Site preference of dopant elements in Nd$_2$Fe$_{14}$B

Munehisa Matsumoto

Institute for Solid State Physics, University of Tokyo, Kashiwa 277-8581, JAPAN

(Dated: 31 December 2018)

*Ab initio* calculations of formation energy and mixing energy for (Nd,$R$)$_2$(Fe,Co)$_{14}$B ($R$ = rare-earth elements other than Nd) are presented to address the site preference of dopants and the corresponding magnetic properties. Contrasting trends between magnetic calculations and non-magnetic calculations are discussed in conjunction with the nature of localized moments in the metallic ferromagnetism at high temperatures. Implications on the optimal heat treatment temperature to maximize the intrinsic properties are discussed referring to the experimental Curie temperature.

PACS numbers: 75.50.Ww, 75.10.Lp

I. INTRODUCTION

Rare-earth permanent magnets are one of the key materials for sustainable solutions of the energy problem. It takes strong magnetization, accordingly strong coercive force that intrinsically originate in the uni-axial magnetic anisotropy, high Curie temperature, and the structure stability for a magnetic material to be useful enough in practical applications of permanent magnets. Unfortunately we often encounter a trade-off between those prerequisites. The champion magnet fabricated on the basis of Nd$_2$Fe$_{14}$B has been a remarkably successful case where strong magnetization and anisotropy comes with robust structure, but a drawback has been its low Curie temperature that is only half of elemental Fe with the body-centered-cubic structure. Most notably, recent developments along the line of 1:12 materials including NdFe$_{12}$N$_3$ and Sm(Fe,Co)$_{12}$ fabricated on a special substrate to go beyond Nd$_2$Fe$_{14}$B have shown a promising route to stronger magnetization and anisotropy than Nd$_2$Fe$_{14}$B in the typical temperature range 300 K \(\leq T \leq 450\) K for practical usage with the reasonably elevated Curie temperature up to 800 K, but at the sacrifice of bulk structure stability.

In order to resolve such trade-off in ferromagnetic compounds for permanent magnets, we look into the issue of structure stability monitoring the trend of ferromagnetism in doped Nd$_2$Fe$_{14}$B to inspect the possibility for gaining both. One of the most popular dopant elements is Co following the celebrated Slater-Pauling curve as the magnetic anisotropy, high Curie temperature, and the robustness of localized magnetic moments in the target materials.

In the next section we describe our *ab initio* methods combining two codes, namely, Korringa-Kohn-Rostoker (KKR) Green’s function method on the basis of coherent potential approximation (CPA) as implemented in AkaiKKR[12] and *ab initio* structure optimization as implemented in another open-source package OpenMX[10]. Main results on doped Nd$_2$Fe$_{14}$B are given in Sec. III and their implications on the nature of localized magnetic moments and heat treatment temperature are discussed in Sec. IV. Final section is devoted for conclusions and outlook.

II. METHODS AND TARGET MATERIALS

A. *Ab initio* calculations for formation energy

We start with looking at the structure stability of R$_2$T$_{14}$B where R=Nd, Sm, Dy, and Y and T=Fe or Co with calculating the formation energy \(\Delta E_f\) which is defined as follows:

\[
\Delta E_f[R_2T_{14}B] = E_{tot}[R_2T_{14}B] - 2E_{tot}[R] - 14E_{tot}[T] - E_{tot}[B] \quad (1)
\]

Here \(E_{tot}[M]\) is the calculated energy for a given material M yielded from *ab initio* structure optimization utilizing OpenMX within the standard pseudopotential data provided therein[11]. Results from magnetically polarized and non-magnetic calculations are used for discussions without taking into account the relativistic effects. Even though spin-orbit interaction is crucial in getting MCA, the non-relativistic set up should be good enough to address the structure stability and ferromagnetism considering their dominating energy scales. We
take GGA-PBE exchange correlation to describe the electronic structure dominated by ferromagnetic 3d-electrons most correctly. For rare-earth elements we use pseudopotentials with open-core approximation. The basis set we took was Nd8.0_0C-s2p2d2f1, Sm8.0_0C-s2p2d2f1, Dy8.0_0C-s2p2d2f1, Y8.0-s3p2d2f1, Fe6.0S-s2p2d1, Co6.0S-s2p2d2f1, and B7.0-s3p3d2. There is some subtlety with the partial core correction (PCC) in the open-core approximation which is set by the following entry in the input to OpenMX:

```plaintext
<scf.pcc.opencore
 Nd 1
 Fe 0
 B 0
scf.pcc.opencore>
```

