Effect of $R$-site substitution and pressure on stability of $RFe_{12}$: A first-principles study

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We theoretically study structural stability of $RFe_{12}$ with the ThMn$_{12}$ structure ($R$: rare-earth elements, La, Pr, Nd, Sm, Gd, Dy, Ho, Er, Tm, Lu, Y, Sc and group IV elements, Zr, Hf) based on density functional theory. The formation energy has strong correlation with the atomic radius of $R$. The formation energy relative to the simple substances decreases as the atomic radius decreases except $R = \text{Sc and Hf}$, while the formation energy relative to $R_2Fe_{17}$ and bcc Fe has a minimum for $R = \text{Dy}$. The present result is consistent with the recent experimental reports that partial substitution of Zr at $R$ sites stabilizes the $RFe_{12}$-type compounds with $R = \text{Nd or Sm}$. Our result also suggests that partial substitution of Y for Nd or Sm is a possible way to enhance the stability of the ThMn$_{12}$ structure. Under hydrostatic pressure, the formation enthalpy decreases up to $\approx 6 \, \text{GPa}$, then turns to increase at higher pressures.

I. INTRODUCTION

Saturation magnetization and magnetocrystalline anisotropy are key quantities that define performance of a magnet compound. High content of iron is considered preferable for the former quantity, while rare-earth elements are used as a source of the latter in many cases. From this viewpoint, $RFe_{12}$-type compounds ($R$: a rare-earth element) with the ThMn$_{12}$ structure have been studied as promising magnet compounds for a long time. $RFe_{12}$ contains higher atomic percentage of Fe (92 at.%) than other magnet compounds, e.g., Nd$_2$Fe$_{14}$B (82 at.%) and $R_2Fe_{17}$ (89 at.%). A quantitative prediction was presented by a theoretical work for NdFe$_{12}$N then, confirmed by an experimental realization of NdFe$_{12}$N by epitaxial growth. Here, N is introduced to enhance the magnetic properties and effect of other typical elements are also theoretically studied to improve the magnetic properties.

One issue is that $RFe_{12}$ are considered to be thermodynamically unstable, and partial substitution for Fe atoms is essential for stabilization of a bulk system with the ThMn$_{12}$ structure. In the absence of stabilizing elements, the $R_2Fe_{17}$ phases are typically generated instead of $RFe_{12}$. The Ti element is a typical stabilizing element. SmFe$_{11}$Ti$_{14}$ and NdFe$_{11}$Ti$_{22}$ were synthesized around 1990. A disadvantage of the introduction of stabilizing elements is significant reduction of the saturation magnetization. As a matter of fact, both SmFe$_{11}$Ti and NdFe$_{11}$TiN are inferior in magnetization to Nd$_2$Fe$_{14}$B (e.g., summarized in Table 1 of Ref. [15]).

In order to save the reduction of the magnetization, search for another stabilizing element has been conducted. Stabilization by substituting Fe with several elements (V, Cr, Mn, Mo, W, Al, Si) are reported so far, but the reduction of the magnetization is still large. It is theoretically suggested that Co can stabilize the ThMn$_{12}$ structure keeping a large magnetic moment. Though high magnetization in Sm(Fe,Co)$_{12}$ films has been experimentally reported recently, the thermodynamic stabilization by doping Co is yet to be confirmed.

Recently, (Nd,Zr)(Fe,Co)$_{11.5}$Ti$_{0.5}$N$_a$ and (Sm,Zr)(Fe,Co)$_{11.5}$Ti$_{0.5}$ were synthesized by the strip casting method, which is more practical in industrial applications than the epitaxial growth. Although these compounds contain smaller amount of Ti than previously synthesized $RFe_{12}$-type compounds without Zr, the ThMn$_{12}$ structure is realized. It suggests that partial occupation of Zr at the $R$ sites contributes to the stabilization of the ThMn$_{12}$ structure. Therefore, substitution of $R$ (not Fe sites) is another possible route for stabilizing $RFe_{12}$-type compounds.

