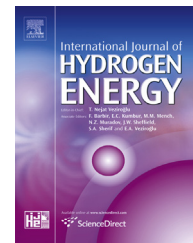Available online at www.sciencedirect.com

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Hydrides of YPd$_3$: Electronic structure and dynamic stability

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ABSTRACT

Ternary intermetallic YPd$_3$ is known to exhibit superior hydrogen storage capacity compared to pure palladium. To understand the characteristics of YPd$_3$ on hydrogenation, the ground state electronic and dynamical properties were computed by two computational methods, the full potential linearized plane wave and projector augmented wave methods within the density functional theory. Hydrogen can be inserted in YPd$_3$ at various octahedral sites, giving rise to model structures YPd$_3$H and YPd$_3$H$_4$ which retain the L1$_2$ crystal structure. The calculated energy bands confirm the metallic nature of YPd$_3$ and also exhibit greater dispersion of bands with increase in hydrogen content. Large variations in the optical constants such as transmittance is observed (by ~40% in the violet region) with insertion of hydrogen, YPd$_3$ may have thus have applications as a sensing device for monitoring hydrogen for using hydrogen safely. The electronic component γ obtained from the temperature dependent specific heats, is related to the density of states at the Fermi level which may be co-related to instability of hydrides.

The modes at Γ-point in YPd$_3$H and at X and M-points in YPd$_3$H$_4$ give rise to high peaks in the imaginary frequency regime which could drive the dynamical instabilities. From the formation energies and phonon modes it is found that the monohydride YPd$_3$H is more stable, thus occupation of the octahedral sites at 2Y4Pd by hydrogen atoms results in greater dynamic instability in YPd$_3$.

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Introduction

Hydrogen storage is one of the key challenges in the development of hydrogen economy due to its low volumetric energy density. Metal hydrides provide an efficient and safe means of storing hydrogen as solid fuel, with sufficiently high volumetric and gravimetric densities. Such solid state hydrogen storage systems are expected to be ideal for applications as hydrogen powered fuel cells vehicles (FCVs). Extensive theoretical and experimental studies have been carried out to identify materials with optimum stability and hydrogen storage capacity. The electronic structure and heats of formation were computed by density functional theory to study the stability of 3d and 4d transition-metal hydrides [1,2]. Similarly, the dynamic stability of palladium hydrides and its vacancy ordered defect phase Pd$_3$VacH$_4$ was studied by density functional perturbation theory [3]. The Fermi surface of

dilute hydride of palladium has been determined from de Haas-van-Alphen measurements to study the effect of hydrogenation [4]. The optical properties of Pd films exposed to hydrogen were studied by transmittance and reflectance spectroscopy [5].

Alloying of palladium with other metals is of special importance since metal/alloy-hydrogen systems can be used as hydrogen storage materials in batteries or fuel cells (FCs). In this context the Pd–Pt alloys system along with other binary alloys such as Pd–Ag, Pd–Cu etc. have been the subject of numerous studies. The crystal and magnetic structure of ternary alloy $PdMn_3$ which may have good hydrogen storage properties was prepared by Rodic et al. and analysed by neutron powder diffraction method [6]. The position of hydrogen atoms in the metal lattice of binary alloys PdCu and PdAg was determined by neutron scattering studies. Self-consistent density functional calculations were also performed using Amsterdam density functional band-structure package (ADF-BAND) to calculate the absorption energy as a function of hydrogen content in the alloys of Pd-Ag [7,8]. The absorption energy of hydrogen in the series of ternary alloys Pd_3M (M = Cd, Ag, Ag, Cu, Ni, Pt, Pb) was calculated by Ke et al. using ADF-BAND and Vienna *ab initio* simulation packages (VASP) [9]. Similarly, the role of hydrogen in magnetic and electronic structure of binary Y–Fe alloys was studied by using the general potential linearized augmented plane wave (LAPW) method [10]. Stability of hydrogen in nickel based binary intermetallics with yttrium (FeB structure) and its hydrides with CrB structure was also studied by *ab initio* methods such as pseudo potential based VASP and scalar relativistic ASW method [11]. Lukaszewski et al. investigated the electrosorption of hydrogen in some Pd alloys with noble metals. The binary Pd–Pt and ternary Pd–Pt–Rh alloys were found to be most suitable for electrochemical experiments due to the fact that hydrogen sorption can take place at room temperature without corrosion of electrode materials [12]. It has been shown by electro catalytic analysis that Pt, Pd/Pt and Pd based catalyst structures facilitate formic acid oxidation in silicon based formic acid micro fuel cells [13]. Long et al. have established the uses of Pt, Pt/Pd based bimetallic and multimetallic nanocatalysts for applications in FCs, especially for commercialization in proton-exchange membrane FCs (PEMFCs) and direct methanol FCs (DMFCs), which offer potential applications as portable devices at low temperatures ranges for cell phones, compact computers and automobiles [14,15].

Hydrides of Y or Pd and their alloys have been well studied by a number of workers, whereas fewer studies of the properties of Y–Pd intermetallic are available in literature. The electronic structure of YPd_3 and $ScPd_3$ along with x-ray photoemission spectroscopy (XPS), brehmsstrahlung isochromat spectroscopy (BIS) and neutron-diffraction measurements are available [16–19]. Since hydrogen is absorbed in alloys by filling of various interstitial sites in the crystal, the hydrogen concentration is quite high, which makes the hydrides of ternary metal YPd_3 attractive hydrogen storage material compared to pure palladium or yttrium or other binary alloys. Transmittance and reflectance of thin films of Y/La coated by Pd were measured with and without hydrogen atmosphere using a double-monochromator spectrophotometer and crystal structure analysed by x-ray diffraction [20,21]. The hydrogen sensing properties of Pd/Y films could be clearly observed from the enhanced optical properties. In this paper, our aim is to study the effect of hydrogen insertion on the electronic structure of the YPd_3 alloy. The results will be useful in guiding us to understand the suitability of Y–Pd alloy for hydrogen storage along with hydrogen sensing characteristics.

The ground state electronic properties of YPd_3 and its hydrides were computed by full potential linearized augmented planewave (FP-LAPW) method. The projected density of states (DOS) and energy bands provide valuable insight into modification of energy bands due to hydrogenation. We also report the optical and transport properties for the first time to understand the effects of hydrogenation. The thermodynamical properties of the Y–Pd intermetallic were calculated within the quasiharmonic approximation (QHA) by the projector augmented wave (PAW) method which is based on density functional theory. We have reported the phonon calculations for YPd_3 for the first time using force constant method, with forces calculated using PAW method.

Methodology

In this paper, two computational methods within the density functional theory (DFT) were used in a complementary manner. For calculating the ground state electronic properties, we have adopted the method of full potential linearized augmented plane waves and local orbitals (lo) (Wien2K code) [22], based on the density functional theory (DFT). For the calculations we have used the generalized gradient approximation (GGA) to the exchange-correlation energy proposed by Wu and Cohen [23]. The self-consistent energy and charge distributions were calculated numerically and the electronic and optical properties were derived from the converged configuration. In the Brillouin zone, k-point integration was carried out using the tetrahedron method in the irreducible Brillouin zone (IBZ) to obtain convergence. The $R_{MT}K_{max}$ was set equal to 7 for the convergence parameter for which the calculation stabilizes and energy convergence was achieved. Here R_{MT} is the smallest muffin-tin radius and K_{max} is the cut-off wave vector of the plane-wave. The maximum radial expansion l_{max} was set to be 10. A mesh with 56 k-points for YPd_3 and YPd_3H and 84 k-points for YPd_3H_4 was used in the IBZ. The energy cut-off between the core and valence states was set at -6.0 Ry.

The Vienna *ab initio* simulation package (VASP) [24], has been used to perform the structure optimization and to evaluate the Hellman-Feynmann forces. The projector augmented wave formalism implemented in this package gives very accurate results. The electronic exchange and correlations were treated by using the generalized gradient approximation (GGA) of Perdew, Burke and Ernzerhof (PBE) [25]. The 4d electrons of Y and Pd have been included as valence electrons. The electronic wave functions were expanded in a plane wave basis with a cut-off of 250.925 eV and fine FFT grid was chosen with spacing around 0.5 A. The Brillioun zone sampling was done with a Monkhorst-Pack **k**-point grid of $4 \times 4 \times 4$. The Fermi surface was treated by the Methfessel–Paxton method with a smearing of 0.2 eV.