Electronic structure of the hydride Pd3FeH

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A self-consistent calculation of the electronic structure of Pd3FeH is presented, using the linear combination of muffin-tin orbitals method. We first briefly discuss the paramagnetic phase of the hydride. We then proceed to the discussion of the ferromagnetic phase of Pd3FeH. The analysis of the energy bands and densities of states gives a good understanding of the influence of hydrogen in this compound. We show any hydrogen uptake drastically decreases the magnetic moments of Pd3Fe. We also find a marked increase in the linear coefficient of specific heat, showing great alterations in the physical properties of Pd3Fe upon hydrogenation.

I. INTRODUCTION

The role of hydrogen absorption in metals, metallic compounds, and alloys has received considerable attention in the last few years because of its potential technological applications for hydrogen storage. As a consequence, theoretical studies of hydrogen in metals have been published, where questions as to the nature of the metal-H and H-H interactions as well as the modifications of the electronic and magnetic properties of metals and metallic alloys upon hydrogenation have been addressed. A large amount of experimental work has been devoted to many of these aspects and also to many technological applications.[1] Some of these applications are concerned with the storage of hydrogen by metallic matrices which can be used as chemical heat pumps, as electrodes in fuel cells, or in solar-energy applications. Hence, due to these very interesting potential applications for metallic hydrides, it appears important to study the influence of hydrogen on the electronic structure of certain metallic alloys. Two of the forerunners in this respect are Ti-Fe and Pd-Fe alloys. While Ti-Fe alloys have received considerable attention in Pd-Fe alloys these questions have not been addressed. We therefore analyze in the present paper the system Pd3FeH.

Pd3Fe in the ordered phase has a Cu3Au structure which is a fcc lattice with Fe atoms located in its corners and Pd atoms at its face centers. It is known that ordered Pd3Fe alloys are capable of absorbing hydrogen through electrolytic loading and that the resultant ternary hydride phase is observed to retain the structure of Pd3Fe with approximately the same lattice constant.[2-3] In the structure of Pd3Fe there are two types of octahedral interstitial sites: one is at the center of the conventional cubic unit cell where the octahedron is formed by six Pd atoms with a local environment identical to that of pure Pd metal. The other octahedron is formed by two Fe and four Pd atoms, the latter disposed in the same plane. These interstitial sites are in the middle of the cube edges. It is known that pure metallic Pd strongly absorbs hydrogen and that Fe does not; therefore, on geometrical grounds, we can argue that the cube-center octahedral sites are more likely to be occupied by H atoms than the cube

edges. This assumption is supported by the fact that in the disordered phase of Pd-Fe, which has a fcc structure with sites randomly occupied by Pd and Fe atoms with concentrations $c = 0.75$ and $1 - c = 0.25$, respectively, there is no noticeable H absorption detected.[3] This may be attributed to the small probability of occurrence of octahedral sites without Fe atoms as first neighbors. Because of the above-mentioned facts we have modeled our Pd3FeH calculation with the hydrogen placed at the octahedral site at the cube center since this position is the most likely to be occupied.

In a recent publication[4] we studied the electronic structure of the intermetallic compound Pd3Fe using the linear muffin-tin orbital (LMTO) method of Andersen,[5-7] which is a first-principles method, and we made a very careful analysis of the ferromagnetic phase. In the present paper we address the question of the formation and stability of hydride phases in this compound. We first consider the question of the stabilization of the paramagnetic phase by hydrogen absorption. We then analyze the influence of hydrogen on the ferromagnetic phase and obtain a dramatic reduction in magnetic moment upon hydride formation.

As in our previous work,[4] we also employ here the LMTO method to study the electronic structure of Pd3FeH. Since the LMTO method has been described in great detail in many publications (for example that of Skriver[7]) we shall limit ourselves to a description of particular details of the present calculation. We have used the self-consistent LMTO formalism without spin-orbit interaction and the combined correction terms were not included. The one-electron potentials were self-consistently obtained with 220 k points for both the paramagnetic and ferromagnetic calculations, using the tetrahedron method.[8] As we have mentioned, Pd3Fe absorbs hydrogen without any substantial alteration in its lattice parameter; hence we used the experimental lattice parameter for this alloy, $a = 3.849$ Å. The spheres around the Pd and Fe atoms were taken to be of equal size, and their radii were $S = 2.8189$ a.u. For the spheres around the H atoms we used the value $s = 1.3308$ a.u. The resultant overlap between the atomic spheres is $0.070a$ for the Pd and H spheres; $0.068a$ for Pd-Pd and Pd-Fe spheres (where a is

