



Study of the structure and lattice vibrations of $\text{Ce}_6\text{Rh}_{30}\text{Si}_{19}$ and $\text{A}_6\text{Pt}_{30}\text{Si}_{19}$ (A = Th, U)

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ABSTRACT

We present an atomistic study on the phase stability, site preference and lattice constants of the rare earth or actinium intermetallics $\text{Ce}_6\text{Rh}_{30}\text{Si}_{19}$ and $\text{A}_6\text{Pt}_{30}\text{Si}_{19}$ (A = Th, U). The calculated preferential occupation site of one Si atom is found to be the *2b* site in $\text{Ce}_6\text{Rh}_{30}\text{Si}_{19}$ and $\text{A}_6\text{Pt}_{30}\text{Si}_{19}$. The Si atom is located at the sites *2b* with occupancy close to 50%. Our calculated lattice constants agree with a report in the literature. The total and partial phonon densities of states are evaluated first for these complicated defect structures. The analysis of the inverted potentials explains qualitatively the contributions of different atoms to the vibrational modes.

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1. Introduction

Ternary alloys and intermetallic compounds of the R–T–X systems (R: rare earth or actinide element, T: transition metal, X: element from the III or IV group) have recently become an interesting research topic, since many of them exhibit unusual properties, such as anomalous magnetism, Kondo behavior, and/or intermediate valency [1–7]. The Ce–Rh–Si system is known to be exceptionally rich in ternary phases [8–17]. Phase equilibria in this system are characterized by significant mutual solubilities between cerium silicides and cerium–rhodium compounds, as well as by extended homogeneity regions of some of the ternaries. It has been shown in Ref. [18] that up to 6.5 at.% of Si can substitute Rh in the binary compound CeRh_2 , hence forming $\text{Ce}(\text{Rh}_{1-x}\text{Si}_x)_2$ phases. With further substitution along the line one obtains ternary compounds $\text{Ce}_{33.3}\text{Rh}_{58.2-55.2}\text{Si}_{8.5-11.5}$ (unknown structure type) and $\text{Ce}_2\text{Rh}_{3+x}\text{Si}_{1-x}$ ($\text{Y}_2\text{Rh}_3\text{Ge}$ -type), each with its specific homogeneity region. Finally, the formation of pseudobinary phases $\text{Ce}(\text{Rh}_x\text{Si}_{1-x})_2$ is observed with up to 10 at.% of Rh substituted for Si in the binary compound CeSi_2 . The first work on the analysis of atomic arrangement in $\text{Ce}_6\text{Rh}_{30}\text{Si}_{19}$ was reported by Tursina et al. in conjunction with their magnetic properties [17]. In the search for new ternary Th, U intermetallics with Pt offer a good promise as Pt is a constituent element of many intermetallic compounds. The structure

of the ternary compound $\text{U}_6\text{Pt}_{30}\text{Si}_{19}$ was determined by Chotard et al. [19], but no $\text{Th}_6\text{Pt}_{30}\text{Si}_{19}$ were published.

If the possibility of phase formation is known beforehand, the search for new intermetallic compounds would be more efficient. The atomic radius and the enthalpy of formation were widely used to predict the phase formation [20]. However, these methods can only give a semi-experimental estimation of the phase formation and often these methods are inaccurate. It is a shortcut to explore phase stability and site preference from the viewpoint of energy through computer simulation, which combines interatomic potentials with different crystal structures. But it is the structural complexity and particularly, the difficulties in acquiring potentials of rare-earth compounds that frustrates attempts to adopt this method. Chen and Ren [21] proposed the lattice inversion method to obtain the interatomic pair potential, which is very timesaving and effective. And it has been applied successfully to study the site preference of ternary additions [22,23] and lattice vibrations [24,25] for rare earth and actinide compounds. In addition, the calculation of vibrational frequencies by computational methods is becoming increasingly important in many areas [26,27].

The third element not only plays a fairly important role in the phase formation, but also influences greatly the physical properties of the Ce–Rh–Si and A–Pt–Si systems. The possible application of the Ce–Rh–Si and A–Pt–Si systems in many fields has inspired us to study the effect of the third element on the phase formation of compounds. In this paper, we investigated the stabilizing effects of the third Si element on $\text{Ce}_6\text{Rh}_{30}\text{Si}_{19}$ and $\text{A}_6\text{Pt}_{30}\text{Si}_{19}$ (A = Th, U) with the interatomic pair potential obtained with Chen's lattice inversion method. And the lattice vibrational properties for these rare earth

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and actinide compounds are evaluated first, from which the Debye temperature is obtained. These are explorations for the structures of complex materials using the interatomic potentials.

