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LETTER TO THE EDITOR

Electronic properties and the maximum hydrogen absorption capacity of the novel hydride Na_2PdH_2

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Abstract. We have investigated the electronic structure of the recently synthesized hydride Na_2PdH_2 by means of a calculation of the energy bands and densities of states using the linear muffin-tin orbital method. The metal–hydrogen bonding features, the Fermi-energy-related properties and the maximum hydrogen content of the system are discussed.

The search for hydrides of intermetallic compounds of general formula $\text{M}'\text{MH}_x$ where M is a transition metal and M' an alkali or alkaline-earth element has led to the synthesis of materials with potential technological applications such as Mg_2NiH_4 [1]. More recently hydrides such as Li_2PdH_x , Li_2PtH_x [2] and also Na_2PdH_2 and Li_2PdH_2 [3] have been synthesized. Besides being materials of possible technological interest, these systems present interesting characteristics from a theoretical point of view, in relation to (i) the possible coexistence of two different types of metal–hydrogen bonds; (ii) their electrical properties, varying between those of the insulating ionic alkali and alkaline-earth hydrides and the metallic transition metal hydrides.

In this letter we present a theoretical study of the electronic structure of the novel hydride Na_2PdH_2 . We focused essentially on the electrical properties, bonding features, and on the maximum hydrogen absorption capacity of this compound. X-ray data on powdered samples and inelastic neutron scattering studies on deuterated single crystals [3] have shown that this ternary compound crystallizes within the $I4/mmm$ space group; the body-centred tetragonal cell which contains two formula units is shown in figure 1. In this structure each Pd atom is surrounded only by two H atoms located along the c -axis, thus forming PdH_2 linear bonds with short Pd–H distances of 1.68 Å. It is worth noticing that the sites in the basal planes of Pd atoms at $(a/2)$ (1, 0, 0) and $(a/2)$ (0, 1, 0) are empty. If these sites could be occupied by H atoms, the compound Na_2PdH_4 would form in the K_2NiF_4 structure. We have tried to explain from our calculations why these sites remain vacant, thus limiting the maximum capacity of H absorption.

We have used the linear muffin-tin orbital method (LMTO) in the atomic sphere approximation (ASA) [4] to calculate *ab initio* the energy bands and densities of states of the hydrides under study.

In order to understand the specific role of the H atoms in the lattice, and since the pure intermetallic compound does not form without hydrogen, we first considered the fictitious compound called hereafter ' Na_2PdH_0 ' which is derived from the hydride

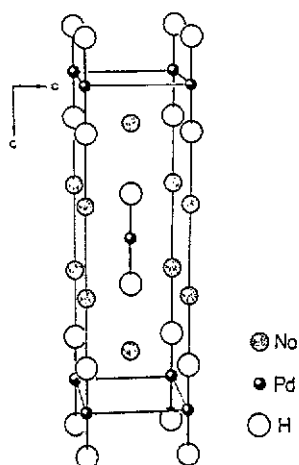


Figure 1. The crystal structure of Na_2PdH_2 from Noreus *et al* [3].

