

Theoretical Study of the Rare Earth Compounds $\text{LaFe}_{13-x}\text{T}_x$ ($\text{T} = \text{Cr}, \text{Cu}, \text{Ga}, \text{Mn}, \text{Ni}$) and Curie Temperature Variation

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ABSTRACT

The phase stability and site preference of the intermetallics $\text{LaFe}_{13-x}\text{T}_x$ ($\text{T} = \text{Cr}, \text{Cu}, \text{Ga}, \text{Mn}, \text{Ni}$) with NaZn_{13} -type structure have been investigated by lattice inversion potentials. The calculated results indicate that each of the stabilizing elements Cr and Mn significantly decreases the cohesive energy of $\text{LaFe}_{13-x}\text{T}_x$ and plays a role in stabilizing the 1:13 structure. The calculated lattice parameters of $\text{LaFe}_{13-x}\text{T}_x$ ($\text{T} = \text{Al}, \text{Si}$) compounds are in good agreement with the experimental data. Qualitative analyses are carried out on the behavior of the Curie temperature and magnetocrystalline anisotropy. All the results indicate that the pair potentials based on the lattice inversion method can effectively give a deeper insight into the structure and property of complex materials.

Keywords: Rare Earth Compounds, Interatomic Potentials, Site Preference, Computers Simulation

1. Introduction

Recently rare earth transition metal intermetallic compounds with NaZn_{13} -type structure have attracted considerable attention owing to their potential application and intriguing magnetic properties [1-4]. In rare earth-transition metal intermetallic compounds the strong magnetic coupling between 3d atoms gives rise to the large magnetization. It seems that the novel R-T intermetallic compounds with excellent magnetic properties are always related to a high content of 3d transition metal. Among all binary R-M intermetallic compounds only LaCo_{13} crystallizes in the cubic NaZn_{13} -type structure (space group Fm-3c). The LaFe_{13} compound does not exist. Generally, the positive heat of alloying between La and Fe is considered to be the reason why no LaFe_{13} binary compound exists. Up to now, many compounds with NaZn_{13} -type structure have been obtained in R (T, M)₁₃ systems ($\text{R} = \text{rare earth}, \text{T} = \text{Fe}, \text{Co}, \text{Ni}$ and $\text{M} = \text{Al}, \text{Si}$) by elemental substitution. By now ternary compounds $\text{LaFe}_{13-x}\text{Si}_x$ ($1.3 < x < 2.6$) [5] and $\text{LaFe}_{13-x}\text{Al}_x$ ($1 < x < 7$) [6] are known. Besides, recently the $\text{NdFe}_{13-x}\text{Be}_x$ compounds ($2 < x < 4$) have been synthesized.

The cubic symmetry of the structure usually implies a lack of significant magnetocrystalline anisotropy, so that intermetallic compounds with the NaZn_{13} -type structure

cannot be used for permanent magnets. Much larger magnetocrystalline anisotropy is expected in materials with a strong anisotropic crystal structure. It has been observed that in some range of Si or Al concentrations the crystal symmetry of the R(M,T)₁₃ compounds transforms from cubic (NaZn_{13} -type) to tetragonal in the $\text{LaCo}_{13-x}\text{Si}_x$ and $\text{PrFe}_{13-x}\text{Si}_x$ compounds ($\text{Ce}_2\text{Ni}_{17}\text{Si}_9$ -type) [7] or to orthorhombic in the $\text{LaFe}_{13-x}\text{Al}_x$ compounds [8] and hence creates an opportunity for developing magnetocrystalline anisotropy in 1:13 alloys.

In this work, a series of inter-atomic pair potentials in $\text{LaFe}_{13-x}\text{T}_x$ were determined using a general lattice-inversion technique with a first principles-based crystal cohesive energy calculation. In this way, the stability of $\text{LaFe}_{13-x}\text{T}_x$ and the site preference were evaluated and analyzed. Section 2 given an introduction to the methodology for the calculation. Section 3 shows the calculated results and give a comparison with the results of the experiments. The conclusions and the further discussion are given in the Section 4.

