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Crystal structure prediction of uranium hydrides at high pressure: A new hydrogen-rich phase

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ABSTRACT

Uranium hydride is a novel hydrogen-rich system which contains $5f$ electrons. Uranium hydride can not only be used in the nuclear fuel industry, but also be a candidate of high superconducting-temperature materials. In this paper, we have searched the stable uranium hydride structures by using particle swarm optimization method and first-principles calculations. Besides UH_8 and UH_9, we find that UH_{17}, which contains larger hydrogen content than most hydride materials reported before, is also stable at high pressure. The atomic structures, electronic structures and phase diagram of uranium hydrides are provided, and we find that all of the discovered uranium hydrides are metals with negligible magnetic moments.

1. Introduction

Since Ashcroft proposed the theoretical prediction of high-temperature superconductivity in solid metallic hydrogen in 1968 [1], extensive researches on hydrogen-rich superconductors, such as SiH_4 [2,3], GeH_4 [4], SiH_4–H_2 [5,6], GeH_4–H_2 [7], PbH_4–H_2 [8], CaH_6 [9], H_2S–H_2 [10], and YH_{10} [11] systems at high pressure, have been carried out both theoretically and experimentally. Up to now, the highest known Tc is 203 K for H_xS [12]. Recently, theoretical research predicted that the superconducting transition temperatures of some actinide hydrides, such as UH_8 and ThH_{10} [13,14], can be as high as 193 K.

Also, actinide hydrides have important applications in the nuclear fuel preparation industry [10]. On the one hand, uranium is widely used as nuclear materials. On the other hand, heated uranium metal can react with hydrogen to produce uranium hydrides [15], which are convenient starting materials to create reactive uranium powder along with various uranium carbide, nitride, and halide compounds [16]. In addition, actinide-based materials have attracted much interest due to the existence of $5f$ electrons. Therefore, exploring the crystal structures and phase transitions of uranium hydride under different pressures is important for both fundamental scientific research and nuclear industry applications.

At present, the main focus of uranium hydride system is on UH_3, which has two allotropes, i.e. α-UH_3 and β-UH_3 [17–19]. The crystal structure and phase transition have been reported through X-ray diffraction measurement [20–22]. However, the phase transition temperature and the stability of α-UH_3 remain controversial due to the lacking in adequate investigations. Furthermore, there are no experimental reports for other uranium hydride compounds. Recently, using *ab initio* evolutionary crystal structure prediction, Yanilkin et al. have predicted new superconducting uranium hydride compounds, such as U_2H_{13}, UH_7, UH_8, U_2H_{17} and UH_9 [14]. Along this line, more theoretical and experimental works are expected to occur in the near future.

In this paper, crystal structure prediction of uranium hydrides at high pressure has been performed using first-principles calculations. The phase diagram of uranium hydride under high pressure ranging from 0 to 300 GPa is shown in our work. From phase diagram, we have predicted three stable phases (UH_8, UH_9, UH_{17}), among which the new stable phase UH_{17} contains larger content of hydrogen than other reported hydride materials. Finally, the electronic properties and magnetic properties of the stable phases are also analyzed.

2. Computational models and methods

For uranium hydride system UH_x, we have considered a wide range of stoichiometries, i.e., x equals 0.5, 1, 2, 3, …, 18, and

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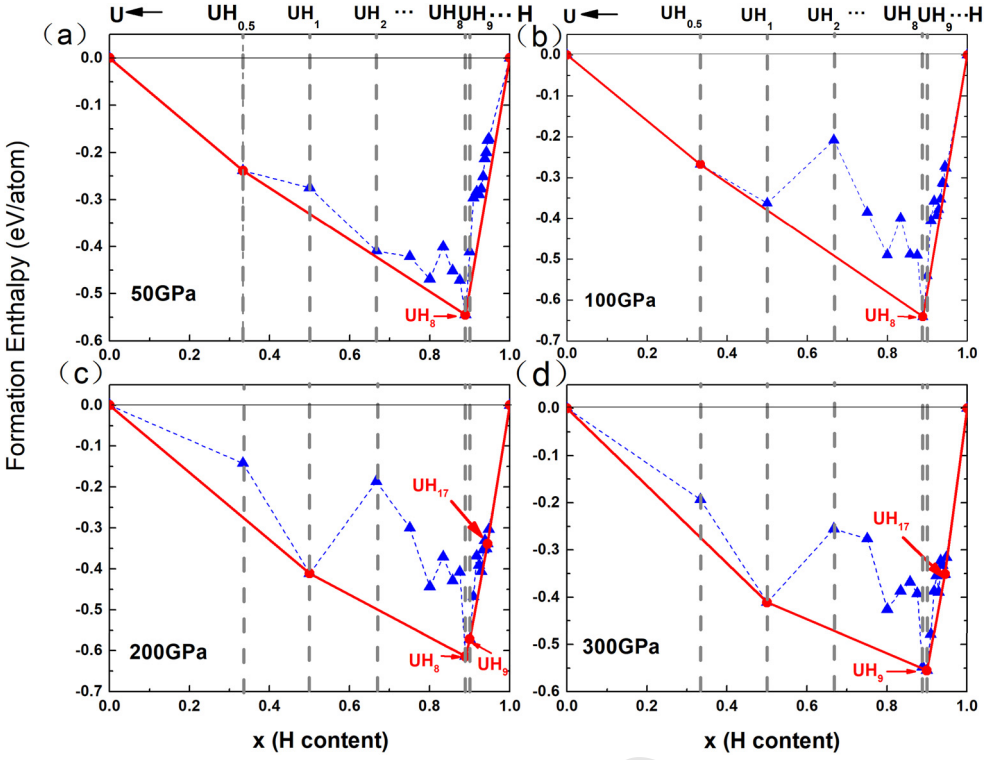

