fe, while the parallel configuration is set within Fe and Nd, respectively. We checked that the structural stability is hardly affected by magnetic configurations.

The internal coordinates of the cubic structures except the trivial fcc random alloy for Nd0.67Fe0.33 alloys are listed in Table I. Varied compositions in Nd0.67Fe1−x and Nd0.67Fe0.33−M alloys were examined using the 2 × 2 × 2 supercell. The variation of the composition was examined both by the substitution of atoms, e.g. the substitution of Fe by Nd, and by the formation of vacancies, where energetically more stable crystalline structures were adopted. The special quasirandom structure (SQS) method was adopted to

---

**Table I.** Varied compositions in Nd–Fe–B sintered magnets lies not only in the physical property of the main phase, Nd2Fe14B, but also in microstructures, e.g. the chemical composition, the magnetism and the thickness of subphases.9–13 In particular, among the subphases in Nd–Fe–B sintered magnets, grain-boundary (GB) phases consisting mainly of Nd and Fe have impact on achieving the high coercivity. This is attributed to the fact that the electronic states of microstructure interfaces between the main phase and GB phases are responsible for the pinning effect to prevent the magnetization reversal caused by thermal fluctuation.14,15 Recent investigations have demonstrated that doping of metallic elements such as Al, Co, Cu, and Ga greatly modifies the microstructure including the GB phase improving the coercivity.20,21 In this sense, the atomic configurations and the magnetism of the GB phase is of significant importance.

It has been reported the chemical composition, the structure, and the magnetic state of GB phases strongly depend on the surface index of the main phase grains.22–24 In particular, the GB phase facing at the (001) surface of the main phase is crystalline, containing approximately 60–70 at% of Nd and nonmagnetic at room temperature.23 Even though the structure of this crystalline Nd–Fe GB phase has been reported as the fcc type for Ga-added Nd–Fe–B permanent magnets from the nanobeam-electron-diffraction pattern and the fast-Fourier-transform pattern of the high-angle annular dark field images of scanning transmission electron microscope,24 more details of the structure are yet to be identified.

In this letter, we systematically investigate the structure for Nd–Fe alloys as fcc-type GB phases by first-principles calculations. Among the tested crystal structures of Nd0.67Fe0.33, fluorite, half-Heusler, cuprite, fcc, and quasi-sphalerite, the fluorite structure is found to be most stable. Furthermore, we find that the crystal structure of the fluorite NdFe1−x is stable for a wide composition range of approximately 0.6 < x < 1, even though the structural phase transition into another phase is expected for large x. The fluorite crystal structure for 0.67 ≤ x ≤ 1 has negligibly small distortions with the Fe-vacancy formation. For x < 0.67 having structures with the substitution of Nd at the 8c sites by Fe, the distortion of the fluorite structure becomes larger as x becomes smaller. The formation energy for this phase is always positive, which means that the separated pure phases of double hcp (dhcp) Nd and bcc Fe are more stable at the zero temperature. To stabilize the binary fluorite alloys, the entropy of mixing is necessary as the finite-temperature effect. In addition, we examine the effect of a third element for Al, Cu, Co, and Ga with its composition y up to approximately 20 at%. We identify that the ternary Nd–Fe–Ga alloy with the fluorite structure is more stable than the corresponding Nd–Fe binary structure, where Nd–Fe–Ga can even have negative formation energies. In this case, Ga atoms preferably occupy Fe sites.

Our first-principles calculations of Nd0.67Fe1−x and Nd0.67Fe0.33−M (M = Al, Co, Cu, and Ga) alloys are based on density function theory using pseudopotentials and pseudo-atomic-orbital basis functions as implemented in the OpenMX code.25 In all calculations, the Perdew–Burke–Ernzerhof exchange-correlation functional was within the generalized-gradient approximation was used. As basis sets, s2p2d2 configurations were adopted for Nd, Fe, Al, Co, Cu, and Ga with cutoff radii of 8.0, 6.0, 7.0, 6.0, 6.0, and 7.0 Bohr, respectively. Semicore orbitals of 3s and 3p in Fe, Al, Cu, Co, and Ga as well as 5s and 5p in Nd were treated as valence electrons. An open-core pseudopotential was used for Nd atoms, where 4f electrons were treated as spin-polarized core electrons. As for convergence criteria, the maximum force on each atom and the total-energy variation are 10−3 Hartree/Bohr and 10−5 Hartree, respectively. Collinear spin structures neglecting the spin–orbit coupling of the valence electrons are considered with the energy cutoff of 500 Ry and the k-point grid of 5 × 5 × 5 for the 2 × 2 × 2 cubic unit cell. The initial spin configuration has the antiparallel structure between Nd and Fe, while the parallel configuration is set within Fe and Nd, respectively. We checked that the structural stability is hardly affected by magnetic configurations.