2. Calculation Methods

In general, any interatomic pair potential can be obtained by a strict lattice inversion of cohesive curve, and the cohesive energy curves can be obtained either by first

principle calculation or by experimental data fitting. The lattice inversion theorem is focused on explaining how to use Chen's lattice inversion theorem to obtain the interatomic pair potential from the first principle cohesive energy curve. A brief introduction of the lattice inversion theorem is proposed as follows [9]: Suppose that the crystal cohesive energy obtained by the first principle calculation is expressed as:

$$E(x) = \frac{1}{2} \sum_{n=1}^{\infty} r_0 \Phi[b_0(n)x] \quad (1)$$

where x is the near-neighbor distance, $r_0(n)$ is the n neighbor coordination number, $b_0(n)x$ is the distance between the central reference atom and its n th neighbor, and $\Phi[b_0(n)x]$ is the pair potential. A multiplicative closed semi-group $b(n)$. In the process, a lot of virtual lattice points are involved, but the corresponding virtual coordination number is zero. In the $b(n)$, for any two integers m and n , there is a sole integer k such that $b(k) = b(m) b(n)$. Hence, equation (1) can be rewritten as

$$E(x) = \frac{1}{2} \sum_{n=1}^{\infty} r \Phi[b_0(n)x] \quad (2)$$

where

$$r(n) = \begin{cases} r(b_0^{-1}[b(n)]n) & b(n) \in \{b_0(n)\} \\ 0 & b(n) \notin \{b_0(n)\} \end{cases} \quad (3)$$

Then the general equation for the interatomic pair potential obtained from the inversion can be expressed as

$$\Phi(x) = 2 \sum_{n=i}^{\infty} I(n) E[b(n)x] \quad (4)$$

where $I(n)$ has the characteristics of

$$\sum_{b(n)/b(k)} I(n) r \left[b^{-1} \left[\frac{b(k)}{b(n)} \right] \right] = \delta_{k1} \quad (5)$$

$I(n)$ is uniquely determined by a geometrical crystal structure, not related to the concrete element category. Thus, the interatomic pair potentials can be obtained from the known cohesive energy function $E(x)$. The interatomic pair potential in distinct atoms can be obtained by the same inversion method, and they are used to study the rare earth intermetallics structures. Which are close to the Morse function, that is:

$$\Phi(x) = D_0 \left\{ e^{\left[-\gamma \left(\frac{x}{R_0} - 1 \right) \right]} - 2e^{\left\{ -\gamma/2 \left(\frac{x}{R_0} - 1 \right) \right\}} \right\} \quad (6)$$

where D_0 is the depth of potential of potential, R_0 , γ are parameters. Some important potential are show in the **Table 1**.

3. Calculation Results

The structure of $\text{LaFe}_{13-x}\text{T}_x$ ($\text{T} = \text{Ga, Ni, Mn, Cr, Cu}$) compounds are simulated by the energy minimization process and realized by the conjugate gradient method with 14 Å as the cut-off radius of the potentials. The results are taken by the arithmetic average for 30 stochastic configurations. To avoid statistic fluctuation, the model is taken as a $2 \times 2 \times 2$ super cell.

3.1. Phase Stability and Lattice Constants of $\text{LaFe}_{13-x}\text{T}_x$ ($\text{T} = \text{Cr, Cu, Ga, Mn, Ni}$)

Although the pure LaFe_{13} compound is unstable, it can be considered as the eigentstructure of $\text{LaFe}_{13-x}\text{T}_x$ and their interstitial compounds. In the calculation procedure, the initial lattice constants of LaFe_{13} are randomly chosen in a certain range. Under the control of the interatomic pair potentials, the energy minimization is carried out by using the conjugate gradient method. The results show that the space group maintains Fm-3c or I4/m-cm with NaZn₁₃-type structure in the tolerance range of 0.001 - 0.1 Å.

