STRUCTURE PREDICTION OF NOVEL Fe-BASED RARE-EARTH INTERMETALLICS

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Abstract

The scheme of the structure prediction for SmFe$_5$→SmFe$_{12}$, SmFe$_5$→Sm$_2$Fe$_{17}$ and SmFe$_5$→Sm$_3$Fe$_{20}$ based on \textit{ab initio} interatomic pair potentials are presented for a series of novel iron-based rare-earth compounds. The calculated results are in good agreement with experimental results. The implication of such agreement is the scheme's potential application in the structure design of similar novel iron-based rare-earth compounds.
1 Introduction

In the past decade, the discovery of a series of novel iron-based rare-earth ternary intermetallic compounds have been given great attention.\textsuperscript{1-4} Compounds of the forms \(R(Fe,T)_{12}\) with either hexagonal or tetragonal structures, \(R_2(Fe,T)_{17}\) with either rhombohedral or hexagonal structures, \(R_3(Fe,T)_{29}\) with monoclinic structure are a few of such compounds, all of which can be considered as derivatives of binary structures \(RFe_{12}, R_2Fe_{17}\) and \(R_3Fe_{29}\). Furthermore, these binary compounds, stable or metastable, can be represented as derivatives of the generating compound \(RFe_5\), providing that a certain proportion of \(R\) atoms is replaced by \(Fe-Fe\) dumbbell \(2\). Some examples for evolution processes are as follows.

\[
\begin{align*}
2(RFe_5) & \rightarrow RRFe_{10} \rightarrow RFe_2Fe_{10} \rightarrow RFe_{12} \text{ where } R \text{ atom substitution ratio is } 1/2; \\
3(RFe_5) & \rightarrow R_2RFe_{15} \rightarrow R_2Fe_2Fe_{15} \rightarrow R_2Fe_{17} \text{ where substitution ratio is } 1/3; \\
5(RFe_5) & \rightarrow R_3R_2Fe_{25} \rightarrow R_3Fe_4Fe_{25} \rightarrow R_3Fe_{29} \text{ where substitution ratio is } 2/5.
\end{align*}
\]

However, these algebraic relations can explain the stoichiometry of existing compounds. For certain cases of existing rare-earth intermetallics, some phenomenological geometrical relations on the space group or very rough lattice parameters can also be obtained\textsuperscript{3}, but the orientation and length of each dumbbell and the accurate atomic site distribution still remains unclear. For \textit{ab initio} calculation of electronic properties of materials, for new materials design, or for discovery of new phases in complex materials, it is necessary to know all of these structure information. In the present work, we report briefly how it can be obtained based on \textit{ab initio} interatomic pair potentials. It is interesting to note that most of the compounds with forms of \(RFe_5, RFe_{12}\), and \(R_3Fe_{29}\) are metastable phases, and the technique of current experiments is insufficient to study metastable compounds. Therefore, on the one hand, in experiment a certain content of ternary elements must be added to obtain stable phases based on the time-consuming trial and error method, which is the reason why two series of rare-earth compounds \(R(Fe,T)_{12}\) and \(R_3(Fe,T)_{29}\) were delayed to be found until the end of 80's and the middle of 90's, respectively. On the other hand, a theoretical scheme for prediction and design of the composition and structure of these new compounds becomes desirable. For simplicity, only the evolution processes from \(SmFe_5\) to \(SmFe_{12}\) and to \(Sm_3Fe_{29}\) are discussed in little detail.
2 The mechanism of structure formation of \( R_m(Fe, T)_n \) based on \textit{ab initio} pair potentials

2.1 Scheme for \textit{ab initio} pair potentials\textsuperscript{6–9}

The \textit{ab initio} cohesive energy \( E(x) \) for a crystal can be obtained by an ASW calculation instead of a norm-conserving pseudo-potential method. On the other hand, \( E(x) \) also can be expressed as a sum of interatomic pair potentials \( \Phi(x) \) as

\[
E(x) = \left(\frac{1}{2}\right) \sum_{n=1}^{\infty} r(n)\Phi(b(n)x)
\]

where \( x \) is the nearest neighbor distance among atoms, \( r(n) \) is the \( n \)th coordination number, \( b(n) \) represents the relative distance between the origin and the \( n \)th set of lattice points, \( \Phi(x) \) is the pair potential function. Inverting the above formula based on a generalized Dirichlet inversion formula, we have\textsuperscript{7}

\[
\Phi(x) = 2 \sum_{n=1}^{\infty} E(b(n)x)
\]

where the inversion coefficient \( I(n) \) satisfies

\[
\sum_{b(d)|b(n)} I(d)r(b^{-1}|b(n)|b(d))) = \delta_{nl}
\]

Several \textit{ab initio} interatomic pair potentials \( \Phi(x) \) are shown in figure 1, which already demonstrates effectiveness to metals and intermetallics.