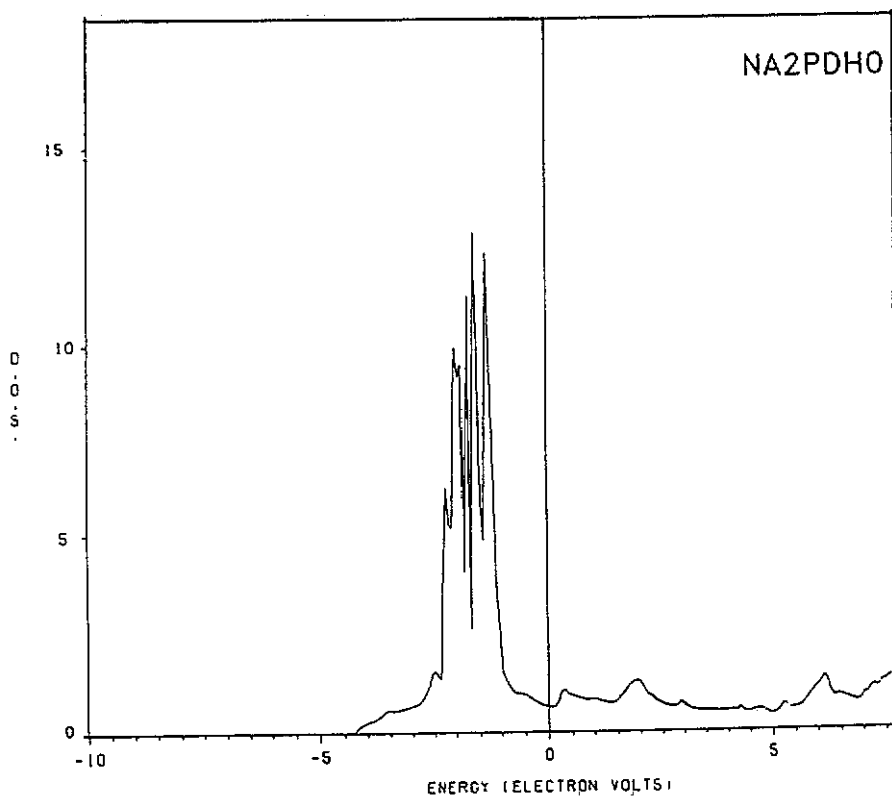


Figure 2. The total density of states (states $\text{eV}^{-1}/\text{cell}$) of ' Na_2PdH_0 '. (H atoms have been removed from Na_2PdH_2 in the structure given in figure 1.) Energies are in eV; the Fermi level, which is indicated by the vertical line, is taken as the origin.

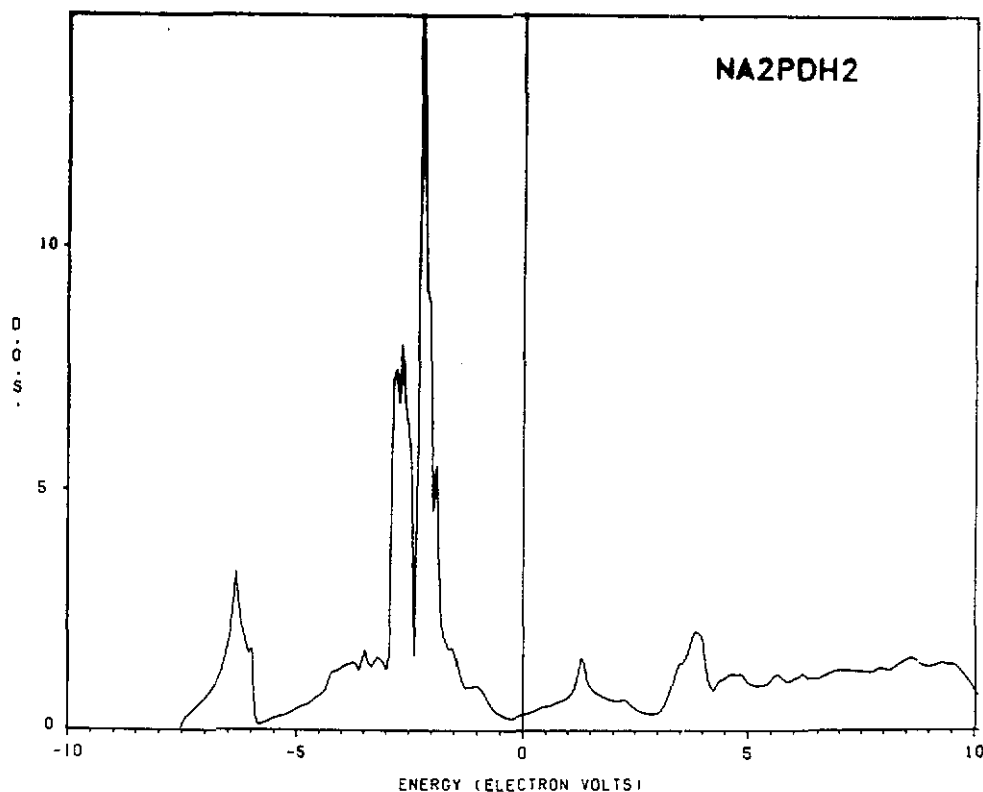


Figure 3. The total DOS (states $\text{eV}^{-1}/\text{cell}$) of Na_2PdH_2 . Energies are in eV; the Fermi level, which is indicated by the vertical line, is taken as the origin.