In the present work, we theoretically examine a series of $R$-elements—$R = \text{La, Pr, Sm, Gd, Dy, Ho, Er, Tm, Lu, Y, Sc, Zr, Hf}$—as possible stabilizing elements that occupy the rare-earth sites in $RFe_{12}$. We calculate the formation energy of $RFe_{12}$ relative to (i) the simple substances, and (ii) $R_2Fe_{17}$ and the bcc Fe based on density functional theory, and analyze the $R$ dependence. The obtained result is discussed in connection with the experiments on partial substitution of Zr for $R = \text{Nd or Sm}$. We then study effect of hydrostatic pressure as a possible method for stabilizing $RFe_{12}$. The paper is organized as follows. The computational methods are described in Sec. II. Calculated formation energy of $RFe_{12}$ and effect of hydrostatic pressure are presented in Sec. III. The paper is concluded in Sec. IV.

II. CALCULATION METHODS

We perform first-principles calculation by using QMAS (Quantum MAterials Simulator), which is based
on density functional theory and the projector augmented-wave method. We use the Perdew-Burke-Ernzerhof (PBE) formula in the generalized gradient approximation for the exchange-correlation energy functional. The 4f electrons of Pr, Nd, Sm, Gd, Dy, Ho, Er, Tm atoms are treated as spin-polarized open core states and those of Lu atom is treated as core states. The number of occupied 4f states is fixed to 2(Pr), 3(Nd), 5(Sm), 7(Gd), 9(Dy), 10(Ho), 11(Er), 12(Tm), 14(Lu). The electron configuration is determined by Hund’s first rule. For light rare-earth elements (from Pr to Gd), all 4f electrons are assumed to be in minority spin states. For heavy rare-earth elements (from Dy to Tm), the minority spin states of 4f orbitals are fully occupied by seven electrons and the other electrons are in majority spin states. Note that the local spin moment at R is antiparallel to the total spin moment. The spin-orbit coupling is not included in the self-consistent calculation.

We study RFe12 with the ThMn12 structure for R = La, Pr, Nd, Sm, Gd, Dy, Ho, Er, Tm, Lu, Y, Sc—rare-earth elements—and R = Zr, Hf—group IV elements. Preferential sites for the group IV elements are discussed in Appendix A. As reference systems, R2Fe17 with the Th2Zn17 structure, and R2Fe17 with the Th2Ni17 structure, and the simple substances of R and Fe are studied. For Fe, the bcc structure is assumed; for R = La, Pr, Nd, Sm, the dhcp structure is assumed; for R = Gd, Dy, Ho, Er, Tm, Lu, Y, Sc, Zr, Hf, the hcp structure is assumed. The structures of RFe12, R2Fe17 and the simple substances are computationally optimized. The calculated lattice constants and the inner coordinates of RFe12 and R2Fe17 are shown in Sec. SA of the Supplemental Material. From the obtained structures of the simple substances, we deduce the atomic radii (rFecalc and rFe) of the elements: a half of the shortest bond lengths are used as the atomic radii. Those values are tabulated in Sec. SB of the Supplemental Material.

III. RESULTS AND DISCUSSION

We first show values of the energy for forming RFe12 from the simple substances R and Fe. Let us denote the formation energy of a substance X by a chemical reaction $X' + X'' \rightarrow X$ by $\Delta E|_{X' + X'' \rightarrow X}$. Figure 1 shows values of $\Delta E|_{RFe12 \rightarrow R + 12Fe}$ as a function of rFe. This energy is calculated by

$$\Delta E|_{RFe12 \rightarrow R + 12Fe} \equiv E[RFe12] - (E[R] + 12E[Fe]),$$

where $E[\cdot]$ denotes the total energy of the system in the bracket per formula unit. There is a trend toward decrease of the formation energy as the calculated atomic radii (rFecalc) decreases. When rFecalc is small, however, this trend does not hold. The value for Sc is exceptionally high. The value for Hf is slightly higher than that for Zr, although Hf has smaller rFecalc than Zr.