2. Methodology

2.1. Method of obtaining the effective potentials

Atomistic simulation has been widely used to study the properties and behaviors of various materials. A major problem in atomistic simulation is determining interatomic potentials. According to Chen's lattice inversion method, the intermetallic pair potentials can be inverted strictly from the cohesive energy curves [21,28]. The cohesive energy $E(x)$ of a crystal can be expressed as a sum of interatomic pair potentials, i.e.

$$E(x) = \frac{1}{2} \sum_{Ri \neq 0} \Phi(Ri) = \frac{1}{2} \sum_{n=1}^{\infty} r(n) \Phi[b(n)x] \quad (1)$$

where x is the nearest-neighbor interatomic distance, $r(n)$ the n th-neighbor coordination number, $b(n)$ the relative distance between the origin and the n th set of lattice points, and $\Phi(x)$ the pair-potential function. Then, the general equation for pair the potential $\Phi(x)$ can be expressed as

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

The coefficient $I(n)$ can be obtained by Chen's lattice-inversion technique [24,25]. For the reader's convenience, several important potentials are shown in Fig. 1.

2.2. Calculation method for DOS and thermodynamic parameters

In the harmonic approximation of lattice dynamics, the secular equation of the lattice vibrations can be written as

$$\det |D_{\alpha\beta, k\mu}(\vec{q}) - \omega^2 \delta_{\alpha\beta} \delta_{k\mu}| = 0 \quad (3)$$

where ω is the angular frequency and q the wave vector. $D_{\alpha\beta}(\vec{q})$ is a dynamical matrix, and its elements are written as

$$D_{\alpha\beta, k\mu} = (M_k M_\mu)^{1/2} \sum_{R_i - R_j} \phi_{\alpha\beta, ik, j\mu} \exp[-i\vec{q} \cdot (\vec{R}_i - \vec{R}_j)] \quad (4)$$

where $\phi_{\alpha\beta, ik, j\mu}$ is the force constant, \vec{R}_i and \vec{R}_j are positions in the i th and j th cell, and k and μ represent different atoms in the same cell. Using the interatomic pair potential, the force constant can be expressed as

$$\phi_{\alpha\beta, ik, j\mu} = \begin{cases} \frac{1}{2} \left[\frac{R_\alpha R_\beta}{R^3} \phi'_{k,\mu}(R) - \frac{R_\alpha R_\beta}{R^2} \phi''_{k,\mu}(R) - \frac{1}{R} \phi'_{k,\mu}(R) \delta_{\alpha\beta} \right] & \text{if } R \neq 0 \\ - \sum_{k \neq \mu} \phi_{\alpha\beta, i\mu, j\mu} - \sum_{i \neq j} \sum_k \phi_{\alpha\beta, ik, j\mu} & \text{if } R = 0 (\vec{R}_i = \vec{R}_j, \vec{r}_k = \vec{r}_\mu) \end{cases} \quad (5)$$

where $R = |\vec{R}| = |\vec{R}_i - \vec{R}_j + \vec{r}_k - \vec{r}_\mu|$, \vec{r}_μ and \vec{r}_k are the relative positions of the different atoms in the same cell, $\phi_{k,\mu}(R)$ is the pair potential between the k th and μ th atoms, and ϕ' and ϕ'' are the first and second derivative of ϕ , respectively.

The phonon dispersion $\omega(\vec{q})$ is given by Eq. (3). Then the DOS $g(\omega)$ can be acquired from $\omega(q)$. The specific heat can be written as

$$C_V(T) = 3Nk_B \int_0^\infty \frac{(\hbar\omega/k_B T)^2 e^{\hbar\omega/k_B T}}{(e^{\hbar\omega/k_B T} - 1)^2} g(\omega) d\omega \quad (6)$$

In the conventional Debye model, the Debye temperature Θ_D can be defined by $\hbar\omega_D = k_B \Theta_D$. The specific heat can be written as

$$C_V = 3Nk_B (T/\Theta_D)^3 \int_0^{\Theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx \quad (7)$$

where $x = \hbar\omega/k_B T$. If we equate Eq. (7) to Eq. (6) or the experimental specific heat, we can obtain the variation of the Debye temperature with temperature [29]. In fact, the Debye temperature reflects the property of the materials at lower temperature and lower frequency. In this approximation, the Debye model is used for acoustic branches [30]. Therefore, ω_D is the cut-off frequency for the Debye model.