the lattice parameter). There is no overlap between the Fe and H spheres. For these choices of radii our results for the converged self-consistent-field (SCF) potentials and charges showed very small charge transfer. The excess charges at the Pd and Fe atoms in the ferromagnetic calculation were $0.0705e$ and $0.0873e$, respectively. These results may be compared with the Pd₃Fe calculation[4] where we obtained $0.0169e$ excess charge at the Fe atoms. Hence, in the hydride case there is a greater charge transfer than in the ordered alloy showing that the H atoms behave as sources of charge for Pd and Fe atoms. This charge transfer alters the electronic distribution and magnetic properties of the alloy as we shall see in the following. In the next section we first present a brief discussion of the paramagnetic calculation of the hydride. Then we present the results for the ferromagnetic phase in terms of band structure and state densities. Finally, in Sec. III we present the main conclusions of this work.
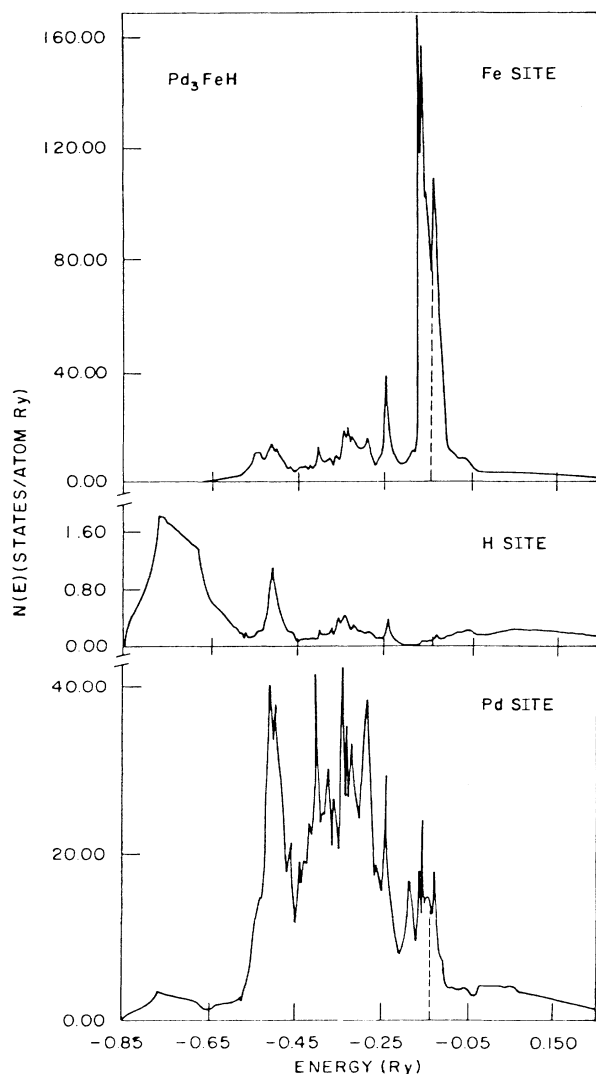

FIG. 1. Site components of the total densities of states $N(E)$ (in states/atom Ry) for paramagnetic Pd₃FeH. The vertical dashed line shows the Fermi level.

II. RESULTS

A. Pd₃FeH — Paramagnetic calculation

The first question we want to answer is: Would hydrogen absorption change the electronic structure of Pd₃Fe enough to stabilize the paramagnetic phase of Pd₃FeH? To this end we first calculated the paramagnetic phase of Pd₃FeH. As our starting point we used charge densities and potentials from our previous calculation[4] for the paramagnetic phase of Pd₃Fe.

The potential parameters of the LMTO method obtained in this calculation show on the one hand that in going from paramagnetic Pd₃Fe to the hydride case, there are no noticeable alterations in the boundary conditions for the crystalline potentials at Pd and Fe sites, and on the other that these subtle alterations occur predominantly at Pd sites. There is also a broadening of the bands (a few percent only) at Pd and Fe sites, which is greater (for s, p, and d bands) at Pd sites. These results can be interpreted to mean that hydrogen interacts more with Pd than with Fe atoms.