In the structure of LaFe_{13} , we first substitute T ($\text{T} = \text{Cr, Cu, Ga, Mn, Ni}$) atom for Fe in each site with different concentrations and then use the energy minimization method to relax the systems under the interaction of the potentials. With different fractions of the third element, $\text{LaFe}_{13-x}\text{T}_x$ may crystallize in the cubic structure with the space group Fm-3c or in the tetragonal structure with the space group I4/mcm. Thus the average cohesive energy of final structure can be investigated and compared. The average cohesive energies of different structures are displayed in **Figure 1**. It can be seen that the crystal energy gradually decrease with increasing content of the ternary element T ($\text{T} = \text{Cr, Cu, Ga, Mn, Ni}$). The structure stability is judged by the energy and tolerance. The tolerance, which represents the displacement of the atomic position in order to retrieve the space group, is an assistant criterion. Numerous calculations show that, when the tolerance is much large than 0.5 Å, the compounds do not exist in experiments. In fact, the site occupation is determined by the energy and the too large tolerance means that the final stable structure has deviated too far from the selected one and that the structure has been changed.

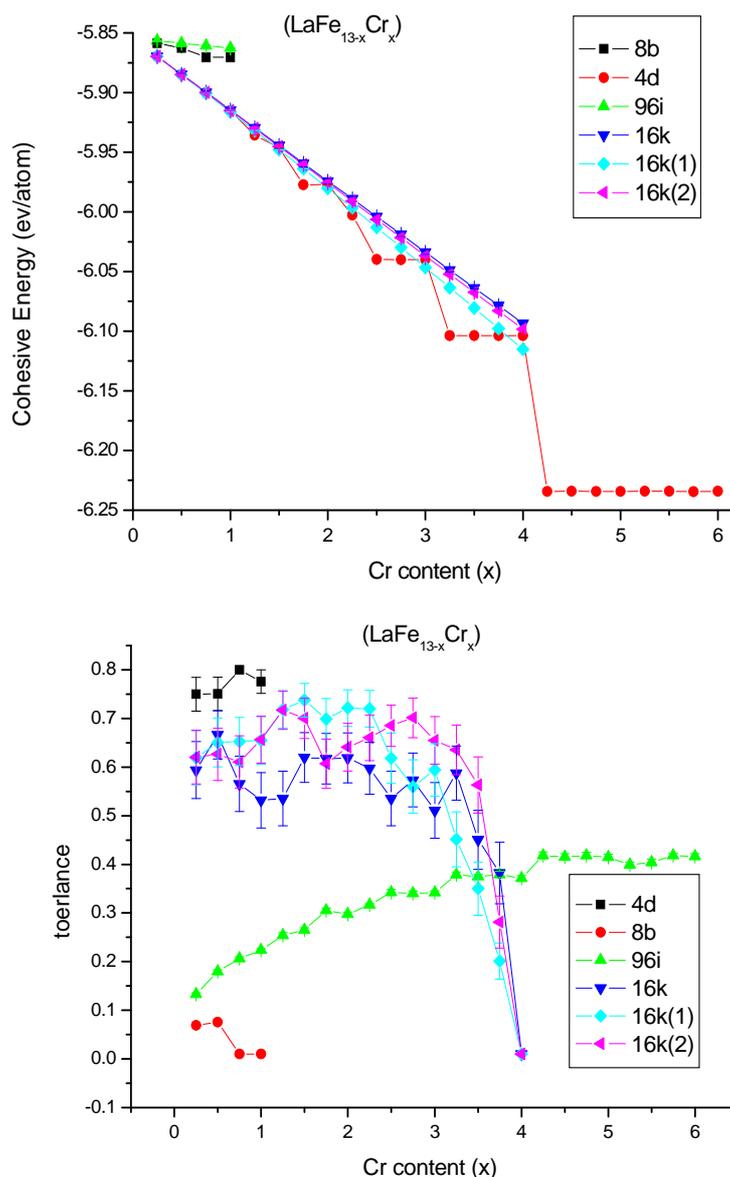
In the calculation, for $\text{LaFe}_{13-x}\text{Cr}_x$, Cr entering into 96i site of the cubic structure has the lowest energy and the tolerance is acceptable for $0 \leq x \leq 3.5$. On the other hand, in the range $0 \leq x \leq 3.5$, the tolerance for Cr entering into 16k site of the tetragonal structure is so large that the tetragonal structure could not exist. However, when $3.5 \leq x \leq 4.0$, the tolerance with Cr entering into 16k site of the tetragonal structure drops sharply and the tetragonal

