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Atomistic simulation on the site preference and mechanical properties of $Th_3Co_{4+x}Al_{12-x}$ and $U_3Co_{4+x}Al_{12-x}$

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Abstract

An atomistic study is presented on the phase stability, site preference and lattice constants of the actinide intermetallic compounds $Th_3Co_{4+x}Al_{12-x}$ and $U_3Co_{4+x}Al_{12-x}$. Calculations are based on a series of interatomic pair potentials related to the actinides and transition metals, which are obtained by a strict lattice inversion method. The lattice constants of $Th_3Co_{4+x}Al_{12-x}$ and $U_3Co_{4+x}Al_{12-x}$ are calculated for different values of x. The site preference of Co atoms at Al sites is also evaluated and the order is given as 6*h*, 4*f*, 2*b* and 12*k* for $Th_3Co_{4+x}Al_{12-x}$, and 6*h*, 4*f*, 12*k* and 2*b* for $U_3Co_{4+x}Al_{12-x}$. In addition, some simple mechanical properties such as the elastic constants and bulk modulus are investigated for the actinide compounds with complex structures.

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Keywords: Interatomic potentials; Actinide compounds; Crystal structure; Mechanical properties

1. Introduction

During the past three decades, U-based intermetallic compounds have been revealed to be a continuous source of materials for the study of unusual physical properties [1–5]. They may exhibit a wide variety of electronic phenomena including heavy fermion behavior, Kondo effect, valence fluctuation, coexistence of magnetism and superconductivity, which still constitutes an important challenge for theory. In theoretical research, Chen et al. have performed studies on the structural properties of 1:5-type compounds and their derivatives [6–17] from the viewpoint of energy. The method combining interatomic potentials with different crystal structures is a shortcut, but can be an effective way of investigating structural stability and site preference. It is accepted that the local atomic environment determines if the energy of a compound is low enough to form a compound with a certain structure. Now, we extend our study to the $Th_3Co_{4+x}Al_{12-x}$ and $U_3Co_{4+x}Al_{12-x}$ compounds. In this paper, interatomic potentials are used to investigate the structural and mechanical properties of actinide compounds $Th_3Co_{4+x}Al_{12-x}$ and $U_3Co_{4+x}Al_{12-x}$.

2. Methodology

2.1. Lattice inversion method

The atomistic simulation has been widely used in the investigation of the structures, defects, and thermodynamic properties of various materials. The key problem with this technique is how to determine the interatomic potentials. In the mid-1990s, Chen used the Möbius inversion theorem in the number theory to obtain interatomic potentials [18,19]. With the lattice inversion theorem, we can do without complicated fitting and parameter adjustment when obtaining the interatomic potentials. Some details

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of the method for obtaining the potentials are given in our previous works [6–17]. The inverted pair potentials are approximately expressed as a Morse function:

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

where D_0, R_0, γ are potential parameters. For the reader's convenience, several important potential parameters are listed in Table 1.

2.2. Second derivative method

There are three basic methods available for calculating mechanical properties in the Cerius2 [20] procedure provided by Materials Simulation Incorporation: second derivative, constant stress minimization and constant strain minimization. All these techniques can be used to obtain the stiffness matrix as well as its inverse, called the compliance matrix. These two matrices are then used to derive the other properties, such as Young's modulus, bulk modulus, Poisson's ratio, and so on. In this work, we use the second derivative method to acquire the mechanical properties of actinide intermetallics.

The second derivative method uses a single-point energy calculation to obtain the second derivatives of the lattice energy with respect to the lattice parameters and the atomic coordinates. The following energy expression is used:

$$U = U_0 + \sum_i \frac{\partial U}{\partial \varepsilon}\varepsilon_i + \frac{1}{2}\sum_{ij}\frac{\partial U^2}{\partial\varepsilon_i\partial\varepsilon_j}\varepsilon_i\varepsilon_j, \quad (2)$$

where U_0 is the equilibrium energy and ε is the strain.