2.2 Process of structure formation

The SmFe\(_5\) with hexagonal structure and the projection along c direction are illustrated in figure 2. In the projection, the small rhombus cell(fig.2.a) represents the unit cell of SmFe\(_5\), the rectangular supercell(fig.2.b) represents the unit cell of prototype of SmFe\(_{12}\) with tetragonal structure, and the large rhombus supercell(fig.2.c) represents the unit cell of prototype of SmFe\(_{12}\) with hexagonal structure.

2.2.1 Structure of tetra- SmFe\(_{12}\)

To construct the tetragonal SmFe\(_{12}\), we extend SmFe\(_5\) primitive cell to \( 2 \times 2 \times 2 \) supercell at first. On each hexagonal layer, a face-centered rectangular periodic structure for the Sm atoms is drawn(left of upper part in fig.3). Then carry out the following substitution for every other layer: In the first case, each Sm atom in the face-center is replaced by a pair of tightly closed Fe atoms with arbitrary orientation and length \((0.1-0.5\,\text{Å})\); in the second case, each Sm atom in the corner is replaced by a pair of Fe atoms (right of upper part in fig.3). Each of these pairs of Fe atoms is called dumbbell. According to this pure geometric model, a tetragonal structure with lattice constants \( 8.721\,\text{Å}, 8.294\,\text{Å} \) and \( 10.068\,\text{Å} \) is the result. But, once the interatomic
potentials $\phi_{Fe-Fe}$, $\phi_{Sm-Fe}$, and $\phi_{Sm-Sm}$ are taken into account. The orientation and the length of the dumbbells change immediately, the site distribution of all the atoms are rearranged, and the lattice constants are adjusted. In the present work, a minimization operation is taken by using the conjugated gradient method. The resulting structure becomes $I4/mmm$ symmetry, with the lattice constants $8.465\ \AA$, $8.465\ \AA$, and $9.62\ \AA$. There are three kinds of Fe atom sites of i, j, and f; among these, half of the i sites are occupied by dumbbells. The comparison of this calculated result with experiment is shown in table 1.

| Table 1. The exp. and cal. data for tetra-Sm(Fe,T)$_2$ |
| --- | --- | --- | --- | --- | --- |
|        | $a_{exp}$ | $a_{cal}$ | $b_{exp}$ | $b_{cal}$ | $c_{exp}$ | $c_{cal}$ |
| SmFe$_{10}$V$_2$ | 8.53 | 8.56 | 8.53 | 8.56 | 9.54 | 9.69 |
| SmFe$_{10}$Cr$_2$ | 8.49 | 8.51 | 8.49 | 8.51 | 9.50 | 9.64 |
| SmFe$_{10}$Si$_2$ | 8.46 | 8.48 | 8.46 | 8.48 | 9.50 | 9.52 |
| SmFe$_{10.5}$Ti$_{1.2}$ | 8.56 | 8.58+ | 8.56 | 8.58+ | 9.58 | 9.69+ |

*Interpolation based on calculation for SmFe$_{10.8}$Ti$_2$

It is also amazing that the large range of variation of initial lattice parameters such as \(\{a, b, c; \alpha, \beta, \gamma\}\) being \(\{2, 2.5, 3; 92, 88, 90\}\), \(\{12, 12, 12; 90, 90, 90\}\) and \(\{2, 2, 2; 60, 60, 60\}\) does not affect the final structure parameters.

