First Principles Study of Pressure Induced Phase Transition, Electronic and magnetic Properties of Plutonium trihydride

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Abstract: The structural phase transition, electronic and magnetic properties of plutonium trihydride is investigated using density functional theory calculations with the generalized gradient (GGA) approximations. The calculated equilibrium lattice parameter and bulk modulus are in good agreement with the experimental results. The electronic structure reveals that plutonium trihydride is half metallic ferromagnet at normal pressure. A pressure-induced structural phase transition from hexagonal to cubic phase is observed in plutonium trihydride. On further increasing the pressure, a half metallic to metallic transition is also observed. Ferromagnetism is quenched in PuH_3 at high pressures.

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1 INTRODUCTION

Understanding the 5f states of actinides (Ac) has always been the physical center of this engaging and challenging field. Among this series, plutonium is the most complex element with many anomalous properties [1]. Experimental and theoretical efforts have been undertaken in order to understand more deeply the nature of 5f electron behavior in Pu material, a comprehensive review of which is provided by Moore et al [2]. Unfortunately, almost no literature is available on electronic-structure and magnetic properties of plutonium trihydride, a class of materials which are comparably important to the more widely studied Pu oxides in the fields of surface corrosion chemistry and the nuclear fuel cycle. In the present paper, ab-initio method is used to explore the structural, electronic and magnetic properties of plutonium trihydride using pseudopotential plane wave method in the DFT + U framework.

2 COMPUTATIONAL DETAILS

We carried out first-principles calculations based on DFT, as implemented in the VASP code (Vienna ab initio simulation package) which uses a plane wave basis set for expansion of effective, single particle Kohn–Sham energy [3]. The generalized gradient approximation (GGA) is used for the exchange and correlation energy functional with the Perdew Burke-Ernzerhof functional (PBE). Valence states in the pseudopotentials are Pu [Rn] $5f^6 6s^2 6p^6 7s^2$ and H $1s^1$, respectively. The energy cut-off 600 eV is used for plane wave expansions in

reciprocal space of PuH_3. Energy calculations in the first irreducible Brillouin zone are performed using a uniform Monkhorst–Pack k point grid for PuH_3. The Hubbard parameter U correction is only applied to Pu 5f electrons in order to include strong-correlation effects. The Hubbard parameter U = 6 eV for PuH_3 are fully accordant with experimental observations [4].

3 RESULTS AND DISCUSSION

3.1 Structural Stability and Ground State Properties

The structural stability of PuH_3 is analyzed by calculating the total energy using VASP code based on density functional theory. The calculated ground state properties like lattice constants a,c (Å), cell volume V_0 (Å^3), valence electron density (VED) ρ (electrons/ Å^3), magnetic moment μ_B, cohesive energy (eV), bulk modulus B_0 (GPa) and its derivative B_0' for PuH_3 with possible considered phases are listed in Table 1 and is compared with the experimental data [5-7]. From Table 1, it is found that the calculated equilibrium lattice constant and bulk modulus are in good agreement with the experimental result. It is also observed that, hexagonal-$P6_3/mmc$ (LaF_3) owing to its highest cohesive energy is the most stable one among the considered phases.

The total energy vs reduced volume plot is given in Fig.1. From Fig.1, it is noted that PuH_3 is stable in hexagonal-$P6_3/mmc$ phase. On further reducing the volume, a structural phase transition occurs from hexagonal to cubic phase in PuH_3.

In order to determine transition pressure, the enthalpy is first calculated using the formula
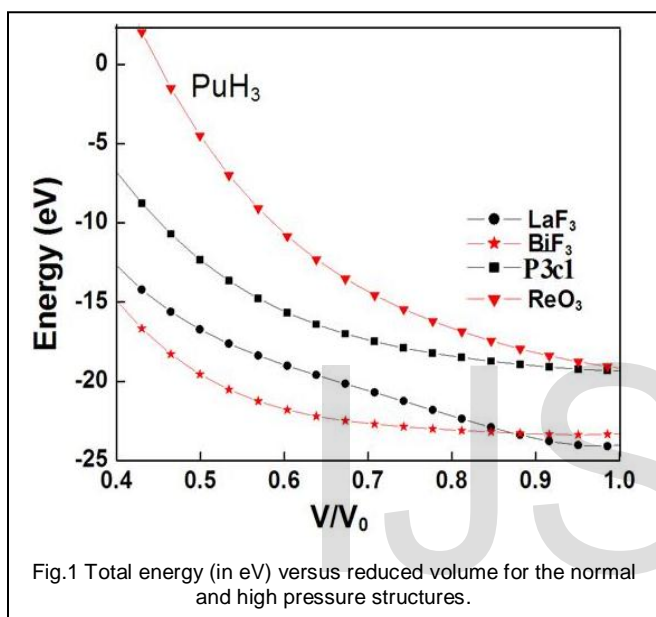
H=E+PV