in case of Nd2Fe14B. Analogous set up is basically recycled for all calculations involving rare-earth elements in the present work. However, a problem in convergence can happen with Sm2Co14B with this particular setup which can be worked around if the calculation is done without PCC. We do both of (a) open-core approximation with PCC and (b) without PCC. Results from the setup in a) is basically taken whenever available.

For the calculations of R2T14B the energy cutoff is set to be 500 Ry and the number of k points was 64. Number of k points was sometimes increased up to 216 to ensure that calculated results with k points being 64 are already converging. The above choice of the computational setup seems to give a reasonable precision in an acceptable computational cost after monitoring the convergence with respect to the richness of the basis set, energy cutoff, and the number of k points. The experimental structure for Nd2Fe14B found in Ref. 3 is taken as the starting structure and ab initio structure optimization has been done for R2T14B.

Energy of the reference elements is calculated in the analogous way, taking the experimental structure of dhcp-Nd, trigonal Sm, dhcp-Dy, hcp-Y bcc-Fe, hcp-Co and α-B as the starting structure. The number of k points for these reference systems is taken to be 512 and the rest of the set up is the same as is done for R2T14B. Unfortunately the structure of the elemental boron comes with polymorphism that is not yet well controlled from first principles. The ground-state energy of Boron may not have been well fixed. Thus the absolute values of the calculated formation energy for R2T14B need be taken with some reservation while the relative trends between materials should be able to be robustly addressed. Thus calculated trend of the formation energy is shown in Fig. 1. The details are described in Sec. IIIA.

B. Ab initio calculations for mixing energy

Calculated formation energy fixes the structure stability at the stoichiometric limits and the structure stability of off-stoichiometric compounds

\[
\Delta E_{\text{mix}}[\text{(Nd1}_x\text{R}_x)_2\text{Fe}\text{(Co)}_{y}_y]_{14}\text{B} = \text{E}_{\text{tot}}[(\text{Nd1}_x\text{R}_x)_2\text{Fe}\text{(Co)}_{y}_y]_{14}\text{B} - (1-x)\text{E}_{\text{tot}}[\text{Nd}_2\text{Fe}_{14}\text{B}] - x\text{E}_{\text{tot}}[\text{R}_2\text{Fe}_{14}\text{B}]
\] (2)

and

\[
\Delta E_{\text{mix}}[\text{Nd}_2\text{(Fe}_{1-x}\text{Co})_{y}]_{14}\text{B} = \text{E}_{\text{tot}}[\text{Nd}_2\text{(Fe}_{1-x}\text{Co})_{y}]_{14}\text{B} - (1-y)\text{E}_{\text{tot}}[\text{Nd}_2\text{Fe}_{14}\text{B}] - y\text{E}_{\text{tot}}[\text{Nd}_2\text{Co}_{14}\text{B}].
\] (3)

The trend of calculated mixing energy can point to the relative site preference of dopants. Whenever needed, the formation energy of (Nd,R)2(Fe,Co)14B can be restored with the following relation

\[
\Delta E_{\text{tot}}[(\text{Nd1}_x\text{R}_x)_2\text{Fe}\text{(Co)}_{y}_y]_{14}\text{B} - 2 \{ (1-x)\text{E}_{\text{tot}}[\text{dhcp-Nd}] + x\text{E}_{\text{tot}}[\text{R}] \} - 14 \{ (1-y)\text{E}_{\text{tot}}[\text{bcc-Fe}] + 0.5y\text{E}_{\text{tot}}[\text{hcp-Co}] \}
\] (4)