The internal coordinates of the cubic structures except the trivial fcc random alloy for Nd0.67Fe0.33 alloys are listed in Table I. Varied compositions in Nd0.67Fe1−x and Nd0.67Fe0.33−M alloys were examined using the 2 × 2 × 2 supercell. The variation of the composition was examined both by the substitution of atoms, e.g. the substitution of Fe by Nd, and by the formation of vacancies, where energetically more stable crystalline structures were adopted. The special quasirandom structure (SQS) method was adopted to

---
Table I. Wyckoff positions for Nd and Fe of Nd–Fe alloys with the composition of Nd$_{0.67}$Fe$_{0.33}$. The number in the labels represents the multiplicity.

| Structure   | Element | Label | x    | y    | z    |
|-------------|---------|-------|------|------|------|
| Cuprite     | Fe      | 2a    | 0.25 | 0.25 | 0.25 |
|             | Nd      | 4b    | 0    | 0    | 0    |
| Fluorite    | Fe      | 4a    | 0    | 0    | 0    |
|             | Nd      | 8c    | 0.25 | 0.25 | 0.25 |
| Half-Heusler| Fe      | 4a    | 0    | 0    | 0    |
|             | Nd      | 4b    | 0.5  | 0.5  | 0.5  |
| Sphalerite  | Fe      | 4c    | 0.25 | 0.25 | 0.25 |
|             | Nd      | 4a    | 0    | 0    | 0    |

determine atomic configurations that are most random within the supercell. For all the examined systems, lattice parameters and atomic positions were relaxed simultaneously. The formation energy $E_{\text{form}}$ for Nd$_{0.67}$Fe$_{1-x}$M$_x$ is evaluated relative to separated single phases with the most stable crystal structures as

$$E_{\text{form}} = E_{\text{Nd,Fe$_{1-x}$M$_x$}} - [\mu_{\text{Nd}} + (1 - x)\mu_{\text{Fe}} + x\mu_{\text{M}}],$$

where $E_{\text{Nd,Fe$_{1-x}$M$_x$}}$ is the total energy of the Nd$_{0.67}$Fe$_{1-x}$M$_x$ alloy per atom and $\mu_{\text{Nd}}$, $\mu_{\text{Fe}}$, and $\mu_{\text{M}}$ are the chemical potentials of dhcp Nd, bcc Fe, and M in the most stable phases, respectively.

First, we discuss the energetic stability of Nd–Fe alloys with the composition of Nd$_{0.67}$Fe$_{0.33}$ for the crystal structures of fluorite, half-Heusler, cuprite, fcc, and quasi-sphalerite. The quasi-sphalerite structure is prepared by forming vacancies for half of the 4c sites of the sphalerite by the SQS method. The four structures except for fcc have the fcc sublattice either with Nd or Fe atoms, while the fcc structure is constructed as the random alloy by using the SQS method. The fluorite, half-Heusler, and cuprite structures are stable, while the fcc and quasi-sphalerite structures are found to be unstable. Figure 1 shows the optimized crystal structures and the corresponding formation energies for Nd$_{0.67}$Fe$_{0.33}$. We have found that all the three structures with this composition keep its initial structure exactly after optimization. Furthermore, it is clearly seen that the fluorite structure is most stable without structural distortions. We argue that the best candidate for the fcc-type GB phase experimentally observed is the fluorite structure, which further support for this argument will be provided in the following discussions. It should be noted that the formation energy for this phase is positive. It means that the separated pure phases of dhcp Nd and bcc Fe are more stable at the zero temperature, while the entropy of mixing can enhance the formation of the fluorite alloys at finite-temperature.

