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First-principles investigations on the electronic structures of U_3Si_2

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ABSTRACT

U_3Si_2 has been widely utilized as a high-power uranium fuel for research reactors due to its high density of uranium. However, theoretical investigations on this material are still scarce up to now. For this reason, the computational study via density functional theory (DFT) is performed on the U_3Si_2 compound in this work. The properties of U_3Si_2, such as stable crystalline structures, density of states, charge distributions, formation energy of defects, as well as the mechanical properties are explored. The calculation results show that the U_3Si_2 material is metallic and brittle, which is in good agreement with the previous experimental observations. The formation energy of uranium vacancy defect is predicted to be the lowest, similar with that of UN. The theoretical investigation of this work is expected to provide new insight of uranium silicide fuels.

1. Introduction

The uranium silicide compound has been licensed as a dispersion type fuel in an aluminum matrix by the Reduced Enrichment for Research and Test Reactors (RERTR) Program since 1988 [1–3]. Nowadays, uranium silicide dispersion fuels have been widely utilized and their safe operation has been confirmed by many applications worldwide, mostly with low enriched uranium (LEU, below 20 wt% ^{235}U) and for uranium densities up to about 4.8 gU/cm^3 [4,5]. As the mostly utilized uranium silicide, U_3Si_2 has been applied to reduce enrichment in the existing research reactors [4]. Relative to U_3Si, U_3Si_2 has been identified to be more stable with the growth of fission-gas bubble at high uranium loading in the fuel meat and burnups, and slower in interaction layer growth between uranium silicide and aluminum [6]. Up to now, plenty of research has been carried out in order to characterize the behaviors of the U_3Si_2 and other uranium silicide compounds that may be options as nuclear fuels. For example, Gan et al. [7] reported the microstructure of the irradiated U_3Si_2/Al silicide dispersion fuel. They found the irradiated U_3Si_2/Al dispersion fuel consists of uniformly distributed fission gas bubbles in U_3Si_2 particles. The estimated average diameter, number density and volume fraction for small bubbles (<1 μm) in the fuel particle are ~94 nm, 1.05 × 10^{20} m^{-3} and ~11%, respectively. Kim et al. [6] compared the interdiffusion of U_3Si_2–Al, U_3Si–Al and USi–Al under irradiation and pointed out that the interaction layer growth rates do not decrease with the decreasing U/Si ratio caused by fission. U_3Si_2 has been also studied in great detail on the crystal structure, and magnetic, electronic and thermal properties. Dwight [8] examined the structure of U_3Si_2, which is determined to be a primitive tetragonal structure of the Cu_3Au-type with ten atoms per unit cell. It is also found that U_3Si_2 is a brittle material with a high melting point at 1665 °C. Remschnig et al. [9] have reported the magnetic behavior of U_3Si_2, and they noticed that the susceptibility of U_3Si_2 has a slight linear dependence on temperature between 5 K and 300 K. Thus they deduced that U_3Si_2 is a paramagnetic material. Miyadai et al. [10] also found that the U_3Si_2 is a Pauli paramagnetic metal at low temperature, in

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good agreement with Remschnig's results [9]. Berche et al. [11] performed a detailed thermodynamic study of the U–Si system in which they provided a series of data on the enthalpies of formation for the U–Si compounds. Yagoubi et al. [12] have studied the structural and electronic properties of USi and USi_2 under high pressure using both experimental and theoretical methods. By experimental investigation, they found that USi and USi_2 can keep their crystal structure under high pressure without any noticeable phase transition. This is in good agreement with their calculated results. In their further computational study, the bulk modules of USi and USi_2 are also predicted. Yang et al. [13] investigated the physical properties of binary uranium silicide alloys by means of density functional theory (DFT) calculations and the structures, elastic properties and the Debye temperature of several U–Si compounds are determined theoretically. Chen et al. [14] have reported their theoretical prediction on the electronic structure of two-dimensional uranium silicide thin film with the plane-wave basis pseudopotential.

Numerous efforts have been devoted in the experimental and theoretical investigation on the uranium silicide up to now. However, the report on the computational study on U_3Si_2 at the electronic structure level has barely been mentioned in the literature. In order to gain a deep insight into the electronic structures for U_3Si_2, which are valuable in the evaluation for the safety and lifetime of the U_3Si_2 fuel, it is necessary to conduct theoretical calculations on the U_3Si_2 compound. In this paper, we present our theoretical investigations on the structures, mechanical properties, and the defect formation energies of U_3Si_2 by the first principles DFT method. Our results may provide theoretical support on the industrial application of the uranium silicide fuel.