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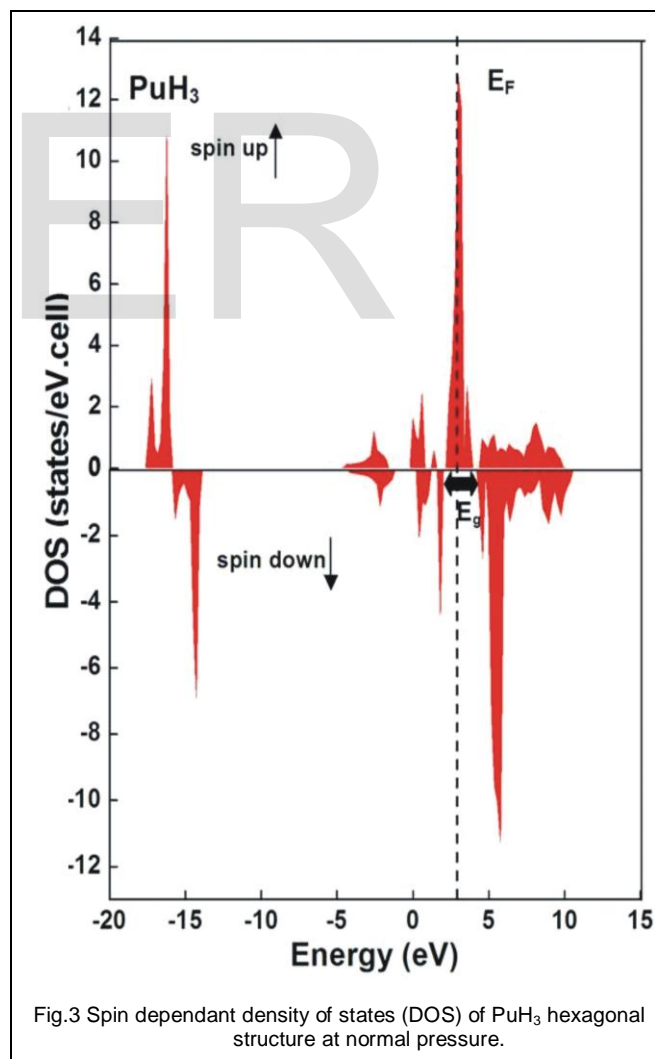TABLE 1

CALCULATED LATTICE PARAMETERS A,C (Å), EQUILIBRIUM VOLUME V_0 (Å^3), VALENCE ELECTRON DENSITY (VED)
P(ELECTRONS/ Å^3), BULK MODULUS B_0 (GPA), PRESSURE DERIVATIVE B_0', COHESIVE ENERGY E_{COH} (EV) AND
MAGNETIC MOMENT μ_B FOR VARIOUS PHASES.

PuH$_3$	a	c	V$_0$	ρ	B$_0$	B$_0'$	E$_{Coh}$	μ$_B$
BiF$_3$	5.338	-	35.48	0.31	94	4.21	13.295	6.0
	5.340[5]							
ReO$_3$	4.451	-	88.45	0.12	76	3.66	9.137	4.99
LaF$_3$	3.62	6.71	79.8		88	3.82		
	3.78[6,7]	6.76[6,7]	74.6[6,7]	0.13	75[6,7]		14.058	6.01
$P\bar{3}c1$	6.021	6.6224	72	0.15	81	4.01	9.327	5.95

Fig.1 Total energy (in eV) versus reduced volume for the normal
and high pressure structures.

The intersection of enthalpy versus pressure curve determines
the transition pressure (Fig.2) as 34 GPa.

