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Internal pressure effect in the series of perovskite structure hydrides: $APdH_3$ (A=Sr,Eu,Yb)

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Abstract

We have investigated the electronic structure and some aspects of the electron–phonon coupling in the $APdH_3$ (A=Sr, Eu, Yb) hydrides using the ab initio augmented plane wave method. The results for the energy bands, the total and partial wave analysis of the density of states, and the electronic contribution, η_H, to the electron–phonon coupling are presented. We have found that all these compounds are metallic with essentially filled Pd-d bands and a small density of states at Fermi level as in PdH. Nevertheless, the calculated values of the hydrogen contribution to the electronic part of the electron–optical phonon coupling constant η_H, although sizeable, are lower than in PdH. This would indicate that these compounds, if superconducting, would have lower values of the superconducting transition temperatures T_c than PdH.

Keywords: Ab initio calculations; Electronic structure; Palladium hydrides; Perovskite structure

1. Introduction

In the present work, we have investigated the electronic structure and the electron–optical phonon coupling in the series of hydrides $APdH_3$ (A=Sr, Eu, Yb) and their evolution as a function of the internal pressure effect associated with the lattice contraction. In fact, the $APdH_x$ (A=Sr, Eu, Yb) hydrides are slightly substoichiometric [1,2] (x=2.7, 2.9 and 2.7 respectively), but in the present work we have considered fully stoichiometric crystals. In the following section we discuss the results of the band structure, total density of states (DOS) and partial DOS of this series of hydrides. Finally, we discuss the calculated values of the electronic part of the electron–optical phonon coupling constant for these materials.

2. Results and discussion

The electronic structure of the three trihydrides is very similar. In Fig. 1 we show the energy bands along some high symmetry directions of the cubic Brillouin zone and the total DOS for only the hydride $SrPdH_3$. The first structure in the DOS at low energy is composed of the first three metal–hydrogen bonding bands. Its width increases from 0.279 Ry (A=Sr) to 0.284 Ry (A=Eu) and 0.302 Ry (A=Yb) as the lattice parameter decreases. This is due to the increased overlap between the orbitals of neighbouring atoms. The second structure in the DOS is a very narrow peak of high intensity due to the essentially nonbonding narrow $Pd-d_{t_{2g}}$ bands. The width of this structure increases also somewhat from 0.053 Ry (A=Sr) to 0.055 Ry (A=Eu) and 0.066 Ry (A=Yb) with decreasing lattice parameter. Finally, the last structure in the DOS is wide and of low intensity; it is due to the two antibonding metal–hydrogen bands. Since the hydrides under study have 15 valence electrons, the first six bands up to the $Pd-d_{t_{2g}}$ narrow manifold are entirely filled, the remaining 3 electrons fill partially the overlapping antibonding metal–hydrogen bands. The hydrides are found to be metallic with a low DOS at E_F, respectively 9.93, 10.03 and 9.13 states of both spins/Ry-unit cell for A=Sr, Eu and Yb. The total DOS at E_F is dominated by the contribution of the Pd-d states, however, in this metal–hydrogen antibonding region, the H-s states are non-negligible since they represent more than 10% of the Pd-d dominant contribution. A small contribution of the Sr-d states at E_F is also present in these compounds, which is of same order of magnitude as that of the H-s contribution. The value of the DOS at E_F is similar to that found for PdH, another hydride with filled Pd-d bands.

The electronic states at the Fermi energy of the metals under study present some similarities with those of super-

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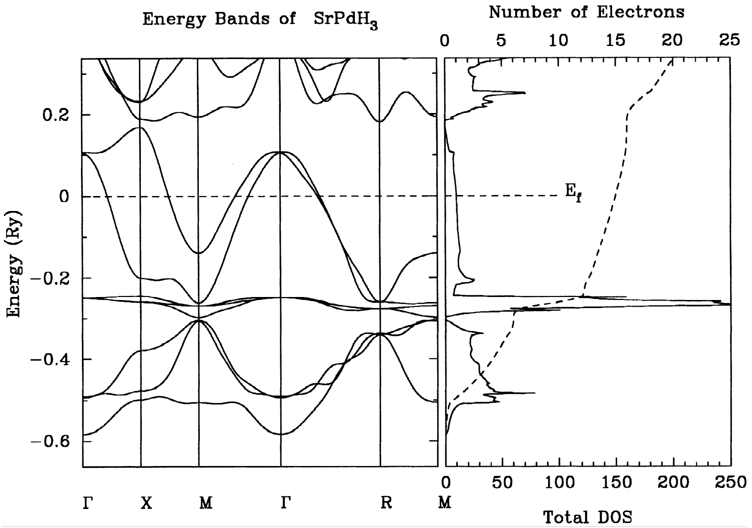

Fig. 1. Energy bands (in Ry) and total density of states (in states of both spins/Ry-unit cell) of $SrPdH_3$.

conducting PdH. Like in PdH, we find that the metal d bands are filled and we obtain a small but sizeable contribution of H-s states at E_F since the Fermi level cuts the metal–hydrogen antibonding states, as in PdH. It has been shown experimentally and confirmed by theoretical investigations [3] that the electron–optical phonon coupling associated essentially with the vibration of the light element hydrogen is responsible for the superconducting properties of PdH and PdD. We have calculated the electronic contribution to λ, denoted hereafter η, by means of the Gaspari–Gyorffy model developed in the framework of McMillan's approximation [4,5]. In Table 1 we summarize the results of η calculated for the five hydrides. The rather weak values η_A for the divalent metal yield, after being weighted by the atomic mass, a negligible contribution to λ. Slightly larger values of the electronic contribution η_{Pd} are found for the Pd atom in these compounds; however these values, as in the case of PdH, are much smaller than those obtained for superconducting transition metals [6,7] and should lead to small values of λ_{Pd}.

In contrast, we find that the hydrogen contributions, η_H, are sizeable for the five compounds, although lower than in superconducting PdH ($\eta_H = 0.64$ eV^{-2} [3]). The trihydrides under study are thus quite similar to PdH, however the calculated values of η_H are about 35% smaller than in PdH. In both cases, a palladium atom remains octahedrally coordinated, however, the coordination of H atoms by Pd atoms is not the same. Whereas in PdH the hydrogens are also octahedrally coordinated by the Pd atoms, in $APdH_3$ compounds they have only two-fold colinear coordination. This substantially weakens the interaction of the H-atoms with Pd atoms in $APdH_3$ and hence reduces the values of η_H. We have no experimental data on the average frequencies of the optic modes $\langle \omega^2 \rangle_H$, however, a hardening of the optic phonons could be expected from the reduced Pd–H distances in these trihydrides. Such hardening would further decrease the value of λ_H. However, since in BCS theory the prefactor in the expression of the superconducting transition temperature T_c is proportional to the average phonon frequencies, we cannot further speculate on the possible values of T_c for these hydrides. Nevertheless, we believe that these trihydrides are interesting candidates for low T_c superconductivity and we hope that the present investigation will stimulate further experimental work in this direction.

Table 1
Electronic part of the electron–optical phonon coupling constant η_α (in eV^{-2})

	η_A	η_{Pd}	η_H
$SrPdH_3$	0.06	0.23	0.43
$EuPdH_3$	0.06	0.23	0.39
$YbPdH_3$	0.05	0.23	0.43

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