2. Methods

In this work, the theoretical calculations are performed based on the density function theory [15,16], using the VASP code [17] with the projector-augmented-wave method. In regard to the exchange correlation potential, the PBE functional [18] is utilized within the generalized gradient approximation (GGA). Due to the strong on-site Coulomb repulsion among the localized U 5f electrons, we use the Hubbard (DFT + U) approximation to estimate the strong correlation effect [19]. In this paper, the cut-off energy of plane-wave is 500 eV and a 9 × 9 × 9 Monkhorst–Pack [20] k-point mesh is adopted. The geometries of the U_3Si_2 system are optimized with the force criterion of 0.02 eV/Å, and the total energy is relaxed until the energy difference is smaller than 10^{-5} eV. In the calculations of defect formation energy, the 2 × 1 × 2 supercells containing 40 atoms are constructed so that the boundary effect on the formation of defects can be negligible, and the K-point for the supercells are chosen to be 2 × 2 × 2 with consideration of both the accuracy and the computational cost.

3. Results and discussions

3.1. The crystal structures of U_3Si_2

The compound U_3Si_2 has a tetragonal structure, and there are ten atoms in the conventional unit cell with the space group of P4/mbm, as shown in Fig. 1. The structure is obviously of Cu_3Au-type with a U atom located in the Cu site and a pair of Si atoms in the position of the single Au atom. In order to examine the ground-state properties of U_3Si_2, we calculated the stable crystalline structures by the DFT + U scheme as adopted in the studies of many other uranium nuclear fuels , such as UO_2, UN, UC and etc. [21–23]. The U value employed in this work is determined systematically by using different U values to predict the lattice parameters of U_3Si_2

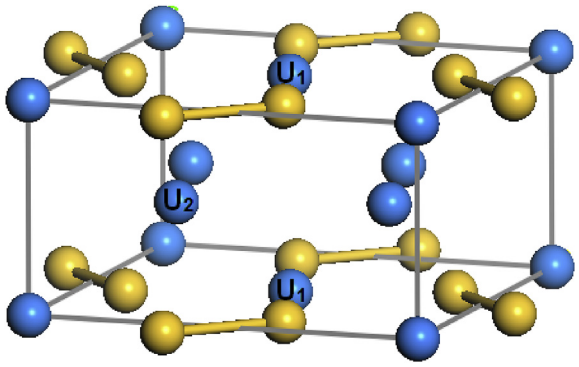

Fig. 1. The crystal structure of U_3Si_2.

and comparing them with experimental observations. The experimental and calculated lattice constants are both displayed in Fig. 2. If the calculations are conducted without the Hubbard correction, (U = 0.0), the predicted lattice constant of *a* is significantly lower than the experimental one (7.14 Å vs 7.33 Å), which is a reflection that Hubbard correction is a necessary procedure for the improvement of prediction on the U_3Si_2 system. According to this work, it is found that when U equals to 4.0 eV, the calculated lattice constant ($a = b$) and the total volume of the unit cell are the closest to the experimental values (lattice a: 7.32 Å vs 7.33 Å [8]; volume: 208.20 $Å^3$ vs 209.63 $Å^3$ [8]). Hence, in this paper the physical properties of U_3Si_2 are all estimated by the GGA + U (U = 4 eV) approach. As shown in Fig. 1, there are two types of U atoms in a unit cell of U_3Si_2, which are denoted as U_1 and U_2 in the figure, respectively. The U_1 atoms are neighbored by Si atoms in the (001) lattice plane of the unit cell. While, the atoms U_2 are located in the (002) plane where only U atoms are present.

From this work, the calculated bond distances of U–Si are from 2.847 to 2.971 Å. The distances of the shortest U–U and Si–Si bonds are found to be 3.308 and 2.386, respectively. The bond lengths of our optimized structures are in accord with the experimental values [24]. According to the interatomic distances, covalent bonds are formed between the two adjacent silicon atoms and the interactions between U and Si atoms are probably ionic bonding. The U–U distance is close to the value of weak bonds in the metallic uranium [25], which may imply that the U–U interaction is likely a

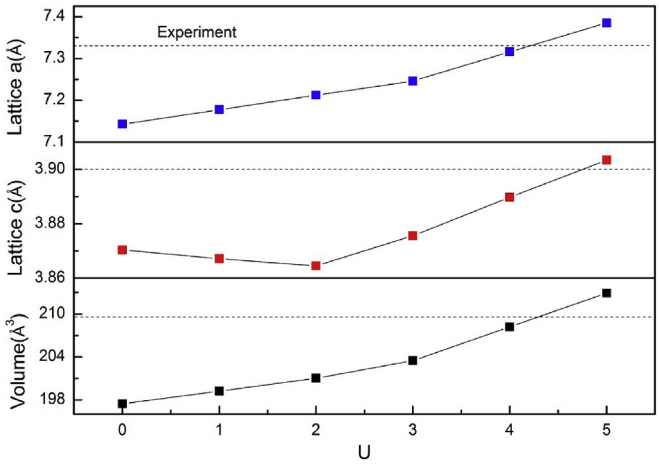

Fig. 2. The lattice parameters a and c (Å) and the volume ($Å^3$) of the unit cell of U_3Si_2 predicted with different U values in the GGA + U calculations. The experimental values are shown as the horizon dash line.