

An atomistic simulation of site preference and vibrational properties of UM_xAl_{12-x} ($M = Fe, Co, Ni, Cr$ and Mn) and $UM_xAl_{12-x}H_x$

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Abstract

A series of lattice inversion pair potentials are used to evaluate the phase stability and site preference for uranium intermetallics UM_xAl_{12-x} ($M = Fe, Co, Ni, Cr$ and Mn) and their related hydrides. Calculated results show that Fe, Co, Ni, Cr or Mn atoms preferentially substitute Al at the $8f$ site. Interstitial H atoms only occupy $2b$ interstitial sites in UM_xAl_{12-x} . Calculated lattice constants are found to agree with a report in the literature. Elastic constants and bulk modulus of UM_xAl_{12-x} and $UM_xAl_{12-x}H$ were also investigated. In particular, the phonon densities of states (DOS) of these actinide compounds were evaluated for the first time.

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1. Introduction

The discovery of heavy fermion-like behavior in the UCu_xAl_{12-x} system [1,2] has aroused interest in the properties of its derivatives. These alloys crystallize in a $ThMn_{12}$ -type tetragonal ($I4/mmm$ SG) structure with four different crystallographic positions: uranium atoms occupy the $2a$ positions whereas Cu and Al atoms are located in the $8f$, $8i$ and $8j$ positions. Since 1990, interstitial atoms such as H, C and N have been introduced into $R(Fe,M)_{12}$ compounds by a gas-solid phase reaction [3,4] and this has resulted in a dramatic change in magnetic properties of 1:12 compounds. Many experimental and theoretical studies have been carried out on $R-Fe-X$ interstitial compounds [5–8]. It has been found that the introduction of both H and N increases the saturation magnetization and the Curie temperature as well as that N changes the easy magnetization direction of the rare earth sublattice. As for $R(Fe,M)_{12}H_x$, the magnetic

properties of $RFe_{11}TiH$, $RFe_{11.35}Nb_{0.65}H$, $RFe_{12-x}Mn_xH$ and $HoFe_{12-x}Ta_xH$ have been investigated [9–12]. Very few data have been reported about the effects of hydrogen insertion on the physical properties of actinide compounds. We have previously reported structural properties for a series of rare earth compounds such as $R(M,T)_{13}$, $R_2(M,T)_{27}$, $R_3(M,T)_{29}$ ($R =$ rare earth metals; $M = Fe, Co, Al, Mn$; $T =$ transition metals) [13–20]. We thus extend our study to ternary uranium-iron-aluminum compounds UM_xAl_{12-x} ($M = Fe, Co, Ni, Cr$ and Mn) and their related hydrides. Lattice vibrations of these compounds were of particular interest. The purpose of this work was to investigate properties such as site preference, elastic constants and the Debye temperature of these actinide compounds.

2. Theoretical methodology

2.1. The lattice inversion method

Over the last 10 years computational techniques have been applied extensively to the investigation of properties

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Table 1
Morse parameters of some lattice inversion 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
Fe–Fe	2.7361	0.7640	8.7529
Mn–Mn	2.7889	0.8318	8.5108
U–Al	3.4682	0.5915	8.8707
U–Fe	3.2024	0.8835	8.6841
U–Ni	3.3033	0.7185	7.9600
Al–Mn	2.8729	0.6127	8.4451
Al–Ni	2.7212	0.5859	9.1625

and behavior of different materials. One of these techniques is atomistic simulation. The key problem with this technique is the determination of interatomic potentials. In the mid 1990s Chen used the Möbius inversion theorem from number theory to obtain interatomic potentials [21,22]. Methods for obtaining these potentials have been reported in our previous work [13–20]. The potentials are inverted from the cohesive energy and can be fitted simply by the Morse function

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

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. The second derivative method

Three basic methods are available for calculating mechanical properties according to the Cerius2 procedure provided by Materials Simulation Incorporated: 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 referred to as the compliance matrix. These two matrices are then used to derive other properties such as Young's modulus, the bulk modulus, and Poisson's ratio. In this work, we use the second derivative method to acquire mechanical properties of uranium intermetallics.

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

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

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

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

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

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

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

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 this volume compressibility:

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

3. Calculated results

3.1. The site preference of UM_xAl_{12-x} and their related hydrides

For the calculation the structural stability of alloys is judged by the minimum energy. The virtual binary UAl_{12} structure can be considered an intrinsic structure of UM_xAl_{12-x} ($M = Fe, Co, Ni, Cr$ and Mn) compounds even though the UAl_{12} cell is essentially metastable. The calculation unit of UM_xAl_{12-x} was a $3 \times 3 \times 3$ cell (702 atoms in total) and was expanded from a $ThMn_{12}$ unit cell. In this process, we substitute Fe for Al atoms at each binary UAl_{12} compound site with different concentrations. The energy minimization method is then applied to relax the ternary system under the interaction of potentials. The average energy of final structures may thus be investigated and compared. We used 30 samples for each case where equivalent sites were randomly occupied by M ($M = Fe, Co, Ni, Cr$ and Mn) atoms. The relationship between the crystal cohesive energy and the stabilizing elements content is shown in Fig. 1. The error bars denote the range of the root mean square error. After comparing these results it is obvious that the various values of cohesive energy correlate to the amount of M atoms and the three different types of Al crystallographic sites. Within the composition range $x < 4$, M atoms randomly occupy the $8i$, $8j$ and $8f$ sites. The figure clearly shows that within $x < 4$ the cohesive energy is lower when Mn, Fe, Co, Cr or Ni atoms are substituted for Al at the $8f$ site rather than at the $8j$ and $8i$ sites. Mn, Fe, Co, Cr or Ni should thus have a preference for the $8f$ site in the $ThMn_{12}$ structure for $x < 4$. Site preferences in UM_xAl_{12-x} compounds are similar to those in Al-based rare earth compounds [19,20]. Based on the above analysis for the composition range $x > 4$ the equivalent $8f$ sites are fully occupied by $M = Mn, Fe, Co, Cr$ or Ni atoms while the remaining M atoms will occupy the $8j$ or $8i$ sites. Calculated results show that the cohesive energy of UM_xAl_{12-x} decreases more rapidly with Fe, Co, Cr or Ni occupation of $8i$ sites than it does with Fe, Co, Cr or Ni occu-

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