Off-stoichiometric compounds can be continuously interpolated between stoichiometric limits via KKR-CPA as implemented in AkaiKKR. Open-core approximation is also taken here for rare-earth elements and the angular momentum cutoff is set to be \(l_{\text{max}} = 2\) which should be sufficient in describing 3d-electron states of Fe/Co and 5d-electron states coming from rare-earth elements. Also with AkaiKKR we collect the data on the basis of non-relativistic calculations. Within OpenMX calculations, discrete substitution of host atoms is inspected on top of which AkaiKKR results are overlapped to ensure the consistency between two codes and the exploration range can be extended continuously. Mixing energy can be exploited with KKR-CPA even with systematic corrections in calculated total energy on the basis of KKR-CPA because the corrections in the terms on the right-hand side of analogous relations to Eqs. 2 and 3 are cancelling.

![FIG. 1. (Color online) Calculated formation energy for pristine R2T14B (T=Fe,Co).](image-url)
out. The advantage of OpenMX results is that formation energy of the stoichiometric compounds and discretely substituted compounds can both be directly addressed while fractional substitution can be more easily addressed via AkaiKKR. We combine these two approaches to cover relevant dopants for possible improvement of magnetic properties of Nd$_2$Fe$_{14}$B. Namely, all magnetic rare-earth elements which reasonably converged on the 2:14:1 structure (Pr, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Eu) are partially replaced Nd and Co to partially replace Fe. Convergence with a fictitious Eu$_2$Fe$_{14}$B seems to involve some problems and the task of answering them is split for other study.

Effects of non-magnetic light rare earth elements, La and Ce, explicitly involve 4f-electrons in the valence state. This is qualitatively different from what we deal with in the present work where 4f electrons are so well localized that energetics can be safely addressed only with 3d-electrons from Fe, 5d-electrons from Nd, and the respective substitutes. Energetics issue involving 4f-electrons in (La,Ce)-based compounds is addressed in a separate work.

### III. RESULTS

Calculated formation energy of R$_2$T$_4$B where R=Nd, Sm, Dy, and Y and T=Fe or Co employing OpenMX is inspected in Sec. III A. In Sec. III B we present results for the mixing energy in Nd$_2$(Fe,Co)$_{14}$B obtained with OpenMX to elucidate the 3d-electron magnetism and energetics. Contrasting outcome from magnetic and non-magnetic calculations is discussed referring to past experimental claims. Then in Sec III C we discuss 5d-electron physics in (Nd,R)$_2$Fe$_{14}$B where R is magnetic and trivalent rare earth elements other than Nd based on both of OpenMX and AkaiKKR results for the mixing energy. Finally in Sec III D calculated formation energy of (Nd,Dy)$_2$(Fe,Co)$_{14}$B as obtained with OpenMX is presented.

#### A. Formation energy of stoichiometric compounds

Calculated energy of the reference elemental materials and the target compounds R$_2$T$_4$B [R=Nd, Sm, Dy, Y and T=Fe,Co] on the basis of OpenMX pseudopotentials and the choice of basis as described in Sec. II is summarized in Tables I and II respectively. The label (a) and (b) for materials involving rare-earth elements denotes explicit incorporation of partial charge correction in open-core approximation has been included (a) or not included (b), respectively, as described in Sec. II A.

Calculated trend of the formation energy is tabulated at the rightmost column in Table I and plotted in Fig. I with the results basically from setup (a). Only for Sm$_2$Co$_{14}$B the results with setup (b) is plotted. Even though the structure stability of Nd$_2$Fe$_{14}$B is well established experimentally, the calculated trend including Nd$_2$Fe$_{14}$B is instructive in that the qualification of Nd$_2$Fe$_{14}$B is revealed in the middle of the overall trend showing that Co-based compounds and heavy-rare-earth compounds are more stable energetically. The trend with respect to rare earth should be attributed to lanthanide contraction while the inter-relation between Fe-based series and Co-based series reflect the competing trend between ferromagnetism and structure stability. The magnetovolume effect expands the lattice and the intrinsic magnetization should be well below a limit that the given crystal structure can hold. In this regard the particular structure of R$_2$T$_4$B is excellent.