Next, we examined the effect of the composition variation from $x = 0.67$ for the fluorite Nd$_{0.67}$Fe$_{1-x}$ alloys. To increase the composition parameter $x$, vacancies are formed by removing Fe atoms or Fe atoms are substituted with Nd atoms. We identified in this case that the fluorite structure is obtained with the Fe-vacancy formation at the 4a site. Structural distortions of the fluorite crystal structure with increasing $x$ are found to be negligibly small in all the cases up to $x = 1$, e.g. for $x = 0.8$ (Fig. 2). As also seen in Fig. 2, the formation energy increases as $x$ increases from 0.67. Note that the formation energy for $x = 1$ is remarkably high, because it has the simple cubic structure. Thus, the structural phase transition into close-packed structures of the Nd sublattice is expected for large $x$. In the case of decreasing $x$ from $x = 0.67$, we examined possibilities that vacancies are formed by removing Nd atoms and Nd atoms are substituted with Fe atoms. We have found that the substitution of 8c Nd sites by Fe is more stable than the Nd-vacancy formation. In contrast with the case of increasing $x$, the crystal structure becomes gradually distorted as $x$ decreases, where an example can be seen in Fig. 2(b). The fluorite-like structure is found to be kept roughly for $0.6 < x$. Under this lower limit, the alloy cannot keep its crystal structure becoming completely amorphous. This result is consistent with experimental observations, where the composition ratio of Nd in the crystalline GB phase was mainly found in a range of approximately 60–70 at%.

Decreasing in $x$ from 0.67, the formation energy increases, where the slope of the curve in Fig. 2(c) is larger than that in the case of increasing in $x$. Summarizing these two cases, the stability of the crystal structure for the fluorite Nd$_{0.67}$Fe$_{1-x}$ is seen for a wide composition range of approximately $0.6 < x < 1$. For this binary system, the entropy effect is necessary to stabilize the fluorite alloys, because the formation energy for this phase is always positive.

In addition to the entropy effect, a third element might promote the formation of crystalline Nd–Fe alloys. Thus, we examined ternary Nd–Fe–M compounds, where we chose M as Al, Co, Cu, and Ga. In calculating the Nd$_{0.67}$Fe$_{0.33}$–M$_x$ alloys, we adapted a $2 \times 2 \times 2$ supercell with 96 atoms, where Fe 4a sites are replaced with M. The sites occupied by M are chosen by the SQS method. Figure 3 illustrates the
formation energies of the fluorite Nd–Fe alloys (0 ≤ y ≤ 0.21). In all the cases, the formation energy is lower than the case of the binary alloy Nd0.67Fe0.33 with the fluorite structure. Furthermore, the negative formation energies of Nd–Fe–Ga alloys indicate that Ga promotes alloying compared with the other alloying elements. This stabilization by the Ga substitution comes from the interaction between Ga 4p states and Nd 5d states. The Mulliken population analysis revealed the transfer of 0.59 electrons from Nd 5d states to Ga 4p states for y = 0.01. Comparing the four alloying elements, we also found that the increase in the number of p electrons monotonically contributes to the stabilization as shown in Table II.

In summary, the best candidate structure for the fcc-type GB Nd–Fe phase was determined to be the fluorite structure from first-principles. This alloy Nd0.67Fe1–x can keep its crystal structure for a wide range of the composition as 0.6 < x ≤ 1.0 with the minimum formation energy at

**Table II.** Change in the number of p electrons Δnp from the bulk state of the alloying element M for y = 0.01.

| Element | Al   | Co   | Cu   | Ga   |
|---------|------|------|------|------|
| Δnp    | 0.11 | −0.20| 0.02 | 0.59 |

Fig. 2. (Color online) Optimized crystal structures of the fluorite Nd–Fe alloys for (a) Nd0.8Fe0.2 and (b) Nd0.625Fe0.375. (c) The formation energies Eform of the fluorite Nd–Fe alloys.

Fig. 3. (Color online) Formation energies of fluorite Nd0.67Fe0.33–yM_y alloys. The dashed line indicates the formation energy of the binary Nd0.67Fe0.33 alloy with the fluorite structure. For y = 0.17, the composition should be read as Nd2/3Fe1/6M1/6.

In contrast, the cuprite Nd0.67Fe1–x alloys having the fcc sublattice with Nd atoms cannot keep ordered structures when Nd composition ratio deviates from x = 0.67, as shown in Fig. 5. The half-Heusler structure was found to be unstable for the variation of the composition as well. As already mentioned, the quasi-sphalerite and fcc Nd0.67Fe1–x alloys cannot keep ordered structures regardless of the composition, even for Nd0.67Fe0.33 and for Nd0.5Fe0.5, where the quasi-sphalerite corresponds to the pristine sphalerite. Thus, the possibilities of cuprite, half-Heusler, fcc, and sphalerite as the crystalline Nd–Fe alloy can be excluded.

