Structural, mechanical, thermodynamic, and electronic properties of thorium hydrides from first principles

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We perform first-principles calculations of the structural, electronic, mechanical, and thermodynamic properties of thorium hydrides (ThH_2 and Th_4H_{15}) based on the density functional theory with generalized gradient approximation. The equilibrium geometries, the total and partial densities of states, charge density, elastic constants, elastic moduli, Poisson's ratio, and phonon dispersion curves for these materials are systematically investigated and analyzed in comparison with experiments and previous calculations. These results show that our calculated equilibrium structural parameters are well consistent with experiments. The Th−H bonds in all thorium hydrides exhibit weak covalent character, but the ionic properties for ThH_2 and Th_4H_{15} are different due to their different hydrogen concentration. It is found that while in ThH_2 about 1.5 electrons transfer from each Th atom to H, in Th_4H_{15} the charge transfer from each Th atom is around 2.1 electrons. Our calculated phonon spectrum for the stable body-centered tetragonal phase of ThH_2 accords well with experiments. In addition we show that ThH_2 in the fluorite phase is mechanically and dynamically unstable.

I. INTRODUCTION

Thorium is one kind of important nuclear materials and together with its compounds has been widely investigated both experimentally and theoretically. Among thorium compounds, thorium hydrides (ThH_2 and Th_4H_{15}) are metallic solids and have potential use for advanced nuclear fuels. In addition, Th_4H_{15} has been reported to have superconductivity with transition temperatures T_c ∼8 K[1] and has been considered as promising candidates for hydrogen storage since its large hydrogen-to-metal ratio[2]. ThH_2 is not superconducting above 1 K[3].

Despite the abundant research on thorium hydrides, relatively little is known regarding their chemical bonding, mechanical properties, and phonon dispersion. Only the optical phonon density of states of ThH_2 and Th_4H_{15} was measured through inelastic neutron scattering[4] and the bulk modulus of ThH_2 was calculated by linear muffin-tin orbital (LMTO) method[5]. Until now the elastic properties, which relate to various fundamental solid-state properties such as interatomic potentials, equation of state, phonon spectra, and thermodynamical properties, are unknown for ThH_2 and Th_4H_{15}. In addition, although the electronic properties as well as the chemical bonding in thorium hydrides have been calculated recently by Shein *et al.*[2] through the full-potential LAPW (FLAPW) method, the study of the bonding nature of Th−H bond involving its mixed ionic/covalent character is still lacking. These facts, as a consequence, inhibit deep understanding of thorium hydrides. Motivated by these observations, in this paper, we present a first-principles study by calculating the structural, electronic, mechanical, and thermodynamic properties of thorium

hydrides. Also, the stability of the metastable phase of ThH_2 (fluorite structure with space group $Fm\bar{3}m$) is analyzed and our calculated results show that the fluorite-type ThH_2 is mechanically unstable. We perform the Bader analysis[6,7] of thorium hydrides and find that about 1.5 (2.1) electrons transfer from each Th atom to H for ThH_2 (Th_4H_{15}).

II. COMPUTATIONAL METHODS

Our total energy calculations are carried out by employing the plane-wave basis pseudopotential method as implemented in Vienna *ab initio* simulation package (VASP)[8]. The exchange and correlation effects are described by the density functional theory (DFT) within generalized gradient approximation (GGA)[9]. The projected augmented wave (PAW) method of Blöchl[10] is implemented in VASP with the frozen-core approximation. The thorium $6s^2 7s^2 6p^6 d^1 5f^1$ and the hydrogen $1s^1$ electrons are treated as valence electrons. Note that although the $5f$ states are empty in elemental Th, this level turns to evolve into a hybridization with the hydrogen orbitals both in the valence band and the conduction band, as well as to prominently contribute to the conduction band (see Fig. 3 below). 9×9×9 and 5×5×5 Monkhorst-Pack[11] k point-meshes in the full wedge of the Brillouin zone are used for ThH_2 and Th_4H_{15}, respectively. Electron wave function is expanded in plane waves up to a cutoff energy of 450 eV, and all atoms are fully relaxed until the Hellmann-Feynman forces become less than 0.02 eV/Å.

In present work, the theoretical equilibrium volume,