Figure 1 shows the total densities of states (DOS) at Pd, Fe, and H sites, obtained using the calculated self-consistent potential parameters. We can see from this figure that the Fe contribution to the total DOS is mainly manifested around and above the Fermi energy, while the Pd contribution is in the region of energies below E_F (the Fermi energy). At H sites we see a small contribution at very low energies, mainly due to s states. These results for the DOS of the hydride may be compared with the results for the pure alloy as follows (see Fig. 1 in Ref. 4). There is a large increase in the DOS at Fe sites around and at the Fermi energy, while the DOS decreases at E_F at Pd sites in the hydride case. We also see that at Pd sites there now appears a small structure in the DOS at low energies (in the range of -0.85 to -0.680 Ry) which has a s-d-hybridized character, broadening the bands at Pd sites. The appearance of these bonding states is due to H-Pd interaction. Hence we may conclude that in the formation of the hydride the H-Pd interaction is more important in altering the electronic properties of the alloy than the H-Fe interaction. Our aim here is to obtain self-consistent-charge densities and potentials to be used in a ferromagnetic calculation of the Pd₃FeH hydride. Concerning the stability of the hydride in a paramagnetic phase our alloy total-energy calculation show that this phase is unstable with respect to the ferromagnetic phase and we comment on the stability of the hydride in the next section.

B. Pd₃FeH — Ferromagnetic calculation

Hydrogen in Pd₃Fe forming the hydride Pd₃FeH is not able to stabilize its paramagnetic phase. We therefore proceed to investigate the influence of H on the ferromagnetic phase of Pd₃FeH. Our starting point was the converged paramagnetic calculation described in the preceding section. The exchange-correlation potential used was the von Barth–Hedin[9] approximation to the local-spin-density theory (the paramagnetic calculation used the Hedin-Lundqvist[10] local approximation).

TABLE I. Potential parameters for spin-polarized Pd_3FeH. Muffin-tin radius for the spheres around Pd and Fe atoms, $S=2.8189$ a.u. For the spheres around H atoms $S=1.3308$ a.u. The potential parameters obtained for spin-polarized Pd_3Fe ($S=2.8434$ a.u.) are shown in parentheses.