Na_2PdH_2 by removing the H atoms while retaining the known crystal structure and lattice constant of the hydride.

The total density of states (DOS) of ' Na_2PdH_0 ' is plotted in figure 2. It is characterized by narrow Pd d states of width smaller than 1.5 eV; these high DOS d states overlap and are hybridized by broad Pd s-p and Na s-p states. ' Na_2PdH_0 ' has 12 conduction electrons; the Pd d bands are filled, and the Fermi energy, E_F , falls in the wide metal s-p band in a low-DOS region. The narrow Pd d bands originate from the large Pd-Pd distances in the planes perpendicular to the *c*-axis ($d_{\text{Pd-Pd}} = 3.599 \text{ \AA}$ compared with 2.75 \AA in FCC Pd); the Pd-Pd distances between square-planar Pd sheets are even larger and thus the interactions are strongly bidimensional; they are mostly due to d-d interactions of the planar $d_{x^2-y^2}$ orbitals.

A comparison of the total DOS of ' Na_2PdH_0 ' (figure 2) and Na_2PdH_2 (figure 3) shows clearly the effect of metal-hydrogen bonding. Besides the lowering of Pd d states which results in a metal-hydrogen bonding band centred at about 4.5 eV below the centre of the Pd d DOS peak, the metal-hydrogen interaction also leads to an important deformation of the Pd d bands in Na_2PdH_2 .

As regards Fermi level properties, it has been pointed out that, using conventional valencies (Na^+ and a d^{10} configuration for Pd), the hydride Na_2PdH_2 could be expected to be an insulator [3]. However, the compound has metallic lustre and metallic conductivity [3]. In our calculation, in agreement with experimental data, Na_2PdH_2 which

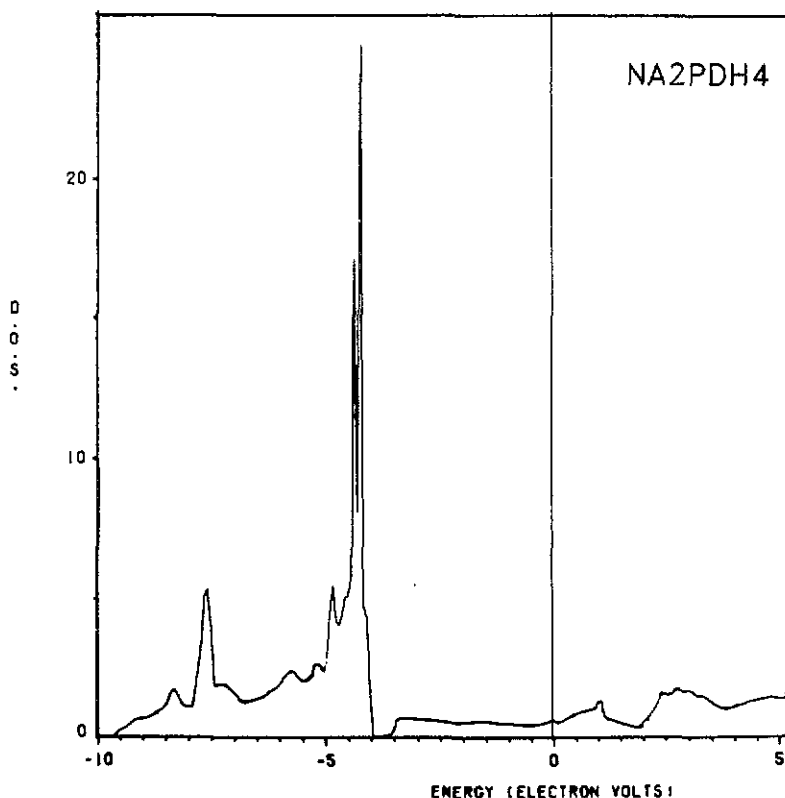


Figure 4. The total DOS (states $\text{eV}^{-1}/\text{cell}$) of 'Na₂PdH₄' (K₂NiF₄ structure). Energies are in eV; the Fermi level, which is indicated by the vertical line, is taken as the origin.

