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# Electronic structure and phase stability of plutonium hydrides: Role of Coulomb repulsion and spin-orbital coupling

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## ABSTRACT

The electronic and magnetic states, chemical bonding and reactions, and phonon spectrum of the plutonium hydrides  $\text{PuH}_x$  ( $x = 2, 3$ ) are investigated by employing first-principles calculations by means of the density functional theory (DFT) +  $U$  approach. The strong correlation and the spin-orbit coupling (SOC) effects on these 5f electrons systems are systematically studied. Results show that both the strong correlation and the SOC play critical roles in correctly describing their ground-state properties. The antiferromagnetic configuration of  $\text{PuH}_2$  is found energetically most stable while for  $\text{PuH}_3$  the ferromagnetic state is the most stable state. Our calculated phonon spectra clearly indicate the dynamical stability of these magnetic configurations. For  $\text{PuH}_3$ , more electrons from the Pu atoms are released to bond with H than that in  $\text{PuH}_2$ . As a result, the lattice constant is contracted by increasing the H concentration. Reacting from metal Pu and molecule  $\text{H}_2$ , more  $\text{PuH}_3$  should be produced than  $\text{PuH}_2$  in low temperature condition.

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## Introduction

Plutonium is a very important component of several materials for nuclear applications. It exhibits six crystal structures between absolute zero and melting point and has attracted many experimental and theoretical investigations due to the unique character of its 5f states, intermediate between localized and delocalized [1]. For its oxides  $\text{Pu}_2\text{O}_3$  and  $\text{PuO}_2$ , the localization behavior of 5f electrons has been confirmed widely by density functional theory (DFT) +  $U$  calculations

[2–5]. However, the DFT +  $U$  can not reproduce the minimum energy state of the nonmagnetic (NM) insulating solution for  $\text{PuO}_2$ . By including the spin-orbit coupling (SOC) in the DFT +  $U$  calculations, in more recent works [6–8], the NM insulating ground-state of  $\text{PuO}_2$  was successfully described.

Concerning plutonium hydrides instead, for  $\text{PuH}_x$  with  $x = 1.99$ , the magnetic susceptibility experiment by Aldred et al. [9] indicated an antiferromagnetic (AFM) order below 30 K. After increasing the hydrogen concentration  $x$  in the range between 2.33 and 3, only ferromagnetic (FM) order was observed even under 4 K. In another experiment, Willis et al.

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[10] reported FM order for  $x = 1.93$  to  $2.65$  until  $T = 1$  K. The differences between the results presented by Willis et al. and Aldred et al. were attributed by Willis et al. to the different samples they used. Besides, the X-ray photoelectron spectroscopy (XPS) measurements of  $\text{PuH}_{2.1}$  by Willis et al. presented a Pu 5f-6d hybridized band  $1.8$  eV below the Fermi level. On the theory side, Eriksson et al. [11] have investigated the chemisorbed state of H on Pu by using the full-potential linear augmented-plane-wave (FLAPW) method. The localized 5f electrons in spin-polarized  $\text{PuH}_2$  were found to induce a substantial conduction-band moment. Later, Ao et al. [12] concluded that the DFT + U gives an equilibrium lattice constant in better agreement with experiments than the pure DFT. In addition, the authors reproduced the lattice contraction for increasing H concentration, which is clearly observed in experiment. By including SOC in the DFT + U, Guo et al. [13] calculated the structural, magnetic, electronic, and elastic properties of face-centered cubic (fcc)  $\text{PuH}_x$  ( $x = 2, 3$ ). They predicted that the fcc  $\text{PuH}_2$  is a metal and the fcc  $\text{PuH}_3$  is a semiconductor with a band gap of about  $0.35$  eV.

However, to our knowledge, some of the ground-state properties of plutonium hydrides are still unclear or debated, and no data for phonon spectrum can be found in literature. Thus, a systematical investigation from first-principles is required. In the present study, the lattice parameter, electronic structure, magnetic state, and phonon spectrum of  $\text{PuH}_x$  ( $x = 2, 3$ ) are calculated by employing the DFT + U/DFT + U + SOC schemes. We discuss to what extent the on-site Coulomb repulsion and the SOC can affect those properties. The nature of the chemical bonding of these two typical Pu–H systems is also presented, both qualitatively and quantitatively. The rest of this paper is arranged as follows. In Section Computational method the computational method is briefly described. In Results Section we present and discuss our results. In Conclusion Section we summarize the conclusions of this work.

