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# Site preference, magnetism and lattice vibrations of intermetallics $\text{Lu}_2\text{Fe}_{17-x}\text{T}_x$ ( $T=\text{Cr, Mn, Ru}$ )

Jin-Chun Li<sup>a</sup>, Ping Qian<sup>a,\*</sup>, Zhen-Feng Zhang<sup>a</sup>, Xiao-Jian Yuan<sup>b</sup>, Yi-Wen Wang<sup>a</sup>, Jiang Shen<sup>a</sup>, Nan-Xian Chen<sup>a,c</sup>

<sup>a</sup> Institute of Applied Physics, University of Science and Technology Beijing, Beijing 100083, China

<sup>b</sup> Department of Applied Physics, Hunan University, Changsha 410082, China

<sup>c</sup> Department of Physics, Tsinghua University, Beijing 100084, China

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## ABSTRACT

We present an atomistic study on the phase stability, site preference and lattice constants of the rare earth intermetallics  $\text{Lu}_2\text{Fe}_{17-x}\text{T}_x$  ( $T=\text{Cr, Mn, Ru}$ ). The calculated preferential occupation site of ternary element  $T$  is found to be the  $4f$  site. The order of site preference is given as  $4f$ ,  $12k$ ,  $12j$  and  $6g$  for  $\text{Lu}_2\text{Fe}_{17-x}\text{T}_x$ . The calculated lattice parameters are corresponding to the experimental results. We have calculated the magnetic moments of  $\text{Lu}_2\text{Fe}_{17-x}\text{T}_x$  compounds. Results show that the calculated total magnetic moment of  $\text{Lu}_2\text{Fe}_{17}$  compound is  $M=37.34 \mu_B/\text{f.u.}$  In addition, the total and partial phonon densities of states are evaluated first for these complicated structures.

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## 1. Introduction

The magnetism of  $\text{Lu}_2\text{Fe}_{17}$  is drawing much attention due to its non-ordinary crystal and magnetic properties [1–6]. The  $\text{Lu}_2\text{Fe}_{17}$  intermetallic compound is an extraordinary member of the family of  $R_2\text{Fe}_{17}$  intermetallics ( $R$ , rare earth). The non-magnetic Lu-element and small volume of crystal cell cause that  $\text{Lu}_2\text{Fe}_{17}$  stays on a verge of stability of ferromagnetism. The magnetic properties of  $\text{Lu}_2\text{Fe}_{17}$  reveal considerable changes upon varying the interatomic distances by means of changing the external (pressure) and internal (hydrogenation, substitution) conditions [7–10].

In the present paper, the effects of  $T$  substitution on the crystal structure, phase stability and site preference of  $\text{Lu}_2\text{Fe}_{17-x}\text{T}_x$  ( $T=\text{Cr, Mn, Ru}$ ) are investigated by using the pair potentials based on lattice inversion technique. In addition, the magnetic properties of  $\text{Lu}_2\text{Fe}_{17-x}\text{T}_x$  compounds with the hexagonal  $\text{Th}_2\text{Ni}_{17}$ -type structure are calculated. The phonon densities of states for  $\text{Lu}_2\text{Fe}_{17-x}\text{T}_x$  ( $T=\text{Cr, Mn, Ru}$ ) are first evaluated. A qualitative analysis is carried out with the relevant potentials for the vibrational modes, which makes it possible to predict some properties related to lattice vibration.

## 2. Methodology

The acquisition of interatomic potentials prepares the groundwork for this research. According to Chen's lattice inversion method, the intermetallic pair potentials can be inverted strictly from the cohesive energy curves [11,12]. A brief introduction to this lattice inversion method is given as follows: it assumes that the total cohesive energy per atom in a perfect crystal can be expressed as the sum of pair potentials, i.e.

$$E(x) = \frac{1}{2} \sum_{R_i \neq 0} \Phi(R_i) = \frac{1}{2} \sum_{n=1}^{\infty} r_0(n) \Phi[b_0(n)x] \quad (1)$$

where  $x$  is the nearest-neighbor interatomic distance,  $R_i$  is the lattice vector of the  $i$ th atom,  $r_0(n)$  is the  $n$ th neighbor coordination number, and  $b_0(n)x$  is the  $n$ th neighbor distance. We extend the series,  $\{b_0(n)x\}$ , into a multiplicative semi-group, then the general equation for pair potential  $\Phi(x)$  can be expressed as

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

in which

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

and the pair potential from the inversion can be expressed as

$$\Phi(x) = 2 \sum_{n=1}^{\infty} I(n) E[b(n)x] \quad (4)$$

\* Corresponding author. Fax: +86 10 62322872.