Calculated formation energy for Nd$_2$Fe$_{14}$B amounting to $-0.7 \sim -0.8$ [eV/(formula unit)] is in reasonable

| material          | $N_{\text{atom}}$ | $E_{\text{tot}}$ [Hartree] | $E_f$ [eV/(f.u.)] |
|-------------------|-------------------|-----------------------------|-----------------|
| Nd$_2$Fe$_{14}$B  | 36                | -105.056                    | -0.77           |
| bcc-Fe            | 1                 | -89.5730                    | -0.65           |
| dhcp-Co           | 2                 | -214.260                    | -1.10           |
| dhcp-Nd (a)       | 4                 | -180.187                    | -1.36           |
| dhcp-Nd (b)       | 4                 | -173.765                    | -1.03           |
| dhcp-Dy (a)       | 4                 | -197.010                    | -0.86           |
| dhcp-Dy (b)       | 4                 | -190.898                    | -1.48           |
|dhcp-Y            | 2                 | -78.7988                    | -2.77           |

| material          | $E_{\text{tot}}$ [Hartree/(cell)] | $E_f$ [eV/(f.u.)] |
|-------------------|----------------------------------|-----------------|
| Nd$_2$Co$_{14}$B  | -6371.612                       | -1.94           |
| Sm$_2$Co$_{14}$B  | -6358.752                       | -1.83           |
| Sm$_2$Co$_{14}$B  | not converging                  | N/A             |
| Dy$_2$Co$_{14}$B  | -6405.562                       | -4.01           |
| Dy$_2$Co$_{14}$B  | not converging                  | N/A             |
| Y$_2$Co$_{14}$B   | -6326.555                       | -2.77           |

TABLE I. Calculated energy with OpenMX on the basis of the standard pseudopotentials and the choice of basis sets as described in Sec. II for each elemental reference material. $N_{\text{atom}}$ is the number of atoms in the unit cell. For all of the data in this table, the number of k points is 512.
agreement with the previous claim\cite{13} $-101$ [kJ/mol] = $-1.05$ [eV/(formula unit)]. As is seen in Table \ref{table1}, the computational setup a) or b) for the open-core approximation in OpenMX can shift the formation energy by 0.1 [eV/(formula unit)]. Even though the ambiguity in the order of $O(0.1)$ [eV/(formula unit)] remains in the absolute value of the formation energy, the relative trends between compounds and position of dopants should be robustly elucidated from first principles as long as we coherently apply the setup of the calculations to all of the data used for discussions.

**B. Nd$_2$(Fe,Co)$_{14}$B**

Calculated mixing energy for Nd$_2$Fe$_{14}$B and Co in Nd$_2$(Fe$_{55}$/56Co$_{44}$/56)$_{14}$B is shown in Fig. 2. We note that the ambiguity in the absolute value of calculated formation energy is cancelled out in the mixing energy. Discrete substitution of Fe by Co is done in OpenMX and one Co atom is put in one of the 56 possible Fe atomic sites in the unit cell. Magnetic calculations show that Fe(8j1) site is most favorable for Co to substitute and Fe(8j2) site is most unfavorable, which is in remarkable agreement with the past experimental claim measured by M"ossbauer effect\cite{15}. The same M"ossbauer measurement\cite{15} claimed less population in Fe(16k1) and some preference in Fe(16k2) which is again in good agreement with the trend in calculated mixing energy on the basis of ferromagnetic ground states while the expected preference of Fe(4c) and avoidance of Fe(4e) seems to be at variance with the experimentally observed slight avoidance on Fe(4c) and preference for Fe(4e)\cite{15}.

Corresponding trends of magnetization is shown in Fig. 3. On top of open-core approximation results, the contribution of two Fe atoms in the formula unit has been restored with $g_J \sqrt{J(J+1)}$ for one Nd atom, where $J = 9/2$ and $g_J = 8/11$. It is noted that all possible ways to dope Co into Nd$_2$Fe$_{14}$B lead to inferior magnetization.