Considering the experimental indication that the R2Fe17 phase is a competing phase, we also calculate the formation energy of RFe12 relative to R2Fe17 and bcc Fe, defined by

$$\Delta E|_{RFe12 \rightarrow R2Fe17 + \frac{7}{2}Fe}$$

defined as Eq. (2) for R = La, Pr, Nd, Sm, Gd, Dy, Ho, Er, Tm, Lu, Y, Sc, Zr, Hf as a function of the atomic radius rFe. The formation energy against R2Fe17 with the (rhombohedral) Th2Zn17 structure and those with the (hexagonal) Th2Ni17 structure are shown.
ues of $\Delta E \mid_{RFe_{12}+\frac{1}{2}R_{2}Fe_{17}+\frac{3}{2}Fe}$ for the two cases. The qualitative behavior is insensitive to the choice of the structures. As $r_{R_{Fe_{12}}}^{calc}$ decreases down to $\sim 1.75 \text{Å}$, $\Delta E \mid_{RFe_{12}+\frac{1}{2}R_{2}Fe_{17}+\frac{3}{2}Fe}$ decreases. It has a minimum for $R = \text{Dy}$, and increase as $r_{R_{Fe_{12}}}^{calc}$ decreases further, which is in sharp contrast with the behavior of $\Delta E \mid_{RFe_{12}+R_{2}Fe_{17}+2Fe}$. The formation energy is positive even for $R = \text{Dy}$. This indicates that one cannot make the $RFe_{12}$ phase more stable than $R_{2}Fe_{17}$, and partial substitution for Fe is necessary for stabilizing the ThMn$_{12}$ structure. However, appropriate choice of $R$ possibly reduces the necessary amount of stabilizing elements that partially substitute for Fe in synthesizing a material with the partial substitution structure.

As mentioned in Sec. I, (Nd,Zr)(Fe,Co)$_{11.5}$Ti$_{0.5}$N$_{a}$ and (Sm,Zr)(Fe,Co)$_{11.5}$Ti$_{0.5}$ have been synthesized $^{23-26}$. The experiments suggest that partial substitution of Zr for Nd and Sm enhances stability in Nd(Fe,Co,Ti)$_{12}$N and Sm(Fe,Co,Ti)$_{12}$, respectively. The question is if there is a better element than Zr that contributes to stabilization of the ThMn$_{12}$ structure. Figure 2 shows that the formation energy (Eq. (2)) is lower for $R = \text{Y}$, Dy, Ho, Er, Tm than for Zr. Among these elements, $R = \text{Y}$ has the closest atomic radius to Nd and Sm, and the lattice constants of YFe$_{12}$ are close to those of NdFe$_{12}$ and SmFe$_{12}$, as we will see below in Fig. 3. This is favorable for forming an alloy. Therefore, we can expect that partial substitution of Y for Nd or Sm enhances the stability of the ThMn$_{12}$ structure.

FIG. 3. (Color online) The lattice constants $a$ and $c$ of $RFe_{12}$ obtained by the structure optimization for $R = \text{La, Pr, Nd, Sm, Gd, Dy, Ho, Er, Tm, Lu, Y, Sc, Zr, Hf}$ as a function of the atomic radius $r_{R}^{calc}$. The left ($a$) and right ($c$) scales are taken so that the value corresponding to a vertical distance in the right axis becomes the value in the left axis multiplied by $c/a$ for $R = \text{Nd}$.

The above results imply that the size of $R$ is essential in the stability of $RFe_{12}$. Figure 3 shows the lattice constants $a$ and $c$. The $a$ axis shortens as $r_{R_{Fe_{12}}}^{calc}$ decreases, while the $c$ axis is insensitive to $r_{R_{Fe_{12}}}^{calc}$. This trend is consistent with the experimental observation that $a$ in (Nd,Zr)(Fe,Co)$_{11.5}$Ti$_{0.5}$N$_{a}$ decreases with increasing Zr concentration, whereas $c$ is insensitive to the Zr concentration $^{24,26}$.

This result motivates us to consider a possibility that applying pressure stabilizes $RFe_{12}$. To discuss the stability under hydrostatic pressure, we estimate the formation enthalpy defined as follows:

$$\Delta H(p) = H[RFe_{12}](p) - \left( \frac{1}{2}H[R_{2}Fe_{17}](0) + \frac{7}{2}H[Fe](0) \right),$$

where $H[\cdot](p)$ denotes the enthalpy of the system in the bracket under pressure $p$. At $p = 0$, $\Delta H(0)$ is equivalent to $\Delta E \mid_{RFe_{12}+R_{2}Fe_{17}+2Fe}$. We perform computational optimization of the structure of $RFe_{12}$, $R_{2}Fe_{17}$ with the rhombohedral Th$_3$Zn$_{17}$ structure and bcc Fe under hydrostatic pressure (pressure dependence of the lattice constants for NdFe$_{12}$ and Nd$_2$Fe$_{17}$ is presented in Sec. SE of the Supplemental Material). The formation enthalpy as a function of the pressure for $R = \text{Nd}$ and Sm is shown in Fig. 4. As the pressure increases, the values of $\Delta H$ decrease up to $p \approx 6$ GPa, then turn to increase when increasing pressure further. Although the pressure cannot lead to a negative enthalpy, it is expected that amount of stabilizing elements for Fe, like Ti, can be reduced by synthesis under the hydrostatic pressure of $\approx 6$ GPa.