E-mail address: [qianpinghu@sohu.com](mailto:qianpinghu@sohu.com) (P. Qian).

where  $I(n)$  is determined by

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

$I(n)$  relates only to the geometrical structure of a crystal but not to the element type. Thus the interatomic pair potentials can be obtained from the known cohesive energy function  $E(x)$ .

In order to obtain the necessary interatomic potentials, some simple and virtual structures are designed. First, let us reckon the structure of binary LuFe as a B2 or CsCl structure with two simple cubic (SC) sub-lattices Lu and Fe taken into consideration. Thus, the partial cohesive energy  $E(x)$  of Lu–Fe is obtained as follows:

$$E(x) = E_{LuFe}^{B2}(x) - E_{Lu}^{SC}(x) - E_{Fe}^{SC}(x) \\ = \sum_{i,j,k \neq 0} \Phi_{Lu-Fe} \left( \sqrt{\frac{4}{3} \left[ \left(i - \frac{1}{2}\right)^2 + \left(j - \frac{1}{2}\right)^2 + \left(k - \frac{1}{2}\right)^2 \right]} \chi \right) \quad (6)$$

where  $x$  is the nearest neighbor distance in the bcc structure,  $E_{LuFe}(x)$  represents the total energy curve with the B2 structure,  $E_{Lu}(x)$  or  $E_{Fe}(x)$  is the total energy function with the simple cubic structure. Thus, the pair potentials between distinct atoms  $\Phi_{Lu-Fe}(x)$  can be obtained directly by using Chen's lattice inversion technique. In the same way, all the other kinds of interatomic potentials can be obtained, and they are used to study the actinide intermetallic structures. The inverted pair potentials are approximately expressed as Morse function

$$\Phi(x) = D_0(e^{-\gamma(x/R_0-1)} - 2e^{-(\gamma/2)(x/R_0-1)}), \quad (7)$$

where  $D_0$ ,  $R_0$ ,  $\gamma$  are potential's parameters. To give an impression, some of the calculated interatomic potentials are shown in Fig. 1.

### 3. Structural and magnetic properties of $\text{Lu}_2\text{Fe}_{17-x}\text{T}_x$

#### 3.1. Calculation of the effective potentials

The  $\text{Lu}_2\text{Fe}_{17}$  intermetallic compounds have the hexagonal  $\text{Th}_2\text{Ni}_{17}$ -type structure of space group  $P6_3/mmc$  [9]. The structure of  $\text{Lu}_2\text{Fe}_{17}$  consists of the Lu–Fe-layers (all the Lu atoms and the Fe atoms on the 12j sites) separated by a distorted Kagome net of Fe atoms on the 6g and 12k sites. The Fe atoms on the 4f sites ("dumbbells") alternate with the Lu(2d) atoms along the *c*-axis parallel to purely Lu chains of the Lu(2b) atoms. The structure can be considered as a natural layered system with Fe-layers (basal planes) with dumbbell-like Fe-pairs between them. Experiments have pointed out that the magnetic properties of  $\text{Lu}_2\text{Fe}_{17}$  compounds can be improved by substitution a third element and that different elements have different effect on the performance [3–5,13–15]. In this part, we investigated theoretically the behaviors of

substitution  $T$  in  $\text{Lu}_2\text{Fe}_{17-x}\text{T}_x$  ( $T=\text{Cr, Mn, Ru}$ ) compounds with the hexagonal  $\text{Th}_2\text{Ni}_{17}$ -type structure, by means of the simulation research based on inverted effective pair potentials obtained through Chen's lattice inversion method. To avoid statistic fluctuation, a periodical super-cell  $(\text{Lu}_2\text{Fe}_{17-x}\text{T}_x)_{4 \times 4 \times 4}$  containing 2432 atoms was taken as a calculation unit. To avoid the random error, the results are taken as the arithmetic average of 50 stochastic samples. In fact, the fluctuation is very small. In the calculation, firstly, we substitute  $T$  atoms for Fe at each site of ternary  $\text{Lu}_2\text{Fe}_{17-x}\text{T}_x$  compounds with different concentration. Then the energy minimization method is applied to relax the quaternary system under the interaction of the potentials. Thus the average energy of the final structure can be investigated and compared.