This is not actually recovered by the volume effects even if the lattice shrinks upon doping of Co. While some doping of Co lead to slightly enhanced structure stability in Fig. 2, ferromagnetism is sacrificed here.

The calculated trend in the magnetization of Co-doped Nd$_2$Fe$_{14}$B is at variance with the Slater-Pauling curve. It may well be the case that Co-induced elevation of Curie temperature can render the room temperature magnetization as a function of Co concentration resembling the Slater-Pauling curve as was reported in some of the past experimental measurements\cite{19}. In the ground state, we conclude that no Slater-Pauling curve would be observed in Nd$_2$(Fe,Co)$_{14}$B with the observed trend in Fig. 3 and also based on CPA data obtained with AkaiKKR. More systematic data for the appearance or the disappearance of Slater-Pauling curve in 4f-3d intermetallics will be presented elsewhere\cite{20}.

**C. (Nd,R)$_2$Fe$_{14}$B [R$\neq$Nd]**

Calculated mixing energy for (Nd,R)$_2$Fe$_{14}$B with R=Sm, Dy, and Y with OpenMX is shown in Fig. 4. Discrete replacement is done in such a way that just one dopant rare earth atom replaces one of the eight Nd atoms in the host Nd$_2$Fe$_{14}$B and \textit{ab initio} structure optimization has been done with OpenMX to yield the energy on the basis of OpenMX pseudopotentials with the setup a) and the choice of basis as described in Sec. II. Preference of dopant Dy for Nd(4f) and calculated mixing energy is in agreement with the results in the previous work\cite{17}. The same thing is done on the basis of continuous replacements following KKR-CPA for which the results obtained with AkaiKKR are shown in Fig. 5 which is a plain extension of what was done for Dy in Ref. 17 toward other rare-earth elements. In the latter 10% of the host Nd atoms are replaced either selectively Nd(4f)/Nd(4g) sublattice or uniformly on a fixed lattice of Nd$_2$Fe$_{14}$B that is known from past experiment.\cite{19}.
The results for R=Sm and Dy look reasonably consistent between OpenMX and AkaiKKR considering the similar replacement ratio 1/8 in the former and 10% in the latter, and also the expected minor effects of lattice variation in the small concentration range of dopants. With AkaiKKR we have basically covered all relevant rare-earth elements and see that except for Pr all dopant rare earth prefers Nd(4f) site. Here we have verified that the difference between magnetic and non-magnetic calculations is minor.

D. (Nd,Dy)2(Fe,Co)14B

Calculated formation energy for (Dy,Co)-doped Nd2Fe14B is shown in Fig. 6. All of the data is taken with setup a) as described in Sec. II.A. Discrete doping OpenMX is done with 1/8 of Nd and 1/56 of Fe being replaced by Dy and Co, respectively. For the convenience of comparison, calculated formation energy from the magnetic calculations as presented in Fig. 2 is included here. The overall trend in Co-position dependence of the calculated formation energy in (Nd,Dy)2(Fe,Co)14B is basically just a shift from what is observed for Nd2(Fe,Co)14B.

We note that presence of Co would affect the site distribution ratio of Dy over Nd(4f) and Nd(4g). Because the energetics in the site preference of Co dominate over the energetics of Dy by a factor of two or three, the seemingly unfavorable situation in Fig. 4 where Dy resides in Nd(4g) site can be less unlikely when Co sufficiently populates Fe(8j1) site.

IV. DISCUSSIONS

A. Localized magnetic moments at high temperatures

We have seen that the results from magnetic and non-magnetic calculations for Co-doped Nd2Fe14B show contrasting trends in Fig. 2. Even stronger contrast is actually seen for mixing energy calculations for Fe-doped SmCo5 with the simpler crystal structure. Calculated
mixing energy for Sm(Co,Fe)₅ is shown in Fig. 7. SmCo₅ makes the cell boundary phase in Sm-Co based magnet which was the champion magnet in 1970’s and is still of practical importance for special-purpose permanent magnet used under extreme conditions. The data is collected with OpenMX where we discretely replaced one Co atom by a dopant Fe atom. There are two sublattices, Co(2c) and Co(3g), and site preference of dopant Fe points to opposite site, namely, magnetic calculations show Fe prefers Co(2c) while according to non-magnetic calculations Fe prefers Co(3g) site. Result of this non-magnetic calculation is consistent with the past calculation. Considering the high Curie temperature of SmCo₅ at 1000 K that can even be higher than temperatures in sample fabrication processes, it looks likely for SmCo₅ to sustain the magnetic nature through the heat treatment processes. On the other hand the low Curie temperature of Nd₂Fe₁₄B could mean that a high-temperature sample fabrication involving Co would be more consistent with the results of non-magnetic calculations in Fig. 2.