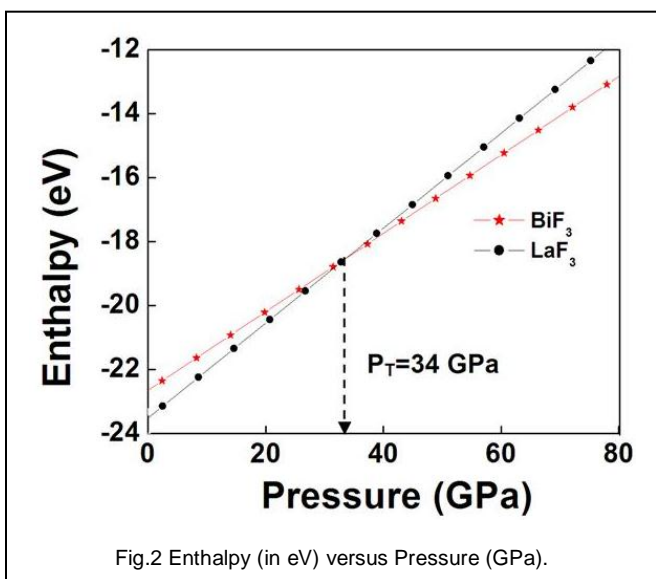Fig.2 Enthalpy (in eV) versus Pressure (GPa).

3.2 Electronic Properties

In order to understand the electronic structure of PuH$_3$, the
spin dependant total density of states (DOS) of the PuH$_3$
(Fig.3) at normal pressure are computed and it is found that,
the minority-spin (spin-down) state exhibit semiconducting
behaviour whereas the majority-spin (spin-up) channel exhibit
metallic behaviour.

Fig.3 Spin dependant density of states (DOS) of PuH$_3$ hexagonal
structure at normal pressure.

The Fermi level is indicated by dotted horizontal line. The energy gap for PuH_3 minority-spin (spin-down) channel is found to be 1.8 eV. For the spin down case (Fig.3), the top of the valence state is formed due to Pu-f states electrons along with a small contribution from Pu-d state and H-s state electrons. The hybridization is found between the Pu-f states, Pu-d states and H-s states below the Fermi level. This hybridization leads to a semiconducting behaviour for the minority-spin case in PuH_3. . On the other hand, the metallic behaviour in the majority-spin channel is mainly due to the contribution from Pu-f state electrons at the Fermi level. Hence, PuH_3 exhibit half metallic behaviour at ambient pressure.

Under high pressure PuH_3 undergoes structural phase transition from hexagonal to cubic phase. Hence, the high pressure density of states is computed with the cubic structure (Fig.4). As pressure increases, no visible changes are observed in the up spin whereas in the down spin channel the distance of separation between the top of the valence state and bottom of the conduction state decreases. The main reason behind the metallic behaviour of the minority-spin case is due to the presence of spikes at the Fermi level, which are formed due to f state electrons of the plutonium atom. A half metallic to metallic transition is found to occur at the pressure of 34 GPa.
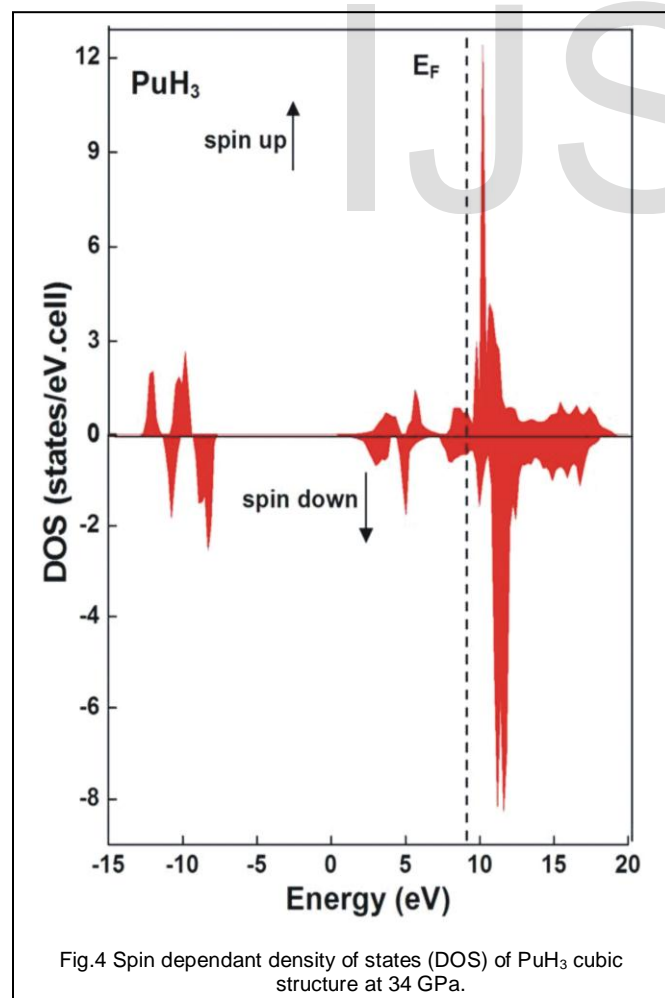