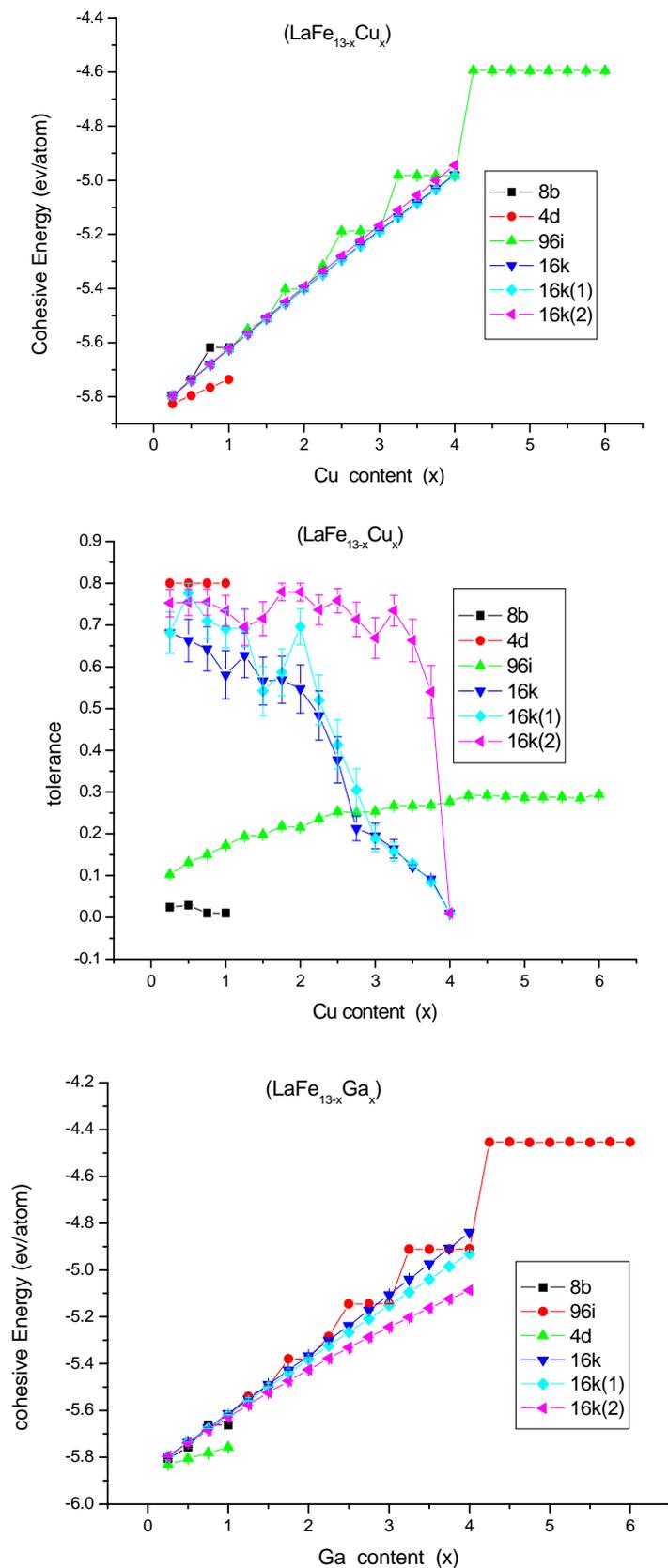
structure is acceptable for $x \leq 3.75$. For $\text{LaFe}_{13-x}\text{Mn}_x$, Mn entering into 8b site of the cubic structure has the lowest energy for $x \leq 3.25$, and the tolerance is acceptable in this range. However, in the range of $3.25 \leq x \leq 4.0$ the tolerance with Mn entering into 96i site of the cubic structure