| | Pd | | Fe | | H | |
	↓	↑	↓	↑	↓	↑
			E_v (Ry)			
s	−0.541 (−0.488)	−0.544 (−0.502)	−0.494 (−0.498)	−0.501 (−0.521)	−0.695	−0.694
p	−0.398 (−0.348)	−0.406 (−0.380)	−0.338 (−0.386)	−0.386 (−0.396)	−0.360	−0.361
d	−0.345 (−0.339)	−0.338 (−0.335)	−0.209 (−0.280)	−0.203 (−0.311)	−0.335	−0.330
			$W_{(-)}$ (Ry)			
s	0.194 (0.156)	0.196 (0.166)	0.177 (0.149)	0.169 (0.126)	0.037	0.036
p	1.085 (1.027)	1.092 (1.058)	0.985 (0.933)	0.967 (0.890)	4.538	4.539
d	0.026 (0.030)	0.016 (0.010)	0.073 (0.133)	0.022 (0.002)	11.351	11.345
			$10S\Phi^2_{(-)}$ (Ry)			
s	3.433 (3.332)	3.432 (3.324)	3.215 (3.140)	3.196 (3.073)	8.978	8.978
p	3.340 (3.240)	3.342 (3.247)	3.042 (2.965)	3.021 (2.898)	12.396	12.397
d	0.384 (0.365)	0.382 (0.358)	0.241 (0.256)	0.224 (0.195)	15.391	15.387
			$\Phi_{(-)}/\Phi_{(+)}$			
s	0.865 (0.862)	0.865 (0.862)	0.856 (0.854)	0.855 (0.851)	0.767	0.767
p	0.712 (0.708)	0.713 (0.710)	0.689 (0.686)	0.687 (0.680)	0.669	0.669
d	0.069 (0.072)	0.064 (0.062)	0.005 (0.045)	−0.026 (−0.028)	0.626	0.626
			$\langle \dot{\phi}^2_v \rangle^{-1/2}$ (Ry)			
s	4.846 (4.651)	4.847 (4.673)	4.284 (4.149)	4.247 (4.016)	7.760	7.759
p	6.570 (6.410)	6.579 (6.451)	5.828 (5.650)	5.775 (5.494)	22.393	22.395
d	1.005 (0.975)	0.998 (0.957)	0.696 (0.733)	0.654 (0.609)	40.744	40.731
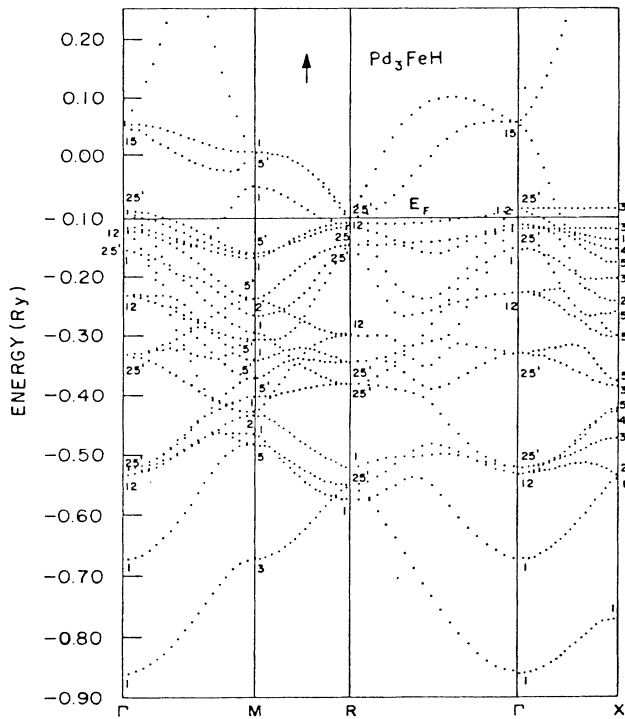
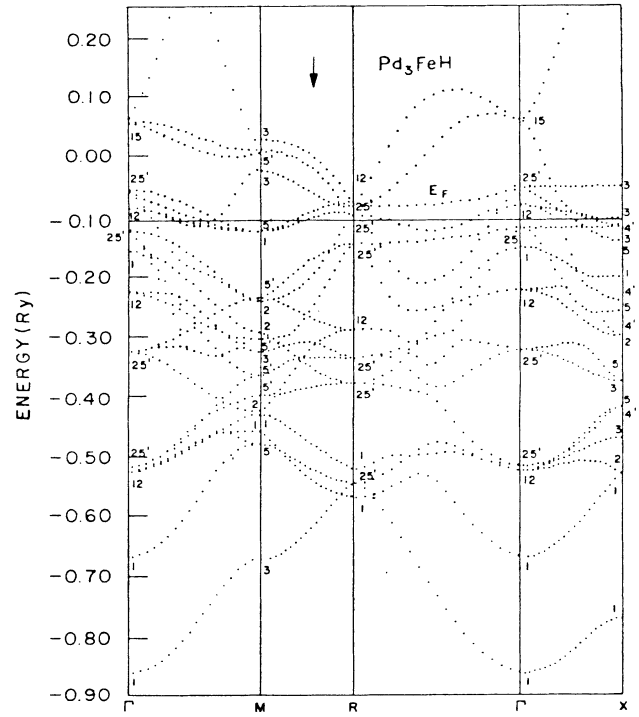FIG. 2. Spin-up energy bands for Pd_3FeH along symmetry lines of the sc Brillouin zone.

FIG. 3. Spin-down energy bands for Pd_3FeH along symmetry lines of the sc Brillouin zone.