When the structure is at the energy minimum (i.e., all first derivatives of the lattice energy are zero), the second derivative term can be used to calculate the components C_{ij} of the stiffness matrix:

$$C_{ij} = \frac{\partial U^2}{\partial\varepsilon_i\partial\varepsilon_j}. \quad (3)$$

The stiffness matrix computed by this method is always symmetric, that is, $C_{ij} = C_{ji}$. Then the compliance matrix, S, is calculated as the inverse of the stiffness matrix:

$$S = C^{-1}. \quad (4)$$

Table 1
Part of Morse parameters of the conversed pair potentials

	R_0 (Å)	D_0 (eV)	Γ
U–U	3.9415	0.6624	7.3445
Al–Al	3.0059	0.4232	8.9191
Co–Co	2.7087	0.6766	8.9030
Th–Th	4.4270	0.5873	7.2648
U–Al	3.4682	0.5915	8.8707
U–Co	3.2024	0.8835	8.6841
Th–Co	3.2856	0.7465	8.6819

The volume compressibility is calculated from the compliance matrix as follows:

$$\beta = S(1,1) + S(2,2) + S(3,3) + 2[S(3,1) + S(2,1) + S(3,2)] \quad (5)$$

and the bulk modulus is the inverse of the volume compressibility:

$$B = \frac{1}{\beta}. \quad (6)$$

3. Calculated results

3.1. Preferential site occupation of Co

The basic features of the crystal structure of the hexagonal $Gd_3Ru_4Al_{12}$ type were first determined by Gladyshevskii [21]. $Th_3Co_{4+x}Al_{12-x}$ and $U_3Co_{4+x}Al_{12-x}$ crystallize in the hexagonal system with a $Gd_3Ru_4Al_{12}$-type structure in which 32 metal atoms are located at the 2*a*, 6*g*, 2*b*, 4*f*, 6*h* and 12*k* symmetry sites of space group $P6_3/mmc$. Actinide atoms are most reasonably placed at 6*h* sites. The site preference of Co atoms in $Th_3Co_{4+x}Al_{12-x}$ and $U_3Co_{4+x}Al_{12-x}$ has been investigated. The calculation unit of $Th_3Co_{4+x}Al_{12-x}$ and $U_3Co_{4+x}Al_{12-x}$ was a $3\times3\times3$ cell (1026 atoms in total) expanded from the $Gd_3Ru_4Al_{12}$ unit cell. Firstly, we substituted Co atoms for Al at each site with different concentrations. Then, the energy-minimization method was applied to let the ternary system relax under the applied potentials. The average energy was taken as a criterion of the stability. Calculations were performed on 30 samples in each case, with the equivalent Al sites randomly occupied by Co atoms. Fig. 1 shows the calculated average energy of $Th_3Co_{4+x}Al_{12-x}$ and $U_3Co_{4+x}Al_{12-x}$ compositions with $Gd_3Ru_4Al_{12}$-type structure. The error bars in Fig. 1 represent the ranges of the root-mean-square errors. It can be seen from Fig. 1 that the substitution of Co for Al at all the four sites 2*b*, 4*f*, 6*h* and 12*k* decreases the cohesive energy of $Th_3Co_{4+x}Al_{12-x}$ and $U_3Co_{4+x}Al_{12-x}$, which means that the Co atoms can play a role in stabilizing the structure. Furthermore, the Co atoms strongly prefer 6*h* sites, which can easily be concluded from Fig. 1 because the average energy decreases more significantly after Co substitution for Al. The order of the site preference is 6*h*, 4*f*, 2*b* and 12*k* for $Th_3Co_{4+x}Al_{12-x}$, and 6*h*, 4*f*, 12*k* and 2*b* for $U_3Co_{4+x}Al_{12-x}$.

3.2. Crystal structure and phase stability of $Th_3Co_{4+x}Al_{12-x}$ and $U_3Co_{4+x}Al_{12-x}$

According to the results of the site preference, using the conjugate gradient method the lattice constants and interatomic distances of $Th_3Co_{4+x}Al_{12-x}$ and $U_3Co_{4+x}Al_{12-x}$ are calculated. The calculated results are presented in Table 2 and Fig. 2. From Table 2, one can find that our calculated results for the uranium system are close to the experimental results [22]. However, so far, there are no