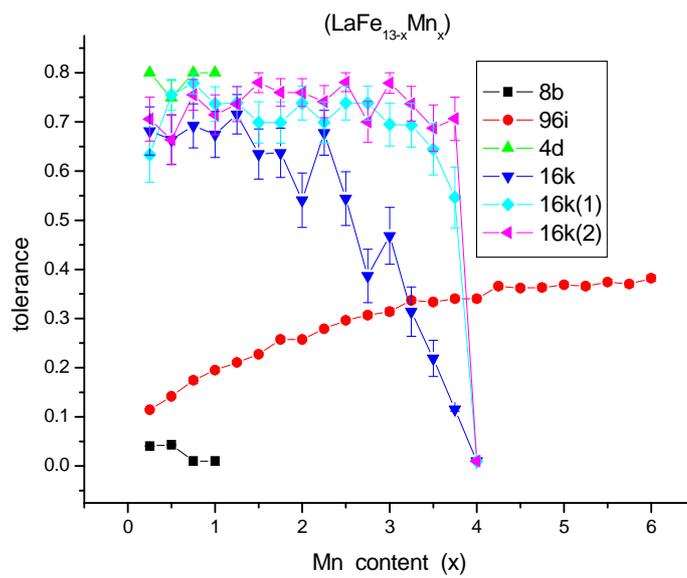
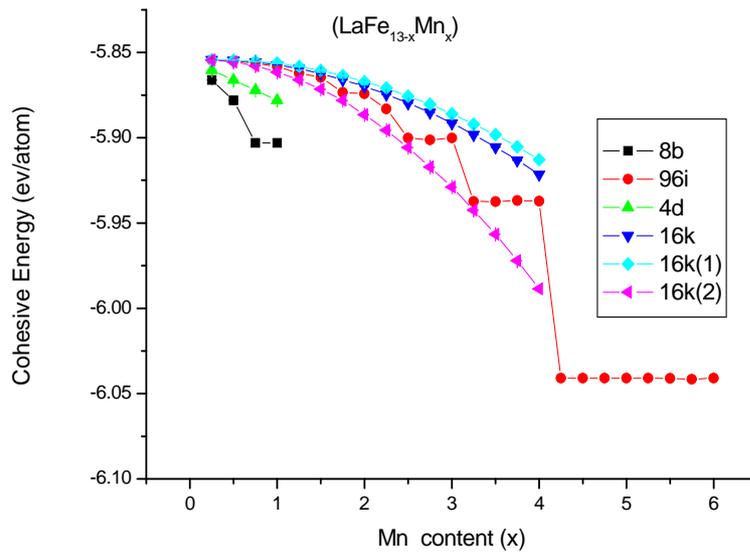
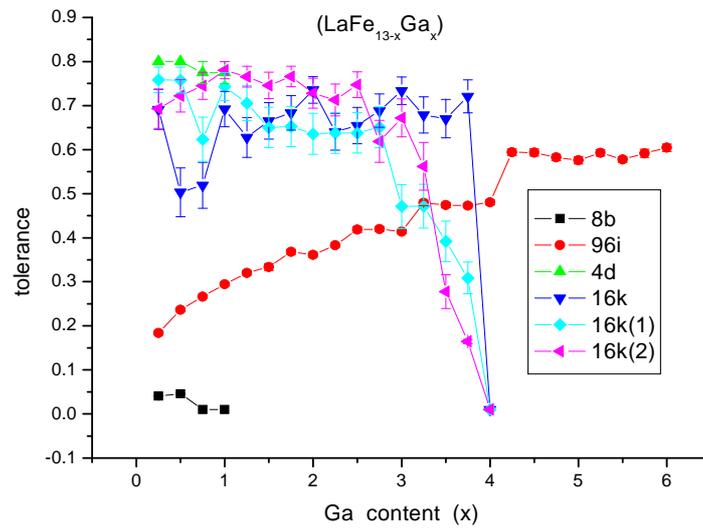
is so large that the cubic structure could not exist, and Mn entering into 16k site of the tetragonal structure. From the **Figure 1**, we can see that Cr, Mn play an important role in stabilization. But Ni, Cu and Ga cannot stabilize LaFe_{13} structure.

