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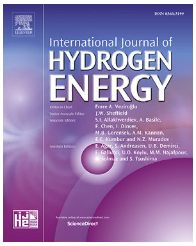

Review Article

Structural, magnetic, and dynamic properties of PuH_{2+x} (x= 0, 0.25, 0.5, 0.75, 1): A hybrid density functional study

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ABSTRACT

Plutonium (Pu) can react with hydrogen to form complicated continuous solid solutions with unusual chemical and physical properties. The PBE0 hybrid density functional under the framework of full-potential linearized augmented plane wave plus local orbitals is employed to investigate the structural, magnetic, lattice vibrations, and thermodynamic properties of face-centered cubic plutonium hydride (PuH_{2+x}, $x = 0, 0.25, 0.5, 0.75, 1$). The decreasing trend with increasing x of the optimized lattice parameters is in reasonable agreement with experimental findings. According to the calculated formation enthalpies of PuH_{2+x} compounds, all PuH_x for both ferromagnetic(FM) and antiferromagnetic (AFM) phase are thermodynamically favorable, and the FM phase plutonium hydride is more favorable than the AFM phases. The characteristic Raman-active and the infrared-active modes at the center (Γ point) of the first Brillouin zone were further assigned and discussed. Finally, the free energy F, internal energy E, vibration enthalpy S, and constant-volume specific heat C_V of PuH_{2+x} are calculated in the range of 0–1000 K.

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Introduction

Plutonium-based materials have numerous novel properties of practical as well as fundamental scientific interest, which are mainly due to the unique characteristics of the 5f electronic states and the nuclear properties of plutonium [1]. Plutonium hydride in particular has generated increasing interest in recent years due to the considerations of long-term storage and safe handling of plutonium metal [2] and the application of plutonium-hydrogen reaction for the recycling of excess weapons-grade plutonium [3]. Concerns exist about the safety of the reaction between the plutonium metal and outgassed water, which forms plutonium hydride during long-term storage of plutonium metal [4–6]. Consequently, a comprehensive knowledge of plutonium-hydrogen reaction and plutonium hydride is desirable.

An increasing number of experimental efforts has been conducted to elucidate the behavior of plutonium hydride. Plutonium is known to strongly absorb hydrogen [7] and a solid PuHx solution can exist over a wide H:Pu range ($2.0 < x < 3.0$) [8]. The conditions under which plutonium hydride is formed have a significant impact on its ignition properties [8,9]. When plutonium hydride is produced slowly at temperatures below 373 K, a face-centered-cubic (fcc) phase forms, which auto-ignites easily in air at room temperature. If formation occurs at temperatures above 673 K and at several bars of hydrogen pressure, the resulting plutonium hydride forms a hexagonal close-packed (hcp) phase, which is not pyrophoric at room temperature [9].

PuH_{2+x} ($0 < x < 1$) crystallizes into the fcc system with the tetrahedral interstitials (H_t) being occupied by H atoms [10]. X-ray diffraction data show that the fcc and hcp phases coexist at $x = 2.8$–3.0 [8,11,12]. The lattice parameters of hcp PuH_3 were also obtained using the nuclear magnetic resonance (NMR) techniques [13].

There are several experiments exploring the chemical thermodynamic properties of plutonium hydrides. Johns et al. [14] first reported the pressure-temperature relationship for the plutonium-hydrogen reaction. The heat required for the formation of PuH_2 and PuD_2 were measured by Mulford et al. [15] according to the reactions: Pu(solid) + H_2(gas) → PuH_2(solid); Pu(solid) + D_2(gas) → PuD_2(solid). Oetting et al. [16] and Colmenares et al. [17] used the calorimetric system to determine the heat of formation of PuH_2 and PuH_3. The pressure dependence of the initiation phase of the plutonium hydride reaction was determined by McGillivray et al. [18] at 298 K, over the pressure range 10–1000 mbar.

When plutonium metal reacts with hydrogen to form plutonium hydride, the magnetic order can be observed due to an alteration of the Pu 5f occupancy states [19,20]. The magnetic susceptibility and X-ray photoemission experiments by Ward et al. [21] and Willis et al. [22] showed a ferromagnetic (FM) order for PuHx ($x = 1.93$, 2.16, 2.24, 2.52, and 2.56) in the temperature range 44 K–67 K. Bartscher et al. [23] reported the FM order for PuDx ($x = 2.25$, 2.33 and 2.65) using the neutron powder diffraction techniques at several temperatures between 20 K and 290 K. However, the magnetic susceptibility experiment by Aldred et al. [24] indicated an antiferromagnetic (AFM) order for $PuH_{1.99}$ below 30 K, which was not consistent with previous experiment results. Willis et al. [22] suggested that the difference may be a result of the samples used. In a recent experiment, FM $PuH_{1.9}$ was also detected by Kim et al. [20] in X-rays and magnetization measurements below 40 K.

However, experimental observations of the formations and properties of plutonium hydrides are scarce because of its instability and radioactive nature [1]. Density-functional theory (DFT) is a ground-state theory can be used to quickly simulate the electronic structure of materials and thereby obtain basic properties at the atomic level with comparable accuracy [25,26]. Therefore, over the last three decades, many first principles techniques from traditional DFT to DFT + U have been performed to explore the electronic structure of Pu hydride. Ao et al. [27–30] first predicted the metal-insulator transition and the lattice contraction of Pu hydride within LDA + U frameworks. The phase transition and electronic and magnetic properties of PuH_3 under high pressure were also predicted by Sudhapriyanga et al. [31] within the GGA + U scheme. Zheng et al. [32] investigated the electronic structure and phase stability of PuH_2 and PuH_3 by means of the LDA + U + SOC approach. Electronic structural and spectroscopic properties of PuHx ($x = 2$, 3, 4) were studied at the atomic level by Balasubramanian et al. [33] based on DFT. Taylor et al. [34] performed density functional computations to investigate the molecular and atomic chemisorption of hydrogen on the δ-Pu (111) surface in its interstitial sites, vacancy, and grain boundary, respectively.

Whereas most experimental and theoretical studies have focused on the structure and magnetic and electronic properties of plutonium hydride, the lattice vibrations and thermodynamic properties of stoichiometric and non-stoichiometric compounds of PuH are still poorly understood. An accurate determination of lattice vibrations is important in studying a wide variety of physical properties of solids, including infrared, Raman, free energy, internal energy, vibration entropy, and constant-volume specific heat properties. In the present study, the structural, magnetic, lattice vibration, and thermodynamic properties of PuH_{2+x} ($x = 0$, 0.25, 0.5, 0.75, 1) are investigated by combining phonon dynamics theory with the PBE0 [35] hybrid functional. Within the harmonic approximation [36], the thermodynamic properties, such as the temperature-dependent enthalpy and

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