Fig. 1. Calculated formation enthalpies of U–H system with respect to the decomposition into solid uranium and molecular hydrogen at pressure 50 GPa (a), 100 GPa (b), 200 GPa (c) and 300 GPa (d). (For interpretation of the colors in the figure(s), the reader is referred to the web version of this article.)

performed variable-composition phase search at pressures of 50, 100, 200, and 300 GPa. High pressure phases were searched by CALYPSO (Crystal structure Analysis by Particle Swarm Optimization) [23] which is based on PSO (Particle Swarm Optimization) algorithm [24,25]. For each compound, our structure searches were performed with each generation contained 40 structures. We usually followed 25–30 generations to find the lowest enthalpy structure. Thermodynamically stable phases of given composition and pressure can be obtained through CALYPSO. In order to get more accurate enthalpies and phase diagram of the obtained compounds, four crystal structures of each compound obtained from CALYPSO which have the lowest energies were picked out and more precise DFT (Density Functional Theory) [26] calculations were executed by using first-principles software VASP (Vienna Ab-initio Simulation Package) [27,28] based on the PAW (Projector-augmented Wave) method [29]. The exchange-correlation potential used in the calculation is generalized gradient approximation [30] (Perdew–Burke–Ernzerhof functional). The cutoff energy is 500 eV, and the spacing between k-points was set to be 0.2 $Å^{-1}$. Convergence thresholds were set as 10^{-6} eV in energy and 10^{-2} eV/Å in force. And a conjugate-gradient algorithm was used to relax the structure.

To describe the precise properties, relativistic effect and correlation effect of the system, spin-orbit coupling was included in our calculation [31] and U $5f$ electrons were treated with an effective Hubbard U. According to the simplified derivation proposed by Dudarev et al. [32], the effective U parameter equals the on-site Coulombic repulsion U minus exchange constant J. In our calculation, J = 0.5 eV was adopted which was commonly used for uranium atoms in UO_2 systems [32–36]. And the on-site Coulombic repulsion U was chosen as U = 2, 4, and 6 eV to test the influence of electronic correlation effect in the presence of $5f$ electrons in uranium atoms.

3. Results and discussion

3.1. Phase diagram

The variable-composition structural searches for UH_x systems were performed at a variety of given U–H stoichiometries with given pressures 50, 100, 200 and 300 GPa. For several most stable compounds predicted by CALYPSO of all the stoichiometries, further crystal relaxations were performed using VASP which is fairly precise. The stability is determined by the formation enthalpy per atom ΔH with the following formula: $\Delta H = \frac{H(UH_x) - H(U) - \frac{n}{2}H(H_2)}{1+n}$, in which $H(UH_x)$, $H(U)$ and $H(H_2)$ are the enthalpies of UH_x system, solid uranium and hydrogen molecule, respectively. The numbers 1 and n in the denominator of the equation are the numbers of uranium and hydrogen atoms in UH_x systems. For certain composition, only the most stable structure is given, which has the lowest formation enthalpy ΔH.

For uranium hydride system UH_x under high pressures, calculated formation enthalpies with respect to the decomposition into solid uranium and molecular hydrogen at each pressure are given in forms of convex hulls, as shown in Fig. 1. Fig. 1 (a)–(d) represent the pressures of 50, 100, 200 and 300 GPa, respectively. The dots on the blue dashed lines represent the most stable phases at each pressure, and the red solid lines are the elemental decomposition line, above which there will be a chance for UH_x to decompose to other phases. The horizontal axis is the content of the H atom in UH_x system, i.e., $x = \frac{n}{1+n}$.

It can be seen that all the formation enthalpies are negative, while most of the investigated UH_x compounds stay above the elemental decomposition line (red solid line), which are energetically metastable with respect to decomposition into solid uranium and molecular hydrogen. The red dots on the hulls are compounds that are energetically stable, which are against decomposition. We can get the most stable phases which are red dots on the hull at each pressure in Fig. 1: $P\bar{4}m2$-$UH_{0.5}$ and $Fm\bar{3}m$-UH_8 for 50 GPa;