has 14 conduction electrons is found to be metallic. This metallic behaviour is due to a small and indirect overlap of band number 7, which is almost fully occupied in Na₂PdH₂, with band number 8, which contains a small electron pocket. In 'Na₂PdH₀' band number 7, which is almost empty except for a small electron pocket, is located entirely below E_F in Na₂PdH₂; it thus brings new states below E_F which can accommodate close to, but less than, two electrons. Band number 8, which is fully empty in 'Na₂PdH₀' cuts E_F in Na₂PdH₂. The total DOS at E_F is low: 5 states $\text{Ryd}^{-1}/\text{unit cell}$; this value is even lower than that of PdH. In Na₂PdH₂, the states at E_F have a large Na p and also a Pd d s and p character; the H s contribution, $n_{\text{Hs}}(E_F)$ is much smaller. Previous calculations of the electron-optical-phonon coupling constant λ_H in metal hydrides [5, 6] performed using the Gaspari-Gyorffy formalism [7] have shown that the electronic contribution, η_H , is sizable only if $n_{\text{Hs}}(E_F)$ is a substantial fraction of the total DOS at E_F . This is the case in PdH and leads to a large value of λ_H and to superconductivity. In Na₂PdH₂, $n_{\text{Hs}}(E_F)$ is much smaller than in PdH and should result in a small value of λ_H . Thus the compound Na₂PdH₂ is not expected to be a superconductor.

In order to understand why the H atoms are not located in the square-planar Pd sheets, we have investigated the electronic structure of the fictitious hydride 'Na₂PdH₄' for which we assumed the same crystal structure and lattice parameters as for Na₂PdH₂. The two additional H atoms per unit cell have been located in the palladium planes midway between the Pd atoms, thus conferring on the hydride the K₂NiF₄ crystal

structure. It is to be noted that in this fictitious structure, all the H-H distances are larger than 2.1 Å, the minimum distance observed in known stable hydrides [8, 9].

The DOS of 'Na₂PdH₄' is plotted in figure 4. Below the top of the Pd d bands, which lies at about 4 eV below E_F in 'Na₂PdH₄', we obtain 7 bands and thus 14 electrons, as in Na₂PdH₂; the electrons introduced by the two additional H atoms in the unit cell of 'Na₂PdH₄' are necessarily accommodated at higher energies, thus shifting the Fermi level higher up in energy—a factor that adversely affects the stability of the hydride and explains why the compound is not stable. This is at variance with the situation for all known stable transition metal hydrides in which one obtains, below the top of the metal d bands, a number of metal-hydrogen- and H-H-derived bands that is equal to the number of H atoms in the unit cell.

The present results, and also our previous investigations of the electronic structure of unstable PdH₂ as a function of d_{H-H} [10], show that besides the effect of the H-H distances, more subtle metal-hydrogen hybridization effects sensitively affect the position of the metal-H and H-H states, and thus the stability of metal hydrides.

Our calculations show that the Pd-hydrogen interactions in the linear PdH₂ complex present in Na₂PdH₂ lead to bonds of covalent nature between the H s and Pd d and to a lesser extent s and p states. In Na₂PdH₂ the Pd d bands are filled; however, due to an important hybridization of the Na and the Pd s and p states, the compound is found to be metallic, in agreement with experimental findings. The Fermi level falls in a low-DOS region at about 1.5 eV above the top of the Pd d peaks.

Our investigation of fictitious 'Na₂PdH₄' (K₂NiF₄ structure) leads us to conclude that the maximum hydrogen absorption capacity in this hydride, Na₂PdH₂, can be ascribed to an electronic origin.

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