The contrast is seen here when some experiments on Nd₂(Fe,Co)₁₄B show remarkable agreement with our magnetic calculations for the preference of Co among the Fe sublattices that dominate the magnetization. Even with the low Curie temperature, high-temperature processes for the sample fabrication preserves the message of magnetic electronic state presumably due to the robustness of localized magnetic moments in Nd₂Fe₁₄B. On the other hand, experimentally found trends for the site preference of Fe and Co in 1:5 materials seem to point to the possibility that Fe prefers Co(3g) site, being consistent rather with the above data from non-magnetic calculations. This presumably reflects the fragility of localized magnetic moments at high temperatures in Co-based 1:5 materials. Low (high) Curie temperature comes from relatively weak (strong) exchange couplings among the robust (fragile) localized magnetic moments in Nd₂Fe₁₄B (SmCo₅) at high temperatures, respectively. It seems that robustness of localized magnetic moments and strength of exchange couplings are traded off. *Ab initio* quantification of this scenario on the basis of local moment disorder (LMD) picture for finite-temperature magnetism is desired.

### V. CONCLUSIONS AND OUTLOOK

We have presented *ab initio* results of the formation energy and mixing energy for doped Nd₂Fe₁₄B. Revealed trends in the site preference compared to experimental observation point to the validity of localized magnetic moment picture for Nd₂Fe₁₄B at high temperatures while fragile nature in the localized moments in SmCo₅ at high temperatures seems to have been indicated. This may be in contrast to the trends in the robustness of localized magnetic moments in the ground state and extra care must be taken in describing the finite-temperature magnetism. Various trade-off situations have been elucidated between structure stability and magnetization, or between high Curie temperature and robustness in localized magnetic moments. At the moment the best we can do is to identify a good compromise and we have provided *ab initio* data that can be of potential use for that.

Referring to the outcome of magnetic and non-magnetic calculations, the heat-treatment temperature in the sample fabrication process compared to the intrinsic Curie temperature can tell which site preference would be realized at least energetically. Two extreme cases, so to say high-temperature limit and low-temperature limit, have been inspected in the present study while the truth for finite-temperature magnetism and structure stability lies somewhere in between - *ab initio* studies based on the LMD picture for finite-temperature magnetism of...
Fe-based ferromagnets\textsuperscript{11,12} would be desirable here.

ACKNOWLEDGMENTS

MM is supported by Toyota Motor Corporation. Helpful comments given by T. Ishikawa concerning the practical precision of calculated formation energy and useful discussions with M. Morishita, T. Abe, H. Akai, S. Doi, A. Marmodoro, M. Hoffmann, A. Ernst, C. E. Patrick, and J. B. Staunton in related projects are gratefully acknowledged. MM benefited from interactions with Y. Harashima, T. Miyake, and T. Ozaki for \textit{ab initio} calculations employing OpenMX. The present work was partly supported by the Elements Strategy Initiative Project under the auspice of Ministry of Education, Culture, Sports, Science and Technology.