Fig.4 Spin dependant density of states (DOS) of PuH_3 cubic structure at 34 GPa.

3.3 Magnetic Properties

Non-spin and spin polarized calculations are performed to obtain total energies of stable phase of PuH_3. The variation of total energies (per formula unit) with relative volume in ferromagnetic (FM) and non-magnetic (NM) states is given in Fig. 5, to check the magnetic stability of PuH_3 at ambient pressure. From Fig. 5, it is found that the ferromagnetic (FM) to non-magnetic phase transition occurs at 168 GPa. Calculation of magnetic moments indicated the presence of six unpaired electrons for the plutonium atoms present in these compounds, the same number as are indicated for the atoms of plutonium metal. The magnetic moment obtained for stable phase of PuH_3 is found to be nearly $6.0\mu_B$ per formula unit as expected (Table 1). This integer value comes out because, for the minority spin direction, the Fermi level (E_F) is situated within a gap, which means that the bands below are occupied by an integer number of spin-up electrons. Since the total number of electrons is an integer as well, a resulting magnetic moment has to be an integer, too.
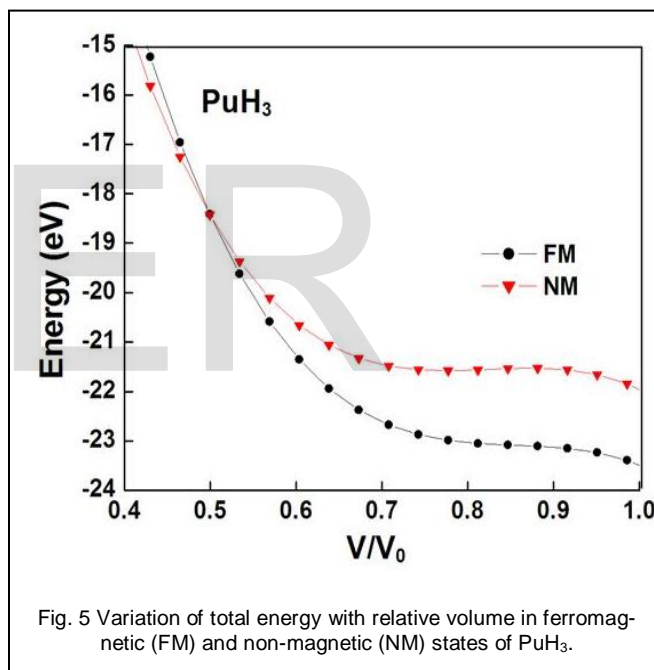

Fig. 5 Variation of total energy with relative volume in ferromagnetic (FM) and non-magnetic (NM) states of PuH_3.

4 CONCLUSION

In conclusion, first principles calculations have been performed using Vienna ab-initio simulation code to investigate the structural, electronic and magnetic properties of PuH_3 with possible considered structures. The calculated ground state properties are in good agreement with the available results. Our results suggest that hexagonal structure is most stable one for PuH_3 at normal pressure. We have also predicted a structural phase transition from hexagonal to cubic for PuH_3 under high pressure. The electronic structure reveals that hexagonal PuH_3 is half - metallic ferromagnet. The calculated band gap is in good

agreement with the available data. As pressure increases, a half metallic to metallic transition in PuH_3 occurs.

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