Table I displays the potential parameters obtained for the spin-polarized case of the hydride Pd$_3$FeH. In order to make a comparison with Pd$_3$Fe we give the potential parameters obtained in our previous[4] ferromagnetic calculation on this compound which are shown in parentheses in this table. From this table we see that subtle alterations have occurred in these parameters so as to accommodate the H atom. The parameters now describe the hydride compound and are important in determining the modification of the electronic properties as H is loaded into Pd$_3$Fe. We observe that the modifications in the potential parameters at Pd sites are, in general, greatest for spin-down electrons and at Fe sites these modifications are greatest for spin-up electrons. These subtle alterations at each site and for each spin direction are due to the interactions between H-Pd and H-Fe atoms, which of course differ for each pair of sites and for each spin direction. They also play an important role in the reduction of the ferromagnetic moments of Fe and Pd atoms in the hydride compound.

The self-consistent spin-polarized potentials give the energy bands for up- and down-spin electrons shown in Figs. 2 and 3, respectively, for some symmetry directions in the Brillouin zone of the simple cubic (sc) lattice with five atoms (i.e., one Fe, one H, and three Pd atoms). Here, as in the case of the Pd$_3$Fe, we can observe that the spin-up bands are almost filled while the spin-down bands are partially empty. Now, it is important to compare these energy bands for the hydride with those obtained for the pure alloy (Figs. 2 and 3 of Ref. 4) in order to get an idea about the influence of the hydrogen-metal interaction in the deformation of the alloy bands. In the hydride case we notice the presence of a low-lying band below the metal d bands that is not entirely separated from the d bands as in some hydrides of transition metals.[11] The Fermi level is raised to higher energies in Pd$_3$FeH filling some d bands of the compound which were previously empty. This filling of the d bands is much greater for spin-down electrons as can be seen in Fig. 3. The low-lying band that appears in Pd$_3$FeH is mostly formed out of states such as Γ_1, M_3, X_1 which were already filled in Pd$_3$Fe and have been lowered by about 2.0 eV (for both spin directions) by the H-Pd and H-Fe interactions. Apart from this fact, we also see that a full branch of alloy states around R_1, located above E_F in Pd$_3$Fe, is lowered by about 6.0 eV due to hydrogen-metal interactions and falls below E_F in Pd$_3$FeH. The lowering of this branch of alloy states (which have p character) is important because they now accommodate 0.14 additional electrons. Hence, although the Fermi level goes up with hydrogenation, only about 0.85 of the one electron brought by the H atom is accommodated at E_F, since some new states appear at low energies in Pd$_3$FeH. The filling of these new states is important to the stability of the compound but, on the other hand, the raising of the Fermi level costs energy. As the stability of the compound comes from the competition of these two factors, we can see that in the case of Pd$_3$FeH, the appearance of additional states at low energies, which hinder the Fermi-level movement up to high energies, is favorable to the stabilization of the compound. Concerning the stability of the hydride phase we

TABLE II. Intrinsic masses obtained for Pd$_3$FeH. The values of μ for Pd$_3$Fe are shown in parentheses.

	s	p	d
		Pd	
↑	0.736 (0.747)	0.817 (0.826)	6.578 (6.896)
↓	0.736 (0.745)	0.817 (0.825)	6.561 (6.793)
		Fe	
↑	0.791 (0.807)	0.905 (0.923)	11.249 (12.657)
↓	0.786 (0.790)	0.901 (0.905)	10.760 (10.637)
		H	
↑	1.257	1.029	0.923
↓	1.257	1.029	0.923

compared the total energies of Pd$_3$Fe and Pd$_3$FeH. We found the difference of total energies E(Pd$_3$FeH)-E(Pd$_3$Fe) $= -15.64\pm0.7$ eV, where -13.6 eV is due to the hydrogen atom. This confirms the stability of the hydride with respect to pure Pd$_3$Fe.