3. Calculated results

3.1. Phase stability and site preference

Chotard et al. [19] have pointed out that $U_6Pt_{30}Si_{19}$ crystallizes with a new type of crystal structure that is hexagonal and belongs to the $P6_3/m$ space group (Fig. 2(a)). There are 11 nonequivalent crystallographic sites in $U_6Pt_{30}Si_{19}$. U atoms occupy 6h sites, and the Pt atoms are in the Pt1(6h), Pt2(6h), Pt3(6h), Pt4(6h) and Pt5(6h) positions. There are four nonequivalent sites, Si1(6h), Si2(6h), Si3(6h) and 2b for Si atoms, and the 2b sites of $U_6Pt_{30}Si_{19}$ are only partially occupied (50%). Tursina et al. [17] reported that Si atoms are located at the 2b(0, 0, 0) and 2a(0, 0, 1/4) sites with a mixable occupancy of 50% in $Ce_6Rh_{30}Si_{19}$. To study the effect of Si atoms on the structural stability of $Ce_6Rh_{30}Si_{19}$ and $A_6Pt_{30}Si_{19}$ (A = Th, U) compounds, we theoretically studied the occupancy behaviors of Si in $Ce_6Rh_{30}Si_{19}$ and $A_6Pt_{30}Si_{19}$ compounds with hexagonal structure.

We are not aware of any reports in the literature on the existence of the ternary structure $Re_6T_{30}Si_{18}$ (Re = Ce, Th or U, T = Rh or Pt), which can be considered the prototype of $Re_6T_{30}Si_{18+x}$. First, we concentrate on the structure of $Re_6T_{30}Si_{18}$. According to experimental [17,19] atomic sites and the lattice parameters of the model, the initial $Re_6T_{30}Si_{18}$ structure is constructed using the modeling software Accelrys Cerius 2. Second, we add the Si atoms to the 2b(0, 0, 0) or 2a(0, 0, 1/4) sites, and then minimize the energy using the conjugate-gradient method based on calculated interatomic potentials with a cut-off radius of potentials of 14 Å. Fig. 1(b) shows the variation of the potential with interatomic distance from 2 to 18 Å. The inset shows the potential curve within the range of 4.5–8.5 Å. The potential Φ_{Rh-Rh} at 8.39 Å is 10^{-5} orders of magnitude, i.e. the interatomic interaction of Φ_{Rh-Rh} is very weaker when the distance is about 8.39 Å. Since all potential curves are rather flat when the distance is larger than 14 Å which means the interaction of potentials than 14 Å can be ignored, the radius of the cut-off is taken as 14 Å.

As a sample system, we chose a $3 \times 3 \times 5$ supercell (2430–2610 atoms in total) as the crystal cell with a periodic boundary to reduce statistical fluctuations. All these configurations are relaxed and the obtained energy is averaged over 40 sample units.

Fig. 3(a) shows the cohesive energy and tolerance of the $Ce_6Rh_{30}Si_{18+x}$ alloys as a function of the Si content 'x'. The error bars in the figure represent the ranges of the root mean square errors. The tolerance, which represents the range of deviation from a space group, is an assistant criterion. Numerous calculations show that, when the tolerance is much larger than 0.50 Å, the structure does not exist. For $x < 0.34$, the energy is the lowest with Si entering the 2b sites of the hexagonal structure, and the tolerance is acceptable. Therefore, the Si atoms will preferentially occupy the 2b sites of $Ce_6Rh_{30}Si_{18+x}$ compounds. Fig. 3(b) and (c) shows the calculated energy of $A_6Pt_{30}Si_{18+x}$ with the hexagonal structure for $x < 1.00$. For $Th_6Pt_{30}Si_{18+x}$ and $U_6Pt_{30}Si_{18+x}$, Si entering the 2b sites has the lowest energy for $x < 0.60$ and 0.53, respectively.

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