\textsuperscript{1}M. Sagawa, S. Fujimura, N. Togawa, H. Yamamoto, and Y. Matsura, J. Appl. Phys. \textbf{55}, 2083 (1984).
\textsuperscript{2}J. J. Croat, J. F. Herbst, R. W. Lee, and F. E. Pinkerton, J. Appl. Phys. \textbf{55}, 2078 (1984).
\textsuperscript{3}For a review, see J. F. Herbst, Rev. Mod. Phys. \textbf{63}, 819 (1991).
\textsuperscript{4}T. Miyake, K. Terakura, Y. Harashima, H. Kino, S. Ishibashi, J. Phys. Soc. Jpn. \textbf{83}, 043702 (2014).
\textsuperscript{5}Y. Hirayama, Y. K. Takahashi, S. Hirosawa, and K. Hono, Scr. Mater. \textbf{95}, 70 (2015).
\textsuperscript{6}For a review, see Y. Hirayama, T. Miyake, K. Hono, JOM \textbf{67}, 1344 (2015).
\textsuperscript{7}Y. Hirayama, Y. K. Takahashi, S. Hirosawa, and K. Hono, Scr. Mater. \textbf{138}, 62 (2017).
\textsuperscript{8}K. Hono and H. Sepehri-Amin, Scr. Mater. \textbf{67}, 530 (2012).
\textsuperscript{9}\url{http://kkr.issp.u-tokyo.ac.jp}
\textsuperscript{10}\url{http://www.openmx-square.org}
\textsuperscript{11}\url{http://www.jaist.ac.jp/~t-ozaki/vps_pao2013/}
\textsuperscript{12}The experimental crystal structure is taken from online database MatNavi\url{[https://mits.nims.go.jp/]} provided by National Institute for Materials Science.
\textsuperscript{13}J. F. Herbst and L. G. Hector Jr., J. Alloys Compds. \textbf{693}, 238 (2017).
\textsuperscript{14}T. Ogitsu, F. Gygi, J. Reed, Y. Motome, E. Schweger and G. Galli, J. Am. Chem. Soc., \textbf{131} 1903 (2009) and references therein.
\textsuperscript{15}R. Zeller, J. Phys. Condens. Matter \textbf{25}, 105505 (2013).
\textsuperscript{16}MM, M. Ito, \textit{et al.}, in preparation.
\textsuperscript{17}K. Saito, S. Doi, K. Ono, J. Alloys Compds. \textbf{721}, 476 (2017).
\textsuperscript{18}L. X. Liao, Z. Alzouian, and D. H. Ryan, Phys. Rev. B \textbf{47}, 11230 (1993)
\textsuperscript{19}Y. Fukuda, A. Fujita, and M. Shimotomai, J. Alloys Compds. \textbf{193}, 256 (1993).
\textsuperscript{20}MM, S. Doi, \textit{et al.}, in preparation.
\textsuperscript{21}K. Uebayashi, K. Terao, and H. Yamada, J. Alloys Compds. \textbf{346}, 47 (2002).
\textsuperscript{22}MM and H. Akai, preprint [arXiv:1812.04842].
\textsuperscript{23}T. Oguchi, K. Terakura, and N. Hamada, J. Phys. F \textbf{13}, 145 (1983).
\textsuperscript{24}A. J. Pindor, J. Staunton, G. M. Stocks, and H. Winter, J. Phys. F: Met. Phys. \textbf{13}, 979 (1983).
\textsuperscript{25}B. L. Gyorffy, A. J. Pindor, J. Staunton, G. M. Stocks, and H. Winter, J. Phys. F: Met. Phys. \textbf{15}, 1337 (1985).
\textsuperscript{26}J. Staunton, B. L. Gyorffy, A. J. Pindor, G. M. Stocks, and H. Winter, J. Phys. F: Met. Phys. \textbf{15}, 1387 (1985).
\textsuperscript{27}J. Staunton, B. L. Gyorffy, G. M. Stocks, and J. Wadsworth, J. Phys. F: Met. Phys. \textbf{16}, 1761 (1986).
\textsuperscript{28}A. M. Gabay, P. Larson, I. I. Mazin, and G. C. Hadijapanayis, J. Phys. D: Appl. Phys. \textbf{38}, 1337 (2005).
\textsuperscript{29}H. Sepehri-Amin, J. Thielsch, J. Fischbacher, T. Ohkubo, T. Schreff, O. Gutfliesch, K. Hono, Acta Materialia \textbf{126}, 1 (2017).
\textsuperscript{30}C. E. Patrick, MM, J. B. Staunton, submitted to JMMM.