Table 1. Some important potential of ($\text{LaFe}_{13-x}\text{T}_x$) system.

	$R_0(\text{\AA})$	$D_0(\text{kcal/mol})$	γ
Fe-Fe	2.73609	17.6177	8.75429
La-La	4.7585	6.7761	6.4607
La-Fe	2.41269	2.38229	6.30159
La-Si	3.4186	13.2643	10.0062
La-Al	3.64488	10.6466	8.89225
Fe-Si	2.7334	15.2938	8.2601
Fe-Al	2.7405	14.9015	9.09675







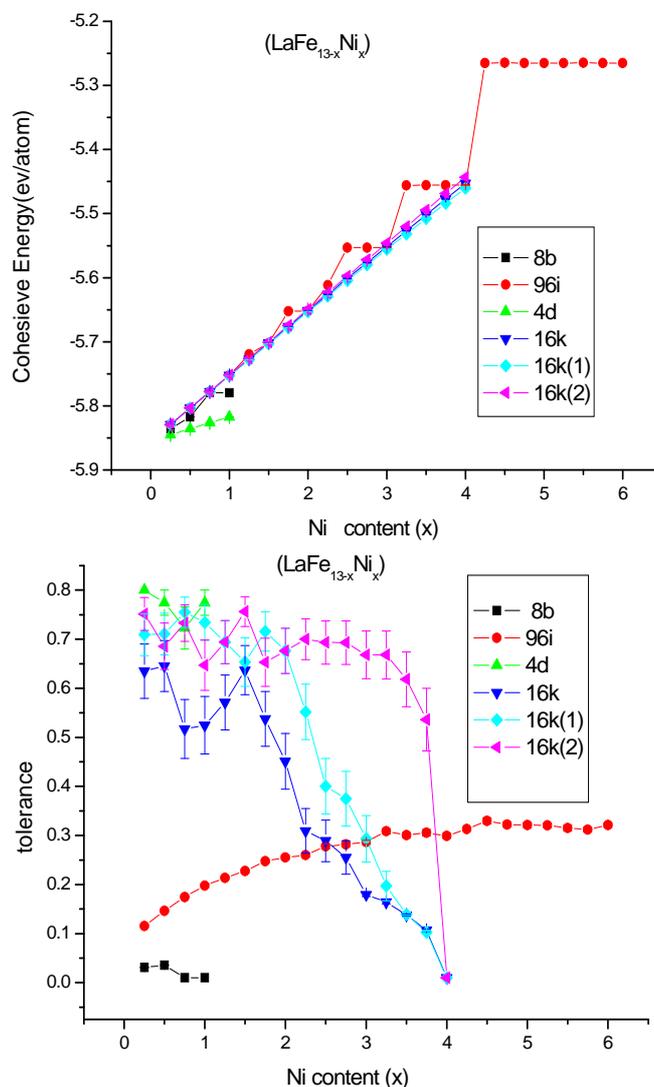


Figure 1. The cohesive energy and tolerance variation with the third element content x in $\text{LaFe}_{13-x}\text{T}_x$ ($\text{T} = \text{Cr, Cu, Ga, Mn, Ni}$) with different space group Fm-3c and I4/mcm.