In summary, the best candidate structure for the fcc-type GB Nd–Fe phase was determined to be the fluorite structure from first-principles. This alloy Nd0.67Fe1–x can keep its crystal structure for a wide range of the composition as 0.6 < x ≤ 1.0 with the minimum formation energy at
Analyzing the formation energies of Nd–Fe–M alloys, we conclude that adding Ga to fluorite Nd–Fe alloys can greatly promote alloying of Nd with Fe. Our new findings in this letter will hopefully trigger further understanding of the microstructure of Nd–Fe–B sintered magnets to improve the coercivity.

Acknowledgments
This work was supported in part by MEXT as ESICMM Grant No. 12016013 and as a social and scientific priority issue CDMSI to be tackled by using post-K computer, and KAKENHI Grant No. 17K04978. The calculations were partly carried out by using supercomputers at ISSP, The University of Tokyo, and TSUBAME, Tokyo Institute of Technology as well as the K computer, RIKEN (Project Nos. hp180206 and hp190169).

ORCID iDs
Yuta Ainai https://orcid.org/0000-0003-2741-1179
Yoshihiro Gohda https://orcid.org/0000-0002-6047-027X

1) M. Sagawa, S. Fujimura, N. Togawa, H. Yamamoto, and Y. Matsuura, J. Appl. Phys. 55, 2083 (1984).
2) M. Sagawa, S. Fujimura, H. Yamamoto, Y. Matsuura, and K. Hiraga, IEEE Trans. Magn. MAG-20, 1584 (1984).
3) M. Sagawa, S. Fujimura, H. Yamamoto, Y. Matsuura, and S. Hirosawa, J. Appl. Phys. 57, 4094 (1985).
4) D. Givord, H. S. Li, and R. Perrier de la Bâthie, Solid State Commun. 51, 857 (1984).
5) J. F. Herbst, Rev. Mod. Phys. 63, 819 (1991).
6) J. M. D. Coey, Magnetism and Magnetic Materials (Cambridge University Press, Cambridge, 2010).
7) J. M. D. Coey, Scr. Mater. 67, 524 (2012).
8) Y. Tatetsu, Y. Harashima, T. Miyake, and Y. Gohda, Phys. Rev. Mater. 2, 074410 (2018).
9) S. Hirosawa, J. Magn. Soc. Jpn. 39, 85 (2015).
10) S. Sugimoto, J. Phys. D.: Appl. Phys. 44, 064001 (2011).
11) T. Nakamura et al., Appl. Phys. Lett. 105, 202404 (2014).
12) Y. Tatetsu, S. Tsuneyuki, and Y. Gohda, Materials 4, 388 (2018).
13) A. Terasawa and Y. Gohda, J. Chem. Phys. 149, 154502 (2018).
14) N. Tsuji et al., Acta Mater. 154, 25 (2018).
15) F. Vial, F. Joly, E. Nevalainen, M. Sagawa, K. Hiraga, and K. T. Park, J. Magn. Magn. Mater. 242–245, 1329 (2002).
16) K. Hono and H. Sepehri-Amin, Scr. Mater. 67, 530 (2012).
17) T. T. Sasaki, T. Ohkubo, Y. Takada, T. Sato, A. Kato, Y. Kaneko, and K. Hono, Scr. Mater. 113, 218 (2016).
18) G. C. Hadjipanayis and A. Kim, J. Appl. Phys. 63, 3310 (1988).
19) K. Niitsu et al., J. Alloys Compd. 752, 220 (2018).
20) Y. Tatetsu, S. Tsuneyuki, and Y. Gohda, Phys. Rev. Appl. 6, 064029 (2016).
21) G. Sadullahoghlu, B. Altuncevahir, and O. Addemir, Acta Phys. Pol. 125, 1172 (2014).
22) W. F. Li, T. Ohkubo, T. Akiya, H. Kato, and K. Hono, J. Mater. Res. 24, 413 (2009).
23) T. T. Sasaki, T. Ohkubo, and K. Hono, Acta Mater. 115, 269 (2016).
24) X. D. Xu, T. T. Sasaki, J. N. Li, Z. J. Dong, H. Sepehri-Amin, T. H. Kim, T. Ohkubo, T. Schrefl, and K. Hono, Acta Mater. 156, 146 (2018).
25) T. Ozaki, Phys. Rev. B 77, 155108 (2003).
26) J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
27) A. Zunger, S. H. Wei, L. G. Ferreira, and J. E. Bernard, Phys. Rev. Lett. 65, 353 (1990).