In Table II we present the intrinsic masses (μ), for the bands of ferromagnetic Pd$_3$FeH. The values of μ for Pd$_3$Fe are shown in parentheses. We observe that there is only a slight alteration in the widths of the bands for both spin directions and sites with hydrogen uptake. In gen-
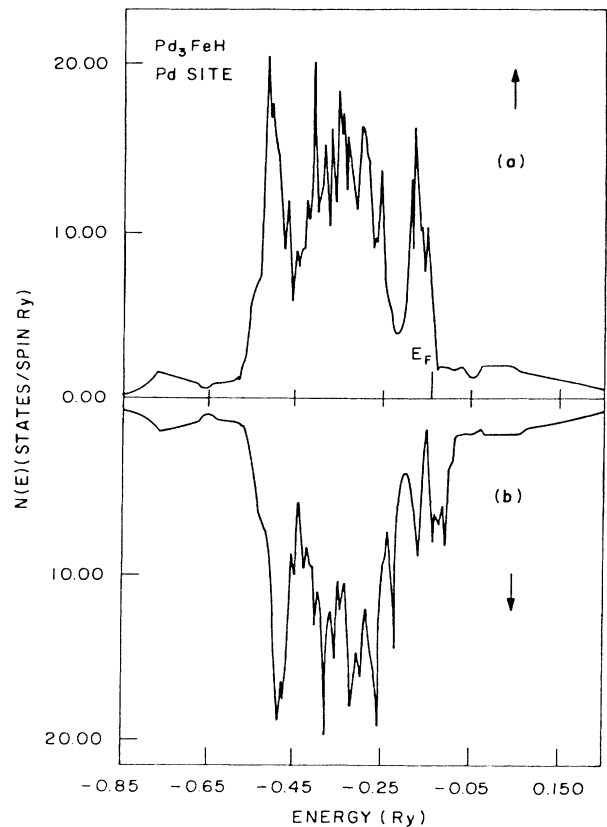

FIG. 4. Total densities of states (in states/spin Ry) (a) spin-up and (b) spin-down electrons at Pd site in Pd$_3$FeH.

eral, there is a small broadening of the bands of the alloy in the hydride case, except for the spin-down d band at the Fe site, where it becames narrower. For spin-down electrons the broadening is great at Pd sites and for spin-up electrons this occurs at Fe sites. This indicates that the H-Pd and H-Fe interactions are different for different spin directions which in fact may alters profoundly the magnetic moments at Pd and Fe sites.

The total densities of states at Pd, Fe, and H sites, for spin-up and -down electrons, are shown in Figs. 4–6. At the Pd site we observe the appearance of a small structure, which is due to new electronic states, located at ~ 0.65 Ry below the Fermi energy. These states do not appear in the Pd_3Fe alloy and are mainly of s character arising because of the mixing of the $1s$ state of hydrogen with the states of the neighboring Pd atoms. We must stress that for Pd and Fe sites the main contribution to the DOS is given by d electrons and that for the H site the largest contribution comes from the s electrons. In the hydride case there is a large increase in the DOS at E_F for spin-up d electrons, increasing the value of γ, the linear coefficient of electronic specific heat. In the Pd_3Fe

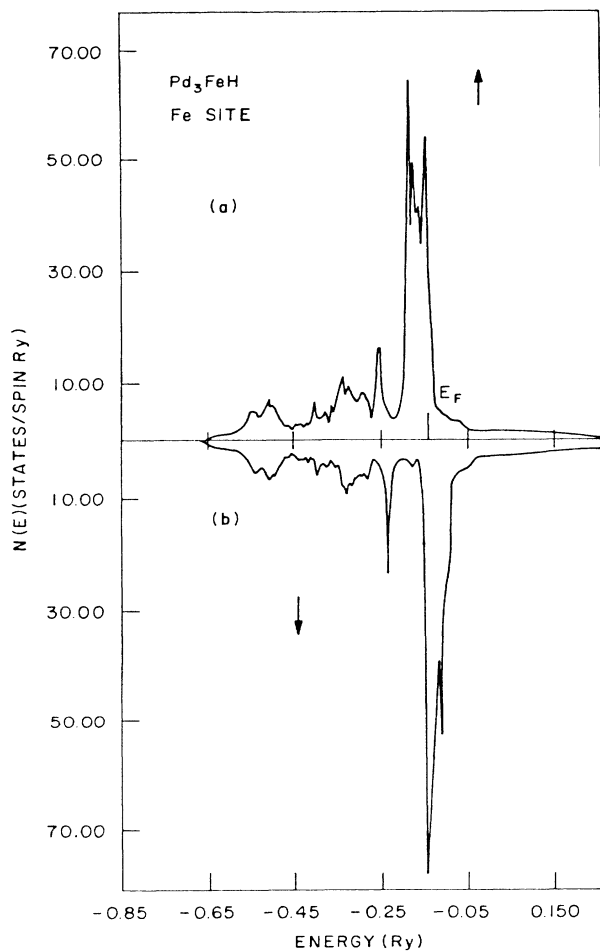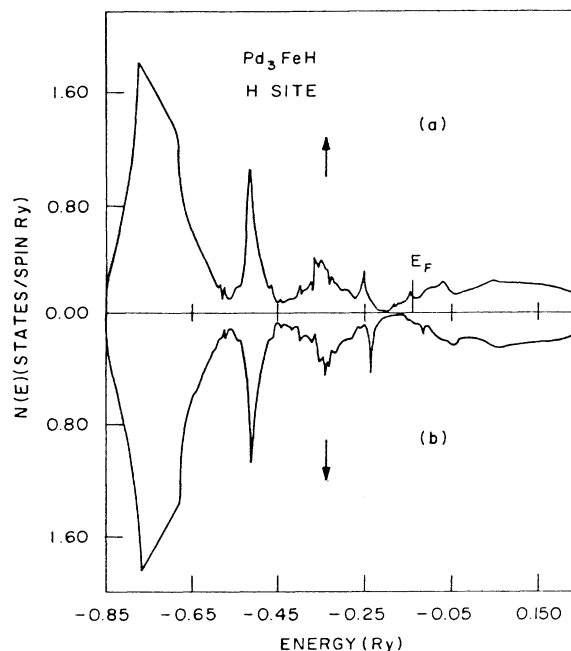FIG. 6. Total densities of states (in states/spin Ry) (a) spin-up and (b) spin-down electrons at H site in Pd_3FeH.