3.2. Fe-Fe Bond Length Change of $\text{LaFe}_{13-x}\text{T}_x$ ($\text{T} = \text{Si, Al}$)

In the cubic NaZn_{13} structure (space group Fm-3c), the rare earth atoms occupy the single 8a sodium site, while the Fe atoms are distributed over the two zinc sites, Fe_1 (8b) and Fe_2 (96i). The Fe_1 atoms are surrounded by an icosahedron of 12 Fe_2 atoms and possess a local symmetry peculiar to an FCC-like lattice. In the tetragonal structure (space group I4/mcm) the Fe atoms occupy four different sites. The Fe_1 atoms (the 4d site) in icosahedron centers are surrounded by 12 Fe atoms in the sites Fe_2 (16k), Fe_3 (16l₁) and Fe_4 (16l₂). Previous investigations [10] have shown that the magnetic properties of the R-Fe-based compounds are determined predominantly by the Fe-Fe interaction, which is sensitive to the Fe-Fe dis-

tance and the number of nearest neighbors. Here, we will theoretically study the effects of Fe-Fe bond length change on the magnetic properties of NaZn_{13} -type intermetallic compounds.

In the experiments, $\text{LaFe}_{13-x}\text{Al}_x$ crystallizes the cubic NaZn_{13} -type structure with the space group Fm-3c in the range $1.04 \leq x \leq 7.15$, and $\text{LaFe}_{13-x}\text{Si}_x$ compounds are of a single phase with the space group Fm-3c in the range $1.4 \leq x \leq 2.6$ [11]. According to our previous works, Si entering into the 96i site could stabilize the cubic structure of $\text{LaFe}_{13-x}\text{Si}_x$ with $x < 3.25$, and for $3.25 < x < 5.25$ Si first enters into the 16l₂ site of the tetragonal structure and with 16l₂ full the rest of the Si enters into the 16k site [12]. Compared with the experiment, the calculated result is good at illustrating the structure transition. Therefore, it is also verified that interatomic pair potential are effect-

Table 2. The crystallographic parameters a and c of $\text{LaFe}_{13-x}\text{T}_x$ (Al, Si) in Å, obtained from experiments (exp.) and calculations (cal.), and Ref. is the source of the experimental data.

	x	a(cal)	c(cal)	a(exp)	c(exp)	Ref.
$\text{LaFe}_{13-x}\text{Si}_x$	2	11.470		11.463		[13]
	3	8.035	11.485	7.994	11.363	
	4	7.997	11.501	7.974	11.542	
	5	7.967	11.595	7.954	11.720	
$\text{LaFe}_{13-x}\text{Al}_x$	2	11.547		11.668		[14]
	3	11.569		11.731		
	4	11.614		11.794		
	5	11.688		11.857		
	6	11.794		11.920		
	7	11.871		11.983		

tive. **Table 2** shows the lattice parameters of $\text{LaFe}_{13-x}\text{T}_x$ ($T = \text{Si, Al}$) obtained from both the experiments [13] [14] and calculations. The results correspond well to experimental data. The bond lengths of Fe-Fe which play an important role in magnetic properties can be evaluated. In this subsection, the dependence of Curie temperature on the Si/Al concentration is analyzed qualitatively.

In the experiment, the value of T_C for the $\text{LaFe}_{11.5}\text{Si}_{1.5}$ compound is 188 K. Just as Givord et al. have pointed out, there are two types of exchange interactions, positive and negative, which depend on the length of Fe-dumbbells. All the exchange interactions could be positive except the case associated with 96i-96i, 96i-8b, since the distances between these iron atoms are small.

In order to study the trend of Curie temperature variation, the distance between special sites and the related exchange interaction should be investigated. **Figure 2** presents the bond lengths in $\text{LaFe}_{13-x}\text{Si}_x$, indicating that the lengths of 96i-96i are shorter than 2.46 Å which can be considered as the threshold of switching exchange interaction. The distances between 96i-96i and 96i-8b decrease with increasing Si content, which are similar to that in the experimental trend. Notice that the bond lengths of 96i-8b are larger than 2.46 Å, then the variation of exchange interaction from 96i-8b pairs can be neglected. As far as iron pairs except 96i-96i are concerned, the positive exchange interactions associated with large bond lengths are weak, even though the introduction of Si atom has the effect of reduction on them. Then the contribution to the exchange interaction from these iron pairs can also be neglected. In the next step, we will focus on the effect of 96i-96i lengths based on the variation of Curie temperature.

