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Electronic structure investigation of the A_2PtH_4 hydrides (A=Na, K) containing $[PtH_4]$ complexes

Emilio Orgaz, Michèle Gupta*

Université de Paris-Sud, URA-446 CNRS, Bât. 415, 91405 Orsay-Cedex, France

Abstract

Ternary platinum hydrides have been synthesized and structurally characterized in recent years. The defective hydride K_2PtH_4 crystallizes within the K_2PtCl_6 structure above 197 K, while at low temperatures, the defective phase presents long range hydrogen ordering. Na_2PtH_4 has been synthesized and shows also hydrogen ordering but of a different nature. We have investigated the electronic structure and bonding in the hydrogen ordered compounds by means of the augmented plane wave (APW) method. The band structure, the total density of states and their partial wave analysis are discussed. We found that these hydrides are insulators and behave essentially as quasi-molecular solids characterized by narrow d-bands and weak $[PtH_4]$–$[PtH_4]$ interactions.

Keywords: Ab initio calculations; Electronic structure; Platinum hydrides

1. Introduction

In recent years, Bronger and Auffermann [1–3] and Kadir and Noréus [4] reported the synthesis of platinum complex hydrides containing square planar $[PtH_4]$ units with short Pt–H distances such as K_2PtH_4, Na_2PtH_4 and $A_2H_2[PtH_4]$ (A=Sr or Ba). The $[PtH_4]$ arrangements (Fig. 1) in these compounds form alternating planes whose orientations differ in the first two hydrides, while an interplane A_2H_2 separates the $[PtH_4]$ slabs in the later. These hydrides were prepared by reacting the alkali (or alkaline earth) metal hydride with platinum powder under hydrogen atmosphere and at moderated temperatures. The resulting powders were investigated by means of X-ray and neutron diffraction.

K_2PtH_6 crystallizes in the antifluorite structure (Fm3m) showing octahedral PtH_6 units with short Pt–H distances (d(Pt–H)=1.64 Å) compared to, for example, PdH (d(Pd–H)=2.04 Å) [5]. The hydrogen defective phase K_2PtH_4, isostructural to K_2PtH_6, presents random occupancy of 2/3 of hydrogen atoms. An ordering transition is observed below 197 K, the transition metal and alkaline metal sublattices preserve their symmetry while the hydrogen atoms adopt a square planar coordination around Pt atoms. These arrangements form alternating planes conferring a tetragonal $P4_2/mnm$ symmetry to this compound. Na_2PtH_4 hydride shows at room temperature essentially the same ordered structure of K_2PdH_4 [6], and belongs to the body centered tetragonal crystal class. The main difference between Na_2PtH_4 and K_2PtH_4 arises from the orientation of the PtH_4 square planar units as shown in Fig. 1. We present in this report our results of the bands structure, total density of states (DOS) and partial wave analysis of the DOS at each atomic site of the H-ordered low temperature phase K_2PtH_4 and Na_2PtH_4 hydrides. These results are an extension of previous work on K_2PdH_4 [7–9], and hydrides of K_2PtCl_6 structure [10,11].

2. Results and discussion

We used the augmented plane wave (APW) method [12] to calculate the energy bands of these hydrides. The crystal potential was modeled in the muffin-tin approximation introducing the exchange term in the local density approximation (LDA). The form of the LDA used was the Slater X_α which has been proved to be adequate to study these kind of materials [10,11], and the effect of self-consistency, not included in the present work, has been shown to result in very minor differences in the palladium system K_2PdH_4 [8,9]. As in our previous calculation [8] and although Pt is a heavier atom, we used a non relativistic hamiltonian. An energy cut-off of 11 a.u. was used to determine the number of reciprocal lattice vectors. This variable set, larger than 700 vectors, was sufficient to insure a 1 mRy convergence in the energy eigenvalues.

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*Corresponding author.

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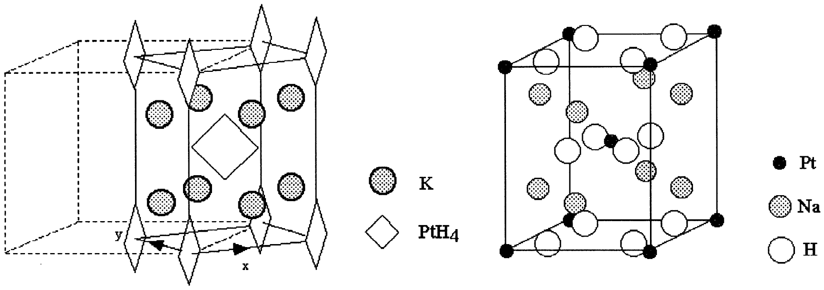

(a) K_2PtH_4 (b) Na_2PtH_4

Fig. 1. Unit cell of ordered hydrides (a) K_2PtH_4 (low temperature phase), (b) Na_2PtH_4 hydride.

The total density of states (DOS) as well the partial wave analysis of the DOS at each atomic site was calculated by means of the linear tetrahedron integration scheme [13]. In order to facilitate the comparison of the electronic structure of the two compounds we have considered the tetragonal cell of Na_2PtH_4 which contains two formula units.

The hydrides under study all show very large transition metal to transition metal distances (d(Pt–Pt)≥5 Å) compared to metallic Pt (d(Pt–Pt)=2.78 Å) or even ternary hydrides as Na_2PdH_2 (d(Pd–Pd)=3.60 Å) [7] but similar to K_2PdH_4 (d(Pd–Pd)=5.83 Å [6]). On the other hand, the Pt–H distances are shorter than in the majority of transition metal ternary hydrides (see Table 1).

Table 1
Lattice parameters and Pt–H distances (in Å) of the platinum ternary hydrides

	a (in Å)	d(Pt–H)
K_2PtH_6	8.176 [2]	1.64
K_2PtH_4	$a=5.582$ [1,2]	1.58
(Low temperature phase)	$c=8.085$	1.59
Na_2PtH_4	$a=5.251$ [3]	1.63
	$c=6.778$	

The energy bands and total DOS of the K_2PtH_4 hydride in the tetragonal H-ordered configuration are plotted in Fig. 2). It is useful to recall that this structure shows two Pt–H distances being almost equivalent (see Table 1). In Table 2 we show the symmetry analysis of the wave function coefficients at $\Gamma\vec{k}$-point for the hydrogen defective hydrides. The valence energy bands and their DOS show six very narrow structures. From the bottom of the energy scale we observe two flat structures close in energy with band widths of 0.12 and 0.29 eV respectively. Each one is composed of two energy bands and is filled with four electrons. They are essentially the result of Pt-d and H-s orbital interactions and have their origin on the Pt-d$_{e_g}$/H-s bonding states observed in the high temperature K_2PtH_4 polytype. Separated from these structures by 3.89 eV a third structure with a band width of 0.99 eV formed by 4 filled bands is the result of H-s/Pt-p interactions as can be appreciated in the PDOS plot. In increasing order of energy, the next sharp peaks in the DOS are composed by three bands each and filled with 12 electrons. These structures have a band width of 0.08 and 0.16 eV respectively and have their origin on the Pt-d$_{t_{2g}}$ non-bonding states. In this hydride, each structure is composed by

