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Phase transitions of actinium dihydride: Pressure-induced charge transfer driving effect

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ABSTRACT

The crystal structures of actinium dihydride (AcH₂) in a wide pressure range of 0–200 GPa have been investigated by using an unbiased structure searching method coupling with first-principles density functional calculations. A series of pressure-induced phase transitions are predicted for AcH₂, as *Fm-3m* → *P4₂/mmc* → *Imma* → *P6/mmm*, and the calculated pressures of the phase transitions are 12, 27, and 68 GPa. Under pressure, the coordination number of H atom increases and the nature of chemical bonds changes. The electronic band structures show that all of the competitive phases are metallic. The pressure-induced charge transfer drives the phase transition. Phonon calculations show the competitive phases are thermodynamically stable within their favored pressure range. Our results elucidate the phase transition mechanisms of AcH₂ under pressure, and have major implications for the high-pressure behaviors of actinide and rare-earth metal dihydrides.

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Introduction

Metal–hydrogen systems constitute a productive field in materials science and have attracted considerable attention from the scientific community because of their promising properties from both fundamental and practical points of views [1–3]. Recently, there is a resurgence of interest in the properties of actinide hydrides because of their potential utility in hydrogen storage and nuclear fuels, particularly under high pressure [4–14]. Actinide hydrides have a broad range of H-to-metal atom ratio, such as 2 for PuH₂ and 3.75 for

Th₄H₁₅, and exhibit fascinating structural and electronic properties. Actinide metals form various binary hydrides within the short span of three elements (Th, Pa, and U). Thorium hydrides, ThH₂ and Th₄H₁₅, have considerably different stoichiometries. Th₄H₁₅ is a superconductor with transition temperature of approximately 9 K [15], whereas ThH₂ does not function as a superconductor until the temperature is down to 1.2 K [16]. The U–H system directly becomes a trihydride without an intervening monohydride or dihydride phase [17]. Uranium trihydride is one of the first ferromagnetic uranium compounds observed, and it exists in two allotropes with the same *Pm-3n* symmetry, i.e., a low

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temperature α -UH₃ phase [18] and a high temperature β -UH₃ phase [19]. With high hydrogen contents, the Pa–H system adopts a cubic hydride isostructure similar to UH₃. With low hydrogen contents, the Pa–H system has a unique Pa₃H₄–Pa₃H₅ solid solution owning both metal–metal and metal–hydrogen bonding [20].

The properties of solids as a function of pressure are of fundamental interest to a wide range of materials science. High pressure can reduce the interatomic distance and change bonding patterns, thus causing profound effects on the physical and chemical properties and generating many new materials that cannot be formed under normal conditions. However, studies of actinide hydrides under high pressure are scarce, thereby hindering their practical applications. To the best of our knowledge, only investigations involving UH₃ under pressure have been conducted. The crystal and electronic structures of β -UH₃ under high pressure were studied through the X-ray diffraction measurements and full potential linearized augmented plane-wave calculations [21]. The β -UH₃ does not undergo phase transition until pressure reaches 29 GPa. The calculated value of the electric field gradient main component at the uranium site is linearly dependent with pressure. Andreev et al. found a highly positive spontaneous volume magnetostriction and a large high-field magnetic susceptibility accompanied by a considerable decrease in magnetic moment and Curie temperature under external pressure [22]. In our previous work, the mechanical and thermodynamic properties of α -UH₃ under pressure were analyzed by first-principles pseudopotential plane-wave calculations based on the density functional theory [23]. The pressure evolution of the elastic constants of α -UH₃ is revealed, and α -UH₃ is found to be mechanically stable at least up to 20 GPa. Under pressure, the low-frequency vibration modes of α -UH₃ slightly change, and the high-frequency vibration modes shift upward.

The preparation of actinium hydride has been reported by Farr et al. [24] The product was obtained at microgram level as a mixture of Ac metal and KCl after the reduction of AcCl₂ by K at 350 °C. By comparing its X-ray diffraction patterns with the LaH₂ analog, actinium hydride has been suggested to adopt a face-centered cubic (fcc) structure with a H/Ac ratio of approximately two. During the hydrogenation reaction to a dihydride, the volume of Ac metal lattice expands by approximately 22%, which is common in fcc rare-earth metal dihydrides [25–28]. The large volume expansion is attributed to negatively charged hydrogen atoms at the tetrahedral sites, which are generated by the charge transfer from the surrounding metal atoms. With the numerous technical difficulties under ambient and high pressures, experimental evidences do not allow a thorough description of the properties of AcH₂; thus, first-principles calculations assume a fundamental role. The development of reliable theoretical simulation would be significantly beneficial, particularly in the field of the nuclear materials, in which adequate experimental data are lacking.

In this work, we report systematic studies of phase transitions of AcH₂ under high pressure using the first-principles calculations. Under high pressure, AcH₂ undergoes cubic-tetragonal, tetragonal-orthorhombic, and orthorhombic-hexagonal phase transitions at 12, 27, and 68 GPa,

respectively. Moreover, the coordination number of H correspondingly becomes larger with increasing pressure, changing from four in the cubic phase to six in the hexagonal phase. The charge transfer, particularly the electronic *s*-*d* transition, drives these phase transitions. Phonon calculations establish the dynamical stability of the interested phases in their favored pressure ranges. In view of the special position of Ac in the periodic table, the obtained high-pressure behaviors of AcH₂ would have significant implications for understanding the high pressure structural characteristics of actinide and rare-earth metal dihydrides.

Computational methods

The structure prediction approach was based on a global minimization of free energy surfaces merging the first-principle total-energy calculations via a particle swarm optimization technique as implemented in the CALYPSO code [29–31]. This method had been successfully predicted structures of various systems ranging from elemental solids to binary and ternary compounds [32–38]. To search for stable high-pressure structures, we have performed calculations with 1–4 formula units (f.u.) per simulation cell at 0, 50, 100, 150, and 200 GPa, respectively. The underlying first-principles structural relaxations were carried out within the framework of density functional theory as implemented in the Vienna Ab-initio Simulation Package (VASP) [39]. In these calculations, the exchange and correlation energy was assessed by the generalized gradient approximation (GGA) in the scheme of Perdew–Burke–Ernzerhof (PBE) [40]. The electron–ion interaction was described by means of projector augmented wave (PAW) [41] with 6s²7s²6p⁶d¹ and 1s¹ as valence electrons for Ac and H atoms, respectively. Candidate structures were selected and then recalculated using a higher accuracy using a Brillouin zone sampling of $2\pi \times 0.028 \text{ \AA}^{-1}$, and a plane-wave basis set cutoff of 350 eV. Iterative relaxation of atomic positions was stopped when the forces generally acting on the atoms were found to be smaller than 0.01 eV/Å. With this criterion, the change in total energy between successive steps was less than 0.01 meV/cell. Phonon calculations were performed by the supercell approach [42]. Real-space force constants of supercells were calculated within VASP, and phonon frequencies and the corresponding phonon density of states were calculated from the constants using the PHONOPY code [43,44].

Results and discussion

The phase stability of AcH₂ within the pressure range 0–200 GPa has been investigated systematically using CALYPSO code. With the only knowledge of chemical compositions, the experimental ambient-pressure fcc *Fm*-*3m* structure can be correctly reproduced [24], justifying the validity of CALYPSO methodology used in the structural searches of AcH₂. In addition to the known *Fm*-*3m* structure, five competitive structures with different symmetries were selected from a large set of structures. The enthalpy difference of competitive structures in the pressure range from 0 to 200 GPa is presented

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