Cerium as a possible stabilizer of ThMn$_{12}$-type iron-based compounds: A first-principles study

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The structural stability of CeFe$_{12}$ is investigated by using first-principles calculation. The formation energies of CeFe$_{12}$ relative to the Ce$_2$Fe$_{17}$ + bcc-Fe phase and to the CeFe$_2$ + bcc-Fe phase are calculated with the assumptions of trivalency and tetravalency for Ce. Those values are compared with corresponding results in RFe$_{12}$ for $R$ = Nd, Sm, and Zr. Our results suggest that the tetravalent Ce is a promising stabilizer of the ThMn$_{12}$ structure. We also show that the stabilizing effect of an element depends as much on the valency as on the size of the $R$ element by investigating RFe$_{12}$ where $R$ is assumed to have a hypothetical valency on the basis of first-principles calculation.

The permanent magnet is one of the most important materials in industries. The range of its application is widespread: the motors in electric vehicles, wind turbine generators, hard disks, and so on. Currently, the most widely used high-performance permanent magnet is NdFeB-based magnets, the main phase of which is Nd$_2$Fe$_{14}$B. Performance of a permanent magnet is determined by the intrinsic properties of the main phase, and by the microstructure formed by the subphases. Intensive research over three decades has improved the performance of the NdFeB-based magnet by controlling its microstructure. However, the performance seems to reach near to its theoretical limit today, hence a new magnet compound for the main phase is required.

Rare-earth compounds with the ThMn$_{12}$ structure have been regarded as potential strong magnet compounds since iron-rich phases, such as SmFe$_{11}$Ti, were synthesized in the late 1980’s.$^{[4,5]}$ Compounds with high iron content, which leads to large magnetization, has been investigated intensely these days. Hirayama et al. have succeeded in synthesizing NdFe$_{12}$N$^{[6]}$ stimulated by a theoretical work on NdFe$_{12}$ and NdFe$_{12}N$.$^{[5]}$ They measured intrinsic magnetic properties, and found that its saturation magnetization, anisotropy field and Curie temperature are higher than those of Nd$_2$Fe$_{14}$B.

The thermodynamic stability has also been one of the central issues in exploration of high-performance ThMn$_{12}$ compounds. Unfortunately, NdFe$_{12}N$ (and its mother compound, NdFe$_{12}$) exists only as a film due to its instability. Introducing another element can stabilize the ThMn$_{12}$ structure, and it affects the magnetic properties significantly. For example, it has already been known in the 1980’s that substitution of Ti for one of 12 Fe sites improves the stability, but it significantly reduces the saturation magnetization.$^{[8,9]}$ Partial substitution of Zr for the rare-earth element has eagerly investigated recently with the expectation of improvement in stability and of small harm in its magnetism.$^{[9-11]}$ In a previous work, we reported first-principle calculation of RFe$_{12}$ for 14 $R$ elements: 12 rare-earth elements (La, Pr, Nd, Sm, Gd, Dy, Ho, Er, Tm, Lu, Y, Sc) and 2 group IV elements (Zr, Hf)$^{[12]}$ On the basis of the calculated formation energy relative to the R$_2$Fe$_{17}$ + bcc-Fe phase, we showed that some elements has potential in stabilizing the ThMn$_{12}$ structure.

In the present work, we investigate potential of Ce as a stabilizer of the ThMn$_{12}$ structure. Cerium is an abundant element, and often called as a “free” rare-earth because it is much more inexpensive than the other rare-earths. It has been attempted to replace other rare-earth elements in the ThMn$_{12}$-type structure with Ce.$^{[13-15]}$
Ce is usually tetravalent\textsuperscript{20} or in a mixed valence state\textsuperscript{21} in rare-earth–iron compounds. This is quite distinct from other rare-earth elements: Most of rare-earth elements are trivalent, and some of them, e.g. Eu and Yb, are divalent, but none of them are tetravalent in R–Fe compounds. Although the magnetism of Ce-doped ThMn\textsubscript{12}-type compounds has been studied well especially in experiments, there is no study on the potential of Ce as a stabilizer of the ThMn\textsubscript{12} structure to the best of our knowledge.

To investigate the possibility, we perform first-principles calculation of the formation energy of CeFe\textsubscript{12}, and compare the result for other RFe\textsubscript{12} compounds. We analyze the result in terms of the atomic radius and valency of the R element, referring to the results of our previous study. We also provide new calculational results in which R is assumed to be tetravalent for the analysis.

We use QMAS, a first-principles calculation code, which is constructed on the basis of density functional theory\textsuperscript{22,23} and the projector augmented-wave method\textsuperscript{24,25}. The exchange-correlation functional is approximated by the generalized gradient approximation of the Perdew–Burke–Ernzerhof (PBE) formula\textsuperscript{26}. 8 \times 8 \times 8 \times 8 k-points are sampled, and the cutoff energy for the plane wave basis is set to 40.0 Ry. The 4f electrons of rare-earth elements are treated as open-core states. Occupation of those open-core states satisfies Hund’s first rule: The minority spin channel is first occupied, then, if electrons remain, the majority spin channel is occupied. For detailed discussion of the reliability of the open-core treatment in calculation of the formation energy, we refer readers to Ref.\textsuperscript{17}.