The non-monotonic pressure dependence shown in Fig. 4 can be explained as follows. Because we are considering zero temperature, the enthalpy under finite pressure $H(p)$ is written as

$$H(p) = H(0) + \int_{0}^{p} dp' V(p')$$

$$= H(0) + V(0) p - \frac{K}{2} p^2 + \cdots,$$

FIG. 4. (Color online) The formation enthalpy defined by Eq. (3) as a function of pressure $p$. The orange circles denote values for $R = \text{Nd}$ and the green squares are for $R = \text{Sm}$. 

$^1$
where $V(p)$ is the volume of the system under pressure $p$, and $K$ is a coefficient that is related to the bulk modulus, $B_0$, by $K = -dV/dp|_{p=0} = V(0)/B_0$. In the first order of $p$, the increase of the enthalpy is proportional to the volume at zero pressure. It follows from the second-order term of $p$ that the softer a phase is, the more easily the phase is stabilized by pressure. This can be expressed in more general form by noting that the higher-order terms are written as $\int_0^p dp' \left( V(p') - V(0) \right)$. It is a general expression of “softness” because it refers to the volume change under a given pressure $p$.

In the second-order approximation, $\Delta H(p)$ in Eq. 6 can be written as

$$\Delta H(p) = \Delta H_0 + \Delta V_0 p - \frac{\Delta K}{2} p^2$$

$$-\frac{\Delta K}{2} \left( p - \frac{\Delta V_0}{\Delta K} \right)^2 + \Delta H_0 + \frac{\Delta V_0^2}{2\Delta K}.$$  

(7)

where

$$\Delta H_0 \equiv H[RFe_{12}](0) - \left( \frac{1}{2} H[R_2Fe_{17}](0) + \frac{7}{2} H[Fe](0) \right),$$

(8)

$$\Delta V_0 \equiv V[RFe_{12}](0) - \left( \frac{1}{2} V[R_2Fe_{17}](0) + \frac{7}{2} V[Fe](0) \right),$$

(9)

$$\Delta K \equiv K[RFe_{12}] - \left( \frac{1}{2} K[R_2Fe_{17}] + \frac{7}{2} K[Fe] \right).$$

(10)

$V[\cdot](0)$ denotes the volume of the system in the bracket per formula unit at $p = 0$; $K[\cdot]$ denotes the coefficient $V(0)/B_0$ of the system.

Within the second-order approximation, the minimum of $\Delta H(p)$ always exists at $p > 0$ when $\Delta V_0 < 0$ and $\Delta K < 0$ hold, or more intuitively speaking, when $RFe_{12}$ is smaller and harder than $R_2Fe_{17}$ at zero temperature. The values estimated from our first-principles calculation are $\Delta K = -0.070 \, \text{Å}^3/\text{GPa}$ and $\Delta V_0 = -1.7 \, \text{Å}^3$ for Nd. This enables us to predict the existence of the dip from the information at zero pressure. Note that, however, Eq. 7 well describes the behavior of the curves in Fig. 4 only for small pressures. The valid range does not cover the argument of the minimum $\Delta H(p)$, $\Delta V_0/\Delta K \approx 24 \, \text{GPa}$. The higher order terms omitted in Eq. 7 takes effect under high pressure, and brings the minimum of $\Delta H(p)$ from 24 GPa to 6 GPa.