### 2.2.2 Structure of rhomb- SmFe$_{12}$

First, using a larger hexagonal supercell equal to the $3 \times 3 \times 2$ original unit cell for SmFe$_7$, the substitution is as follows: on one layer, two Sm atoms in the center part of the rhombus are substituted by two dumbbells; on the next layer, one Sm atom in the corner of rhombus is substituted by a dumbbell. In this case, the substitution ratio is kept as 1:2, but with a different substitutional structure. According to the conventional geometrical relation, the lattice constants are $a = b = 8.721\ \AA$, $c = 8.294\ \AA$, with the space group $P6/mmm$. After the structure evolution based on the same interatomic potentials as mentioned above, the space group remains unchanged, but the resulting lattice constants become $a = b = 8.432\ \AA$, $c = 8.389\ \AA$. This structure is similar to SmZn$_{12}$(fig.4), which might be instructive for designing a new series of iron-rich rare-earth intermetallic compounds.

### 2.2.3 Structure of Sm$_2$ Fe$_{17}$ and Sm$_3$ Fe$_{29}$

The sophisticated geometry for substituting certain fractions of rare-earth elements has been shown in ref.3. Then, based on the same $ab\ initio$ interatomic potentials as above, the calculated results comparing the experiment for Sm$_2$Fe$_{17}$ with rhombohedral structure and Sm$_3$Fe$_{29}$ with monoclinic structure are shown in table 2 and table 3, respectively.
Table 2. The comparison between experiment$^{10}$ and theory for Sm$_2$Fe$_{17}$

<table>
<thead>
<tr>
<th></th>
<th>$a_{exp}$</th>
<th>$a_{cal}$</th>
<th>$c_{exp}$</th>
<th>$c_{cal}$</th>
</tr>
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<tr>
<td>Rhom-Sm$<em>2$Fe$</em>{17}$</td>
<td>8.54</td>
<td>8.501</td>
<td>12.43</td>
<td>12.43</td>
</tr>
<tr>
<td>hex-Sm$<em>2$Fe$</em>{17}$</td>
<td>8.5</td>
<td>8.508</td>
<td>8.3</td>
<td>8.329</td>
</tr>
</tbody>
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Table 3. The comparison between experiment$^{2,3}$ and theory for Sm$_3$Fe$_{29}$

<table>
<thead>
<tr>
<th></th>
<th>$a_{exp}$</th>
<th>$a_{cal}$</th>
<th>$b_{exp}$</th>
<th>$b_{cal}$</th>
<th>$c_{exp}$</th>
<th>$c_{cal}$</th>
<th>$\rho_{exp}$</th>
<th>$\rho_{cal}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sm$<em>3$Fe$</em>{27}$Ti$_2$</td>
<td>10.635</td>
<td>10.62</td>
<td>8.57</td>
<td>8.56</td>
<td>9.72</td>
<td>9.75</td>
<td>96.98</td>
<td>97.2</td>
</tr>
<tr>
<td>Sm$<em>3$Fe$</em>{26.5}$V$_{2.5}$</td>
<td>10.57</td>
<td>10.63</td>
<td>8.52</td>
<td>8.54</td>
<td>9.69</td>
<td>9.77</td>
<td>96.82</td>
<td>97.04</td>
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<tr>
<td>Sm$<em>3$Fe$</em>{24.5}$Cr$_{4.5}$</td>
<td>10.56</td>
<td>10.61</td>
<td>8.51</td>
<td>8.54</td>
<td>9.68</td>
<td>9.75</td>
<td>96.9</td>
<td>97.01</td>
</tr>
<tr>
<td>Sm$<em>3$Fe$</em>{29}$(unrelaxed)</td>
<td>/</td>
<td>10.89</td>
<td>/</td>
<td>8.72</td>
<td>/</td>
<td>9.703</td>
<td>/</td>
<td>98.9</td>
</tr>
<tr>
<td>Sm$<em>3$Fe$</em>{29}$(relaxed)</td>
<td>/</td>
<td>10.58</td>
<td>/</td>
<td>8.488</td>
<td>/</td>
<td>9.724</td>
<td>/</td>
<td>97.075</td>
</tr>
<tr>
<td>Nd$<em>3$Fe$</em>{27.8}$Ti$_{1.2}$</td>
<td>10.65</td>
<td>/</td>
<td>8.59</td>
<td>/</td>
<td>9.75</td>
<td>/</td>
<td>96.9</td>
<td>/</td>
</tr>
<tr>
<td>Nd$<em>3$Fe$</em>{29}$(unrelaxed)</td>
<td>/</td>
<td>11.063</td>
<td>/</td>
<td>8.933</td>
<td>/</td>
<td>9.701</td>
<td>/</td>
<td>100.12</td>
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<tr>
<td>Nd$<em>3$Fe$</em>{29}$(relaxed)</td>
<td>/</td>
<td>10.671</td>
<td>/</td>
<td>8.544</td>
<td>/</td>
<td>9.774</td>
<td>/</td>
<td>97.22</td>
</tr>
</tbody>
</table>