## Computational method

Our first-principles total energy calculations are performed by means of the Vienna ab initio simulation package (VASP) [14], based on the frozen-core projected augmented wave (PAW) method of Blöchl [15]. The exchange and correlation effects are described with the local density approximation (LDA) or generalized gradient approximation (GGA) [16,17], and a cutoff energy of  $550$  eV is used for the set of plane waves. The Monkhorst–Pack (MP) [18]  $9 \times 9 \times 9$  mesh is used in the Brillouin zone (BZ) for the fcc unit cell of both  $\text{PuH}_2$  and  $\text{PuH}_3$ , which turns out to be sufficient to get results converged to less than  $1.0 \times 10^{-6}$  eV. The Pu 6s<sup>2</sup>7s<sup>2</sup>6p<sup>6</sup>6d<sup>2</sup>5f<sup>4</sup> and the H 1s<sup>1</sup> orbitals are treated as valence electrons. The strong on-site Coulomb repulsion among the localized Pu 5f electrons is described by using the LDA/GGA + U approach formulated by Dudarev et al. [19–21], where the double counting correction has already been included as in the fully localized limit (FLL) [22]. In this paper, we study several values of the Hubbard parameter U, while we keep the Hund's exchange parameter fixed to  $J = 0.51$  eV. One can notice that only the difference between U and J is significant, and we will henceforth refer to

it as a single parameter, named U for sake of simplicity. Due to the strong SOC effects on the electronic structure of these plutonium hydrides, as already reported in a earlier DFT study [13], in our present work we also discuss the energy, electronic structure, and phonon spectrum with and without inclusion of the SOC.

## Results

### Atomic and electronic structures of plutonium hydrides

The crystal structures of  $\text{PuH}_2$  and  $\text{PuH}_3$  are shown in Fig. 1.  $\text{PuH}_2$  crystallizes in the fcc fluorite-type structure with space group  $Fm\bar{3}m$  (No. 225). Its unit cell is composed of four formula units (f.u.) with the plutonium atoms and the hydrogen atoms in  $4a(0, 0, 0)$  and  $8c(0.25, 0.25, 0.25)$  Wyckoff sites, respectively [see Fig. 1(a)]. The structure of the fcc  $\text{PuH}_3$  also belongs to the  $Fm\bar{3}m$  space group, as shown in Fig. 1(b). Compared with  $\text{PuH}_2$ , more hydrogen atoms appear in  $\text{PuH}_3$ . They occupy the  $4b(0.5, 0.5, 0.5)$  site and are labeled as H2 in Fig. 1(b). Moreover, we define the hydrogen atoms in the  $8c(0.25, 0.25, 0.25)$  site of  $\text{PuH}_3$  as H1.

In the present work, both spin-unpolarized and spin-polarized calculations are performed. Due to the fact that the NM phase of the two plutonium hydrides is not energetically favorable compared with their FM and AFM phases, as clearly shown in Table 1, we will mainly focus our investigation on the spin-polarized phases. Similarly to our previous studies of the plutonium and uranium compounds [5,23–25], the strong on-site Coulomb repulsion among the localized Pu 5f electrons is here considered within the LDA/GGA + U approach.

For both the FM and AFM phases of the  $\text{PuH}_2$ , the dependence of the total energy (per f.u. at respective optimum geometries), lattice parameter, and bulk modulus on U within LDA/GGA + U is shown in Fig. 2. Similarly to our study of  $\text{NpO}_2$  [26], the Hubbard U correction in the LDA/GGA + U approach leads to an increase of the equilibrium lattice constant, as well as to a decrease of the bulk modulus. Moreover, these Hubbard U-induced changes on the atomic structure will affect the electronic structure and other macroscopical properties. As seen in Fig. 2(a), the total energy of the AFM phase is lower than that of the FM phase in LDA + U for U smaller than  $4.0$  eV. For U larger than this critical value, instead, the FM phase is energetically more stable. In GGA + U the transition from a FM

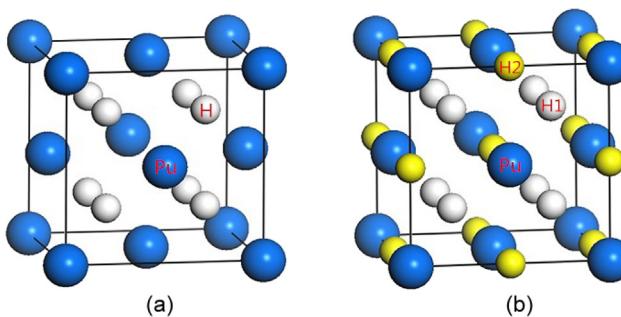


Fig. 1 – Crystal structures of (a) fcc  $\text{PuH}_2$  and (b) fcc  $\text{PuH}_3$ .

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