**IV. CONCLUSION**

We have performed first-principles calculations of $RFe_{12}$ where $R = \text{La, Pr, Nd, Sm, Gd, Dy, Ho, Er, Tm, Lu, Y, Sc, Zr, Hf}$ are considered. The formation energy relative to the simple substances becomes lower as the atomic radius of $R$ becomes smaller except for $R = \text{Sc and Hf}$. The stability of $RFe_{12}$ against the $R_2Fe_{17}$ phase was also discussed. We found that ZrFe$_{12}$ has lower formation energy than NdFe$_{12}$ and SmFe$_{12}$. This is consistent with the experimental results for the synthesis of $(\text{Nd,Zr})(\text{Fe,Co})_{11.5}\text{Ti}_{0.5}\text{Na}$ and $(\text{Sm,Zr})(\text{Fe,Co})_{11.5}\text{Ti}_{0.5}$. We also discussed that Y is a possible candidate to enhance stability of Nd- or Sm-based $RFe_{12}$ compounds. Hydrostatic pressure was also examined as a possible method for stabilization of the NdFe$_{12}$ and SmFe$_{12}$ phase. In both cases, hydrostatic pressure of $\approx 6 \, \text{GPa}$ was found to contribute to the stability of the phases, although the formation energy is still positive.

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**Appendix A: Substitution of group IV elements (Zr, Ti, Hf)**

In order to investigate site-preference of group IV elements $Z = \text{Ti, Zr and Hf}$ for the substitution in NdFe$_{12}$, we calculate ZFe$_{12}$ (2a substitution) and NdFe$_{11}Z$ (8j, 8i and 8f substitution) with structure optimization. Then we calculate the formation energy of them from the simple Fe, Nd and Z phases. In the case of the 2a substitution, we consider the formation energy of ZFe$_{12}$ plus the simple Nd phase from the simple Fe, Nd and Z phases:

$$\Delta E \mid ZFe_{12} + \text{Nd} \leftrightarrow \text{Nd} + Z + 2\text{Fe} = \Delta E \mid ZFe_{12} + Z + 2\text{Fe}.$$  

(A1)

In the other cases, we consider the formation energy of NdFe$_{11}Z$ plus the simple Fe phase from the simple Fe, Nd and Z phases:

$$\Delta E \mid \text{NdFe}_{11}Z + \text{Fe} \leftrightarrow \text{Nd} + Z + 2\text{Fe} = \Delta E \mid \text{NdFe}_{11}Z + \text{Nd} + Z + 11\text{Fe}.$$  

(A2)

Therefore, we nominally use the common reference system (Nd+Z+2Fe) to the cases.
The results are shown in Fig. 5. Ti(8i), Zr(2a) and Hf(2a) are the preferential sites for the substitutions. As for Hf, the 8i site is as stable as the 2a site. The values of ΔE for the substituted systems are much smaller than NdFe12. Therefore, those elements can work positively in stabilization of the ThMn12 phase.

We also evaluate the magnetic moments and magnetizations of the systems considered. Figure 5 shows the magnetic moment \( m \) [\( \mu_B/\text{f.u.} \)] and the magnetization \( \mu_0 M \) [T], where \( \mu_0 \) is the vacuum permeability. The magnetization is estimated from the calculated magnetic moment \( m \), volume \( V \), and the Bohr magneton \( \mu_B \) by \( \mu_0 M = \mu_B m/V \). The values denoted by the open symbols include the value of \( g_J J = 3.273 \mu_B \) as the contribution from the Nd-4f electrons [\( g_J \): the Landé g-factor; \( J \): the total angular momentum of Nd-4f electrons]. The values denoted by the filled symbols do not include the contribution.

The magnetic moment \( m \) (circle) for ZFe12 [denoted by Z(2a)] in the figure, is much less than that for NdFe12. Though it comes mainly from the lack of the Nd-4f moment, the differences are larger than \( g_J J \) of Nd, which can be seen from the difference between the red open circle and the red filled circle. The magnetizations \( \mu_0 M \) are also reduced by the Z substitution as seen in the magnetic moment, but the amount of the reductions in the magnetizations are close to the contribution from the Nd-4f moment. It is because Z substitution shrinks the volume and the shrinkage cancels some of the reduction. Eventually, the reduction in the magnetizations falls close to the Nd-4f moment.

For the substitutions of Ti for the Fe sites (8f, 8i) and 8j), the magnetic moment is drastically reduced, which can be explained by Friedel’s concept of virtual bound state. As for NdFe12 Zr and NdFe12 Hf, the reduction in \( m \) is moderate. However, the reduction in terms of the magnetization, \( \mu_0 M \), are significantly large due to the volume expansion caused by the introduction of Zr and Hf.

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