In the above subsection, the analysis of site preference behavior shows that Si atoms have a pronounced preference for occupying 96i site. On the one hand, the number of 96i-96i (Fe-Fe) dumbbell pairs reduces and the negative exchange interaction with the increase of Si atom,

and in thus beneficial in improving the Curie temperature. on the other hand, bond lengths of 96i-96i pairs decrease with increasing Si content, and thus enhance the negative exchange interaction and lead to a lower Curie temperature. So there is a competing mechanism arising from Si content increase, *i.e.* the variation of Curie temperature is not monotonic with the increment of Si concentration.

Givord *et al.* [15] have shown that the threshold of switching Fe-Fe exchange interaction is 2.45 Å. In other words, if the distance of Fe-Fe is shorter than 2.45 Å, then the exchange interaction would be negative, if it is larger than 2.45 Å, then it would be positive. In the present calculation, the threshold of Fe-Fe exchange interaction is taken as 2.46 Å, instead of 2.45 Å from the experimental analysis. This difference may be caused by a systemic error in derivation of these quasi-*ab initio* interatomic potentials.

4. Conclusions and Discussions

Pair potentials based on *ab initio* calculations and on the lattice-inversion method have been used to calculate the structural properties of a series of $\text{LaFe}_{13-x}\text{T}_x$ ($T = \text{Cr, Cu, Ga, Mn, Ni}$). The results show that Cr and Mn make the cohesive energy decrease markedly, indicating that these atoms can stabilize $\text{LaFe}_{13-x}\text{T}_x$ with the cubic NaZn_{13} -type or its derivative tetragonal structure.

Furthermore, the increase of the Curie temperature of $\text{LaFe}_{13-x}\text{T}_x$ ($T = \text{Si, Al}$) with increasing Si concentration can be qualitatively explained in terms of the distance dependence of the exchange interaction. The presented results indicate that simple pair potentials are useful for studying the structural properties of these kinds of intermetallics.

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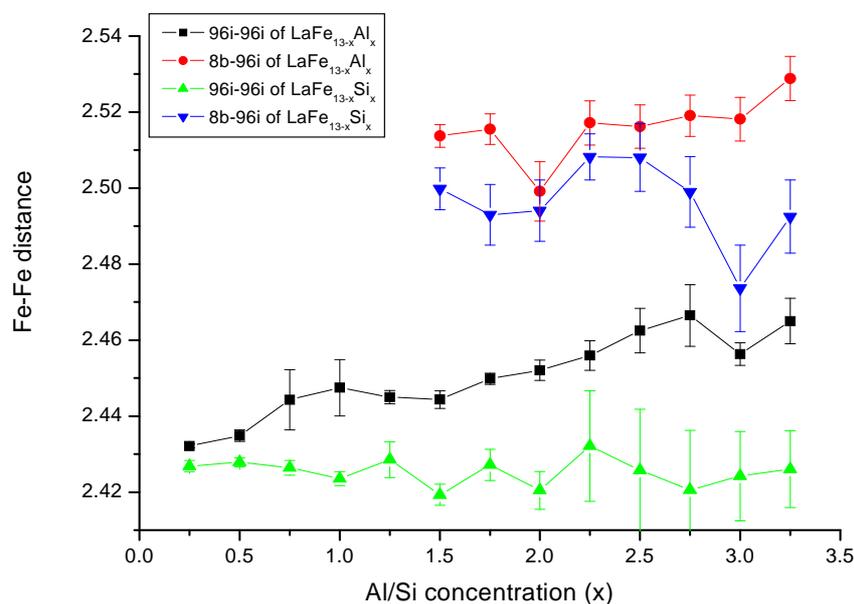


Figure 2. Bond lengths (Å) of Fe-Fe pairs with the ternary element (Al/Si) content in $\text{LaFe}_{13-x}\text{T}_x$ ($\text{T} = \text{Al}, \text{Si}$).

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