Obviously, the calculated result is in good agreement with experiment. In particular, even though the experimental data for metastable phase R$_3$Fe$_{29}$ are lacking, the lattice parameters \{$a, b, c, \beta$\} for R$_3$Fe$_{29}$ can be calculated in the present scheme, which are quite close to experimental data for stable ternary phases. This implies that the energy difference between the binary metastable phase and the ternary stable phases for R$_3$(Fe,T)$_{29}$ is small, when the concentration of ternary additions is low. Figure 5 shows the stabilizing effect of the ternary element Mn and the site preference order being $i, j, f$. All the result indicates the success of our \textit{ab initio} interatomic pair potentials in these cases.

3 Prediction for structure of R$_4$(Fe,M)$_{41}$

For save space as a letter, we would like to mention only a few points. The crystal structure of R$_4$Fe$_{41}$ is monoclinic with space group of A2/m, and the number of distinct atomic sites is 15 instead of 11 for R$_3$Fe$_{29}$ with the same space group. The predicted crystal lattice constants are \{9.728,8.481, 15.136;104.8°\} for Sm$_4$Fe$_{41}$ and \{9.78,8.542,15.26;104.16°\} for Nd$_4$Fe$_{41}$. The detail will give elsewhere$^{11}$.

4 Conclusion and discussion

The present work provides a quantitative method to confirm and to predict the structures of a series of novel iron-based rare-earth compounds by using \textit{ab initio} interatomic pair potentials. Based on energy analysis, the calculated results for lattice structure, phase stability and site preference of ternary elements are all in good agreement with experiment. Also, the resulting structure parameters are topologically invariant. It is worth to note that the preferred substitution order is $f$-site, $j$ * site and $i$-site for Si, instead of $i$-, $j$-, $f$-site for most other ternary elements.
The number of distinct sites for Fe atoms in R\textsubscript{3}Fe\textsubscript{29} is equal to 11. It is difficult to determine the space group of this kind of complex structures such as R\textsubscript{3}(M,T)\textsubscript{29} since the ternary elements play some sophisticated role and the solution of the inverse diffraction spectrum problem cannot distinguish the tiny difference between the space groups A2/m and P2\textsubscript{1} for R\textsubscript{3}(Fe,T)\textsubscript{29}. But the calculation can obtain the change of the space group index with respect to the element type and the concentration of ternary additions, even for some metastable phases. Moreover, the structure with corresponding x-rays diffraction pattern for R\textsubscript{4}(Fe,T)\textsubscript{41} and R\textsubscript{5}(Fe,T)\textsubscript{53} has been performed and prepared for experimental discovery in future. All this show the optimistic future for both materials formation design and performance prediction based on \textit{ab initio} calculation\textsuperscript{4,5} including \textit{ab initio} interatomic potentials. As the last point, it should be mentioned that the current \textit{ab initio} calculation gives deeper cohesive value at equilibrium position and the inversion model does not include the many-body interaction, which might be consider in our future work.

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References


Figure Captions

Fig. 1. Several illustrated interatomic potentials

Fig. 2. The structure of SmFe₅ and its projection.

Fig. 3. The substitution geometry for formation of tetra-SmFe₁₂.

Fig. 4. The substitution geometry for formation of hex-SmFe₁₂.

Fig. 5. The stabilizing effect of Mn atoms in tetra-SmFe₁₂ structure and site preference.

Fig. 6. The predicted structure of monoclinic Sm₄Fe₄I.
Fig. 2
The first layer

the second layer

The final structure of SmFe$_{12}$ with tetragonal symmetry

Fig. 3
The final structure of SmFe$_{12}$ with hexagonal symmetry

Fig. 4
Energy (eV/atom)

\[ s = \sqrt{\sum_{n=1}^{20} \left( X_i^2 - \bar{X}^2 \right)} \]

(SmFe\textsubscript{12m}Mn\textsubscript{16})
Fig. 6