Fig. 2 shows that the calculated average energy and tolerance of  $\text{Lu}_2\text{Fe}_{17-x}\text{T}_x$  for  $x \leq 3.00$ , and the error is omitted in order to make the figure clearer. Here, we suppose that all the ternary elements  $T$  occupy only the same site. The tolerance, which represents the atomic derivation distance can be viewed as the errors in the process of determining the space group of the compound, is an assistant criterion. It can be seen from Fig. 2 that addition of the ternary element Cr, Mn or Ru to  $\text{Lu}_2\text{Fe}_{17}$  as an atom replacing Fe leads to the crystal cohesive energy decrease markedly, illustrating that each of these elements can stabilize the crystal structure. The degree of the decrease in cohesive energy corresponds with the species and occupation sites of the ternary atoms. It shows obviously that the  $\text{Lu}_2\text{Fe}_{17-x}\text{T}_x$  has the lowest energy when  $T$  atoms are substituted for Fe at the 4f sites and the tolerance is acceptable. For  $x \leq 3.00$ , the cohesive energy is lower when  $T$  atoms are substituted for Fe at the 12k, 12j sites than for ones at the 6g sites, and the tolerance is reasonable. This indicates that  $T$  atoms preferentially occupy the 4f sites and avoid the 6g sites, which agrees reasonably well with the experiment results [16,17]. Therefore, the order of site preference is 4f, 12k, 12j and 6g for the hexagonal  $\text{Th}_2\text{Ni}_{17}$ -type structure. When  $x=2.00$  and 3.00, the energy of the 4f and 6g sites rapidly rises and the tolerance suddenly drops down to 0.01 Å. This is because the  $T$  atoms fully occupy the interstitial 4f and 6g sites, and the structure of the system is very symmetric. In other words, in the process of minimization with the conjugate gradient method, the space group of  $P6_3/mmc$  is easy to keep. We cannot draw a conclusion that when  $x=2$  and 3 there exists the most stabilized state, and we can verify this in the reported experimental result [13].

Calculated lattice constants of  $\text{Lu}_2\text{Fe}_{17-x}\text{T}_x$  are listed in Table 1 together with experimental data from literature [13,18,19]. Table 1 shows that our results agree with experimental data. The structure and the lattice parameters of  $\text{Lu}_2\text{Fe}_{17-x}\text{T}_x$  compounds and their carbides are also studied at high temperature. For this, we have performed molecular-dynamics simulations at constant pressure and temperature (NPT) with a  $4 \times 4 \times 4$

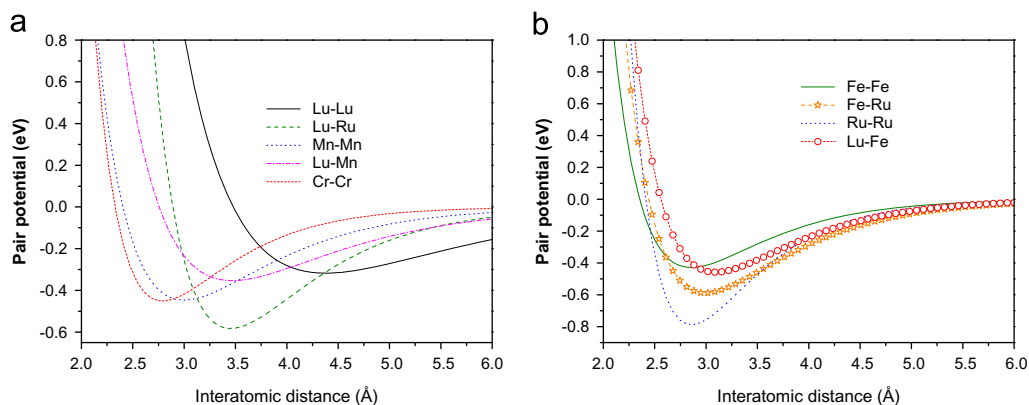


Fig. 1. Some important potentials of Lu–Fe– $T$  system.

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