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The electronic structure of the europium–palladium hydrides

Emilio Orgaz

Departamento de Física y Química Teórica, Facultad de Química, Universidad Nacional Autónoma de México, CP 04510, Coyoacán, México, D.F. Mexico

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Abstract

We have investigated the electronic band structure for a series of europium–palladium-based hydrides. we have computed the energy bands, total and partial density of states of these compounds, by means of the full-potential linearized augmented plane waves method. We found these hydrides to be systematically magnetic with a localized magnetic moment due to the high spin Eu^{2+} atom. The spin polarization on the 4d conduction electrons of palladium is negligible. We speculate about the existence of two new Eu–Pd hydrides isostructural to $EuMg_2H_7$ and $La(Ce)Mg_2H_7$. The crystal data, lattice parameters and interatomic distances were obtained in a partial geometry optimization. These theoretical crystallographic data are consistent with that found in other Pd-based hydrides.

Keywords: Hydrogen storage materials; Intermetallics; Electronic band structure; Europium–Palladium hydrides

1. Introduction

Europium compounds are interesting due to the variety of valence states usually shown by this element. It can be present as divalent Eu^{2+} ($4f^7$, $J=7/2$), trivalent Eu^{3+} ($4f^6$, $J=0$) or even in a mixed valence state [1]. This situation is frequent also in systems such as oxides, borides, sulfides, arsenides, phosphides, silicides and halogenides. Europium forms also a large number of intermetallic phases. Of particular interest result those phases with non-magnetic elements [2] such as palladium. The binary phase diagram Eu–Pd show unambiguously seven intermetallic compounds [3–5]. Pure Pd and Eu yield spontaneously highly stoichiometric hydrides when exposed to gaseous hydrogen. PdH_x is metallic and for $x \geq 0.8$ show a superconductive transition at 9 K. On the other side, EuH_2 is considered a salt-like hydride system. The reactivity of these intermetallics with respect to hydrogen has also been investigated in recent years [6]. Among the known intermetallic phases, four of them form hydrides. Eu_5Pd_2 reacts with hydrogen and decomposes into EuH_2 and Eu_2PdH_4. Eu_3Pd_2 also decomposes under hydrogen now into Eu_2PdH_4 and $EuPdH_3$. EuPd forms directly the perovskite hydride $EuPdH_3$. However, while $EuPd_2$ yields $EuPd_2H_x$ ($x \leq 2$) at low hydrogen pressure and moderate temperatures, it decomposes into $EuPdH_3$ and PdH at higher hydrogen pressures. In conclusion, besides the binary hydrides PdH_x and EuH_2, the Eu–Pd system forms only three known hydrides, $EuPdH_3$, $EuPd_2H_x$ ($x \leq 2$) and Eu_2PdH_4, the last one existing only as a ternary compound.

In the following sections we will present a very brief account of our results for the electronic structure of the Eu–Pd hydrides. We start by pointing out some aspects of the computation method for the band structure. Then, we will describe the electronic structure features of some of the known ordered hydrides; EuH_2, $EuPdH_3$ and Eu_2PdH_4. Finally, we investigate the properties of two highly stoichiometric hypothetical hydrides derived from the C15 intermetallic $EuPd_2$. We conclude this paper with a summary of our most important findings.

2. Methodology

Solid state electronic structure calculations were carried out within the density functional approximation in the framework of band theory. We employed the full potential-linear augmented plane waves method [7]. The exchange part of the crystalline potential was modelled by means of the generalized gradient approximation (GGA) [8] to the local spin density. A large sample of *k*-points of the irreducible wedges of the corresponding Brillouin zones were selected. For this set of points, we computed ab initio

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E-mail address: orgaz@eros.pquim.unam.mx (E. Orgaz).

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the energy eigenvalues which converged to 1 mRy for the valence states. The muffin-tin radii were selected as large as the crystal structure permitted and it was kept similar for all the series. We performed spin polarized calculations, in a self-consistent and semi-relativistic way, for the paramagnetic phases. We do not introduce the spin–orbit correction. The total density of states (DOS) as well as the angular momentum resolved density of states (PDOS) at each atomic site were computed by means of the tetrahedra-integration scheme.

3. Results

EuH_2 crystallizes within the orthorhombic $PbCl_2$ structure [9]. We found that EuH_2 is a semiconductor with a small energy gap of 0.29 eV. This value is consistent with a dark brownish-violet color shown by the hydride [9]. We found this hydride to be magnetic with a magnetization of 7.0 μ_B/Eu-atom. The spin polarization on the hydrogen atom is, as expected, negligible.

$EuPdH_3$ is a metallic hydride and it shows ferromagnetism below 21 K. This compound has been previously investigated by the author using the augmented plane wave method [10,11]. In this previous report, the Eu-f states were not explicitly calculated; however, the present results are in good agreement with it. The DOS plots for this hydride can be consulted in Refs. [10,11]. The actual band structure calculations indicate that this hydride is metallic with a density of states at the Fermi energy of 1.26 states/eV-cell (0.38 states/eV-cell) for the up (down) orientation of the spin. The position of the spin up Eu-f band is close to the Fermi level while the unoccupied spin down Eu-f band appear 4.5 eV above the Fermi energy. We found a total magnetization of 6.9 μ_B per cell (per Eu atom) with a null contribution from the Pd and H atoms. Again, the overall magnetic behavior of this hydride is caused by the Eu atom. It is interesting to note that the formal charge analysis indicates that, if hydrogen atoms appear in the hidrido form and Eu is set to 2+ oxidation state, Pd must be single ionized ($Pd^{(I)}$). This extremal viewpoint explains why the Fermi level cut the antibonding Pd-d/H-s band rising up to a metallic behavior to this compound.

The crystalline structure of Eu_2PdH_4 is characterized by nearly tetrahedral $[PdH_4]^{4-}$ units in a Eu^{2+} framework. The Pd–Pd distances are large (4.77 Å) compared to, for example, metallic fcc palladium (2.75 Å). This hydride orders ferromagnetically below 15 K [6]. We found this dark grey-violet luster hydride semiconducting with a small energy gap of 0.23 eV. The occupied Eu-f localized bands appear close to the Fermi energy with a splitting of about 5 eV with respect to the unoccupied spin down bands (Fig. 1a,b). This yields a high spin situation where all the magnetism is, once again, due to the Eu atoms. The induced Eu-5d spin polarization is a common feature in lanthanide-based compounds. As well as in EuH_2, this is clear in the PDOS plots of Fig. 1b, where a small peak due to Eu-d states appear close to the Fermi energy only for the spin up contribution. This structure in the PDOS plots represents a very small contribution to the total electron counting (≈ 0.03 electrons/Eu-atom). The Pd contribution show the Pd-d/H-s bonding contributions followed by a narrow peaked structure of Pd-d non-bonding states (Fig. 1c,d). At higher energies, the antibonding Pd-d/H-s states appear centered at 2 eV below the Fermi energy. In a strictly tetrahedral geometry, the bonding states involve the H-s, Pd-s and Pd-d orbitals of A_1 and Pd-d of T_2 symmetries. The Pd-d non-bonding states belong to the E irreducible representation of T_d point group. Note that the PDOS plots corresponding to the three non-equivalent hydrogen atoms show a very similar shape (Fig. 1d). This is due to the near tetrahedral geometry that the $[PdH_4]^{4-}$ unit exhibit. $EuPd_2$ absorbs hydrogen and forms disordered hydrides by occupying interstitial sites in the structure. It has been determined that the most favorable interstitial sites are the tetrahedral 2A–2B 96 g, in Wyckoff notation [12,13]. As indicated in the introduction, the $EuPd_2H_x$ ($x \leq 2$) system undergoes a thermal decomposition at 400 K and $p(H_2) = 620$ kPa, yielding $EuPdH_3$ and PdH. At higher hydrogen pressures, it could be possible to stabilize hydrides with a higher hydrogen content. We considered two highly stoichiometric hypothetical phases; $Eu^{2+}Pd_2^{2+}H_6$ inspired by the recently discovered $EuMg_2H_6$ system [9,14], and $Eu^{3+}Pd_2^{2+}H_7$ based on the $La(Ce)Mg_2H_7$ hydrides [15,16]. Both palladium hydrides were considered isostructural to the respective Mg-based hydrides. We base this hypothesis on two considerations. First, the similar radii (crystal and ionic) that Mg^{2+} and $Pd^{1+/2+}$ exhibit [17]. Second, the existence of reported ternary hydrides containing Pd^{2+} as $Na_2Pd^{2+}H_4$ and $K_2Pd^{2+}H_4$ [18–22].

With these hypothesis in mind, we performed a lattice-parameter optimization of both structures; $EuPd_2H_6$ and $EuPd_2H_7$ constrained to the P_4/mmm and $P4_12_12$ space groups, respectively. We found a total energy minima in both cases reflecting a reasonable volume cell, Pd–Pd and Pd–H distances. The band structure calculations performed for the optimized geometry of $EuPd_2H_6$ yield a paramagnetic hydride. The Pd–H distances range from 1.63 to 1.67 Å while the Pd–Pd distance is 3.27 Å. These values are similar to that found experimentally for Na_2PdH_2 [23], but shorter than those found in the $Na_2Pd^{2+}H_4$ and $K_2Pd^{2+}H_4$ phases [18,19]. As in the majority of the hydrides of this class, the Pd–Pd distance is larger than in metallic Pd. The magnetic moment is again localized on the europium atom indicating a Eu^{2+} ($J = 7/2$) state.

In Fig. 2 we show the total DOS computed for this hypothetical hydride. The labels indicate the major orbital contributions in each energy range. This hydride seems to be a paramagnetic metal with a small DOS at the Fermi energy. The magnetic moment is localized on the Eu atom indicating a high spin situation. In this context, the formal

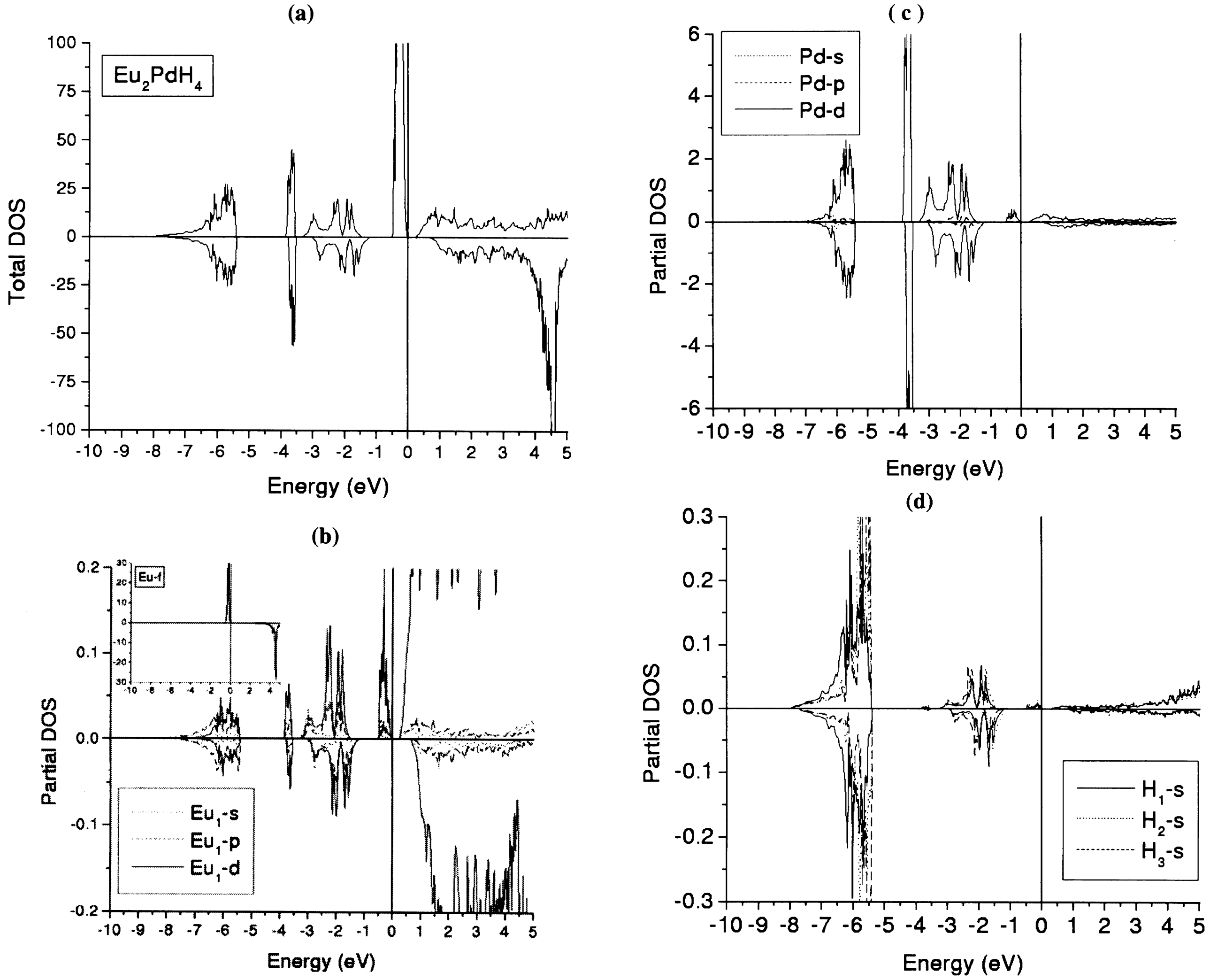

Fig. 1. (a) Total density of states (in states/eV-cell-spin) and (b–d) partial density of states (in states/eV-atom-spin) for Eu_2PdH_4.

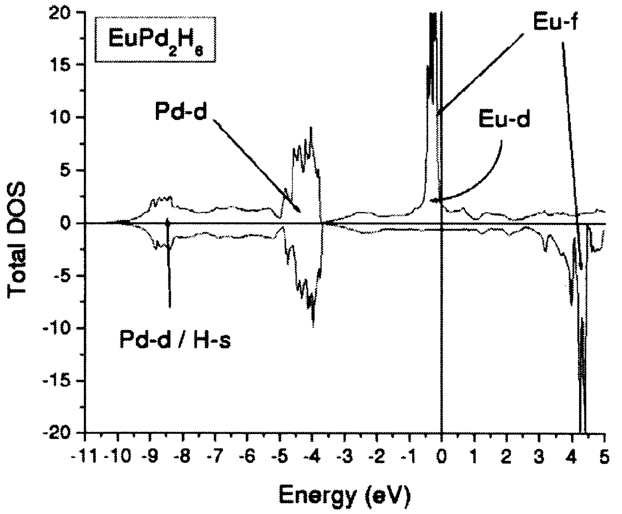

Fig. 2. Total density of states (in states/eV-cell-spin) for $EuPd_2H_6$. The optimized tetragonal lattice parameters are $a = 6.3408$ Å and $c = 12.3645$ Å. The atom relative positions were taken from that found for $EuMg_2H_6$ [9,14].

charges can be assigned in the following way; $Eu^{2+}[Pd_2H_6]^{2-}$.

Our results for the geometry-optimized hypothetical $EuPd_2H_7$ hydride indicate also short Pd–H distances close to 1.9 Å, and a Pd–Pd distance of 3.0 Å. These are similar to the distance found in the Na_2PdH_2 hydride, and more important, of the same order than those observed experimentally in $La(Ce)Mg_2H_7$ [15,16]. In Fig. 3 the total DOS is sketched along with the major orbital contributions in each energy range. This hydride appears to be a paramagnetic metal. Because of a lack of space it is not possible to discuss in more detail the features of the electronic structure of these *hydrides*. However, it seems that these compounds could be synthesized provided that right thermodynamical conditions are attained.

4. Conclusions

In this report we survey the electronic properties of the known Eu–Pd-based hydrides. We found that, sys-

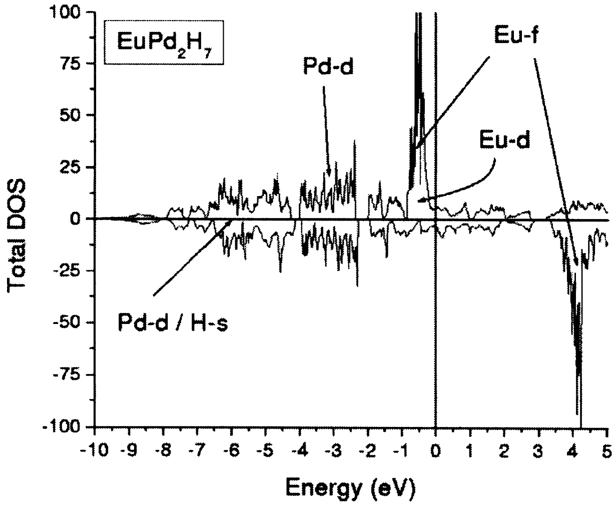

Fig. 3. Total density of states (in states/eV-cell-spin) for $EuPd_2H_7$. The optimized tetragonal lattice parameters are $a = 11.3069$ Å and $c = 17.2317$ Å. The relative atom positions were taken from that found for $LaMg_2H_7$ [15].

tematically, these compounds are magnetic showing a high spin situation owing to the localized Eu-f electrons. Our results indicate that Eu_2PdH_4 is a semiconductor with a small energy gap (0.23 eV). We investigated two hypothetical hydrides: $EuPd_2H_6$ and $EuPd_2H_7$. After a partial geometry optimization for these compounds, we found that the Pd–H, Pd–Pd and Eu–Pd distances are concordant with those found experimentally in other Pd-based hydrides. We found the $EuPd_2H_6$ and $EuPd_2H_7$ compounds are metallic and magnetic as are other existing Eu–Pd hydrides (v.gr. $SrPdH_3$ [10,11]). We hope that these partial results stimulate further experimental investigations regarding the synthesis of hydrides based on $EuPd_2$ with high hydrogen content.

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