First, we show the lattice parameters for CeFe\textsubscript{12}, obtained by the numerical optimization, and also those for Ce\textsubscript{2}Fe\textsubscript{17} and CeFe\textsubscript{2} for comparison. Table \textsuperscript{1} shows the optimized structures of CeFe\textsubscript{12} calculated with the assumption of the Ce\textsuperscript{3+} and Ce\textsuperscript{4+} valency, where the number of occupied 4f electrons are assumed to be one and zero, respectively; Table \textsuperscript{2} shows the result for the rhombohedral Ce\textsubscript{2}Fe\textsubscript{17}; Table \textsuperscript{3} shows the result for the cubic CeFe\textsubscript{2}.

In all phases, the volume is significantly smaller with Ce\textsuperscript{4+} than with Ce\textsuperscript{3+}. It can be attributed to the additional delocalized electron in the Ce\textsuperscript{4+} systems that is fixed to an f-state in the Ce\textsuperscript{3+} systems. The extended electron contributes to cohesion, and makes the difference in volume. The experimental lattice parameters of a = 8.496 Å and c = 12.414 Å have been reported for Ce\textsubscript{2}Fe\textsubscript{17}\textsuperscript{27} (although the structure is annotated to be ‘hexagonal’ in the literature, we take its Bravais lattice as rhombohedral, which has a hexagonal conventional cell, because the given parameters are unreasonably different from other compounds having a hexagonal Bravais lattice). The experimental value of a = 7.302 Å for CeFe\textsubscript{2} have also been reported\textsuperscript{28}.

Our calculated lattice constant with Ce\textsuperscript{4+} agrees well with the experimental values while those with Ce\textsuperscript{3+} deviate significantly from the experimental values. Gabay et al. have reported that the volume of CeFe\textsubscript{3}Co\textsubscript{2}Ti having the ThMn\textsubscript{12} structure is slightly smaller than that of SmFe\textsubscript{3}Co\textsubscript{2}Ti\textsuperscript{18} This tendency agrees with our calculation of CeFe\textsubscript{12} and SmFe\textsubscript{12} (a = 8.497 Å and c = 4.687 Å\textsuperscript{17}) when the tetravalency of Ce is assumed.

Next, we calculate the formation energy of CeFe\textsubscript{12}. We take Ce\textsubscript{2}Fe\textsubscript{17} + bcc-Fe as a reference system because the closest compound to CeFe\textsubscript{12} is Ce\textsubscript{2}Fe\textsubscript{17} in the phase diagram. The definition of the formation energy is

$$\Delta E \equiv E[\text{CeFe}_{12}] - \left( \frac{1}{2}E[\text{Ce}_2\text{Fe}_{17}] + \frac{7}{2}E[\text{Fe}] \right),$$  \hspace{1cm} (1)
where $E[\cdot]$ denotes the total energy per chemical formula of the system in the bracket. This can be also expressed in terms of the formation energy of CeFe$_{12}$ and Ce$_2$Fe$_{17}$ from simple substances by $\Delta E = \Delta E_{\text{CeFe}_{12}} - \Delta E_{\text{Ce}_2\text{Fe}_{17}}$ where they are defined as

$$
\Delta E_{\text{CeFe}_{12}} = E[\text{CeFe}_{12}] - (E[\text{Ce}] + 12E[\text{Fe}]), \tag{2}
$$

$$
\Delta E_{\text{Ce}_2\text{Fe}_{17}} = \frac{1}{2}E[\text{Ce}_2\text{Fe}_{17}] - \left(E[\text{Ce}] + \frac{17}{2}E[\text{Fe}]\right). \tag{3}
$$

We consider both the Ce$^{3+}$ and Ce$^{4+}$ valency in the following, but the valency of Ce in CeFe$_{12}$ and Ce$_2$Fe$_{17}$ are assumed to be the same to each other in Eq. (1). We also take account of the CeFe$_2$ phase, another competing phase which appears in the phase diagram as the next nearest phase of CeFe$_{12}$, with calculation of the formation energy of CeFe$_{12}$ from CeFe$_2$:

$$
E[\text{CeFe}_{12}] - (E[\text{CeFe}_2] + 10E[\text{Fe}]). \tag{4}
$$

In Fig. 1 the formation energies for CeFe$_{12}$ are plotted and the corresponding results for RFe$_{12}$ ($R = $ Zr, Nd, Sc) are shown for comparison. Nd and Sm are typical rare-earths used in permanent magnet compounds, and Zr is recently suggested as a stabilizer of the ThMn$_{12}$-type structure. The values for Ce$^{4+}$Fe$_{12}$ are significantly less than those for NdFe$_{12}$, SmFe$_{12}$ and ZrFe$_{12}$. Although the formation energy against Ce$^{4+}$Fe$_{2}$ is not negative, it is also much less than the values of the other RFe$_{12}$ systems against RFe$_2$. Providing that the CeFe$_2$ phase can be suppressed in a process, which is achieved in synthesis of Ce$_2$Fe$_{17}$ or Sm$_2$Fe$_{17}$ in practice, our result suggest the potential of Ce$^{4+}$ in stabilizing the CeFe$_{12}$ phase.

To analyze the stabilization by a tetravalent element systematically, we consider hypothetical RFe$_{12}$ systems for $R = $ Pr, Nd, Sm, Gd, Dy, Ho, Er, Tm and Lu, with the valency of $R$ assumed to be tetravalent. We show the formation energy of RFe$_{12}$ from R$_2$Fe$_{17}$ + bcc-Fe as a function of $r_{\text{voronoi}}$ in Fig. 2. The results we have reported in Ref. 17 are also plotted in the figure for comparison. $r_{\text{voronoi}}$ is defined as the radius of a sphere whose volume is equal to the Voronoi cell volume of the $R$ site in RFe$_{12}$, which can be regarded as an estimation of the atomic radius of $R$. The data points form two distinct curves, which is differentiated by the valency of the $R$ element. Interestingly, Hf and Zr, which are tetravalent and non-rare-earth elements, also follow this trend. The formation energies become minima around $r_{\text{voronoi}} = 1.62$ Å, and the tetravalent elements tend to yield lower formation energy than the trivalent elements. The valency of the rare-earth elements significantly affects the stability, and is important as well as the atomic size.

We also investigate stability of the tetravalent phase over the trivalent phase. Figure 3 shows the total energy difference per $R$ atom between $R^{4+}$Fe$_{12}$ and $R^{4+}$Fe$_{12}$ (red) and that between $R^{3+}$Fe$_{17}$ and $R^{4+}$Fe$_{17}$ (blue). The values at $R = $ Ce are admittedly positive, which means that the tetravalent state is less stable than the trivalent state. This contradicts the experimental observation of Ce$_2$Fe$_{17}$ and our expectation for CeFe$_{12}$. However, the energy difference systematically decreases as a function of the atomic number of $R$ decreases. This means that there is a trend toward a tetravalent state when $R$ approaches Ce, which is in agreement with the expectation and the experiment. The deviation may be ascribed to theoretical errors coming from our calculational framework using GGA and the open-core treatment, solution of which is an open question at the present stage.

Finally, we investigate the magnetization of CeFe$_{12}$.

FIG. 2. (Color online) The formation energy defined as the $R$Fe$_{12}$ forming from $R_2$Fe$_{17}$ and bcc-Fe [see Eq. (1) for the definition, where Ce should be read as $R$] as a function of the atomic radius, $r_{\text{voronoi}}$ (see the text for its definition). Blue squares are for $R^{4+}$ elements; red circles are for $R^{3+}$ elements.

FIG. 3. (Color online) Total energy difference per $R$ atom between $R^{3+}$Fe$_{12}$ and $R^{4+}$Fe$_{12}$ ($E[R^{4+}\text{Fe}_{12}] - E[R^{3+}\text{Fe}_{12}]$), and that between $R^{3+}$Fe$_{17}$ and $R^{4+}$Fe$_{17}$ (a half of $E[R^{4+}\text{Fe}_{17}] - E[R^{3+}\text{Fe}_{17}]$).
Figure 4 shows the magnetizations of CeFe$_{12}$ and other RF$_{12}$ compounds. All systems has a similar contribution to the magnetization from the valence electrons, and the difference comes mainly from the magnetization of the $f$-electrons. Ce$^{4+}$Fe$_{12}$ has a lower magnetization than Ce$^{3+}$Fe$_{12}$, large part of which is attributed to the local magnetic moment of Ce-4f electrons. Difference in hybridization between Ce and Fe also has a minor but discernible effect on the magnetization.

In conclusion, we performed first-principles calculation for CeFe$_{12}$ with the trivalent and tetravalent Ce. The formation energies of CeFe$_{12}$ from Ce$_2$Fe$_{17} + $ bcc-Fe and CeFe$_3 + $ bcc-Fe are calculated. By comparison with the formation energies of RF$_{12}$ for $R = $ Nd, Sm, and Zr, it is found that the value for Ce$^{4+}$Fe$_{12}$ is lower than the other RF$_{12}$ systems. This result indicates that the tetravalent Ce is a promising stabilizer for the ThMn$_{12}$-type compounds. Our analysis revealed that the tetravalency of Ce is important in its functionality as a stabilizer. We also calculated the magnetization of CeFe$_{12}$. Ce$^{4+}$Fe$_{12}$ has a smaller magnetization than NdFe$_{12}$ and SmFe$_{12}$, but its potential in stabilizing the ThMn$_{12}$ phase is still appealing. We expect fractional doping of Ce can improve the stability of the RF$_{12}$ phase with a small loss of the magnetization. However, the amount of Ce is necessary to be tuned to balance the magnetization and stability, which cannot be predicted by a simple interpolation in general even when the concentration of the dopant is small in practical use. Finding the optimum concentration of Ce is an important open problem, in which we should take account of other stabilizers. We refer those who are interested in such a composition-optimization problem to Ref. [30] one of our previous study with a machine learning technique.

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