alloy we have found[4] that the spin-up electrons form a common d band while the Fe spin-down electrons are almost excluded from Fe sites producing a large localized magnetic moment at these sites. In the case of Pd_3FeH, as we can see in Fig. 5, there is a population of spin-down states caused by the H metal interactions decreasing the

FIG. 5. Total densities of states (in states/spin Ry) (a) spin-up and (b) spin-down electrons at Fe site in Pd_3FeH.
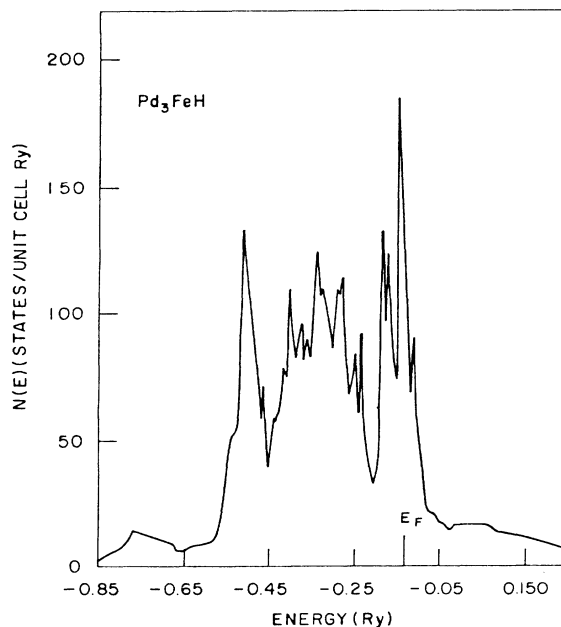

FIG. 7. Total densities of states (in states/unit cell Ry) for ferromagnetic Pd_3FeH hydride (sc structure).

TABLE III. Calculated parameters for spin-polarized Pd₃FeH using the self-consistent potentials. The values calculated for ferromagnetic Pd₃Fe are shown in parentheses. V_{MTZ} are the muffin-tin zeros of the potentials.

	Pd ↓	Pd ↑	m ↑-↓		Fe ↓	Fe ↑	m ↑-↓	H ↓	H ↑	m ↑-↓
n (electrons/spin)	4.96	5.12	0.16(0.38)		3.22	4.93	1.71 (3.10)	0.35	0.35	0.00
n_s (electrons/spin)	0.30	0.30	0.00		0.32	0.32	0.00	0.30	0.30	0.00
n_p (electrons/spin)	0.38	0.37	−0.01		0.37	0.38	0.01	0.05	0.05	0.00
n_d (electrons/spin	4.28	4.45	0.17		2.53	4.23	1.70	0.00	0.00	0.00
N (E_F) (states/spin Ry)	6.51	5.99			59.16	31.91		0.05	0.10	
N_s (E_F) (states/spin Ry)	0.06	0.12			0.16	0.19		0.04	0.08	
N_p (E_F) (states/spin Ry)	0.45	0.24			0.54	0.31		0.01	0.02	
N_d (E_F) (states/spin Ry)	6.00	5.63			58.16	31.41		0.00	0.00	
N (E_F) (states/atom Ry)	12.50 (8.00)				91.07 (20.56)			0.15		
N (E_F) (states/unit cell Ry)			128.57 (44.56)							
γ_{theo} (mJ/mol K²)			21.96 (7.61)							
E_F (Ry)			−0.106 (−0.129)							
V_{MTZ} (Ry)	−0.811	−0.811			−0.723	−0.721		−1.115	−1.114	

difference between the spin-up and spin-down electrons, which alters drastically the local magnetic moments in Pd₃FeH.

In Table III we showed some theoretical parameters obtained for spin-polarized Pd₃FeH. We show some values in parentheses for Pd₃Fe calculated previously.[4] As can be seen from this table there is a drastic reduction of the local magnetic moments at Pd and Fe sites which comes from the filling effect of the d bands for the spin-down electrons by the H-metal interactions. We also found no net magnetization on the H site. The enhancement of the DOS at E_F is much greater at Fe than Pd sites for both spins, and the total density of states (per unit cell) at Fermi level is almost 3 times the value obtained in the case of Pd₃Fe. This can also be seen in Fig. 7 where we show the total DOS for Pd₃FeH. As the Fermi energy goes up about 23 mRy it leaves the valley in the DOS where it was situated lying now at a peak of the DOS. Hence the linear coefficient of the electronic specific heat of Pd₃Fe is substantially increased in the hydride compound, showing that the absorption of hydrogen alters markedly the electronic properties of this compound.

III. CONCLUSION

In this work we employed the LMTO formalism to obtain the band structure of ferromagnetic hydride Pd₃FeH. We found that the electronic and magnetic properties of the compound are altered profoundly by the H-metal interactions. We saw that Pd₃FeH is stable in the ferromagnetic phase and its total energy is lower than that of Pd₃Fe by an amount of 1.150(±0.005)Ry where 1 Ry is due to the total energy of the hydrogen atom. The stability of the compound arises from the competition between two factors, the increase of the Fermi level, which costs energy and the filling of the new low-energy states (below E_F), that appear in Pd₃FeH, which represents a gain in

the stability. We found that there is a mixing of H s with Pd p states filling these previously unoccupied states leading to a smaller increase in the Fermi level, thus less than one electron supplied by H atom is allocated at E_F. This fact, together with the lowering of the metal states could explain the stability of hydrated compound with respect to the pure alloy.

As shown here, the most important feature in the DOS curves are the changes of the density of states below the Fermi energy, corresponding to the appearance of localized H s and Pd s hybridized states. As we have seen these differences in the DOS of the Pd₃FeH and the pure compound cannot be explained within the rigid-band model, as well as other simplified models as the anionic and protonic models, where the later is related to the rigid-band model. However, we found a drastic reduction of the magnetic moments at Fe and Pd sites, with the addition of H which is due to the filling of the spin down d bands at these sites. This reduction may be viewed as a result of a "filling effect" which accommodates part of the extra charge brought in by the H atom and, consequently, increasing the Fermi energy. Our theoretical calculations of the magnetic properties of Pd₃FeH hydride are in reasonable agreement with recent experimental measurements of Corrêa et al.[12] in Pd₃FeH₀.₇ hydride where they found a drastic reduction in magnetic moment (per unit cell) of 4.56μ_B in Pd₃Fe to 0.86μ_B in the hydride compound. However, in their work they suggest the appearance in the hydride of both ferromagnetic and antiferromagnetic interactions, which we did not consider in our model for Pd₃FeH.

In this calculation also we found that the thermal properties of the pure alloy are markedly altered by hydrogen absorption. As we have seen, there is a large increase in the DOS at E_F, hence increasing γ, the linear coefficient of the electronic specific heat. This enhancement of the γ coefficient may be verified experimentally, and we believe that our calculation will be helpful to experimentalists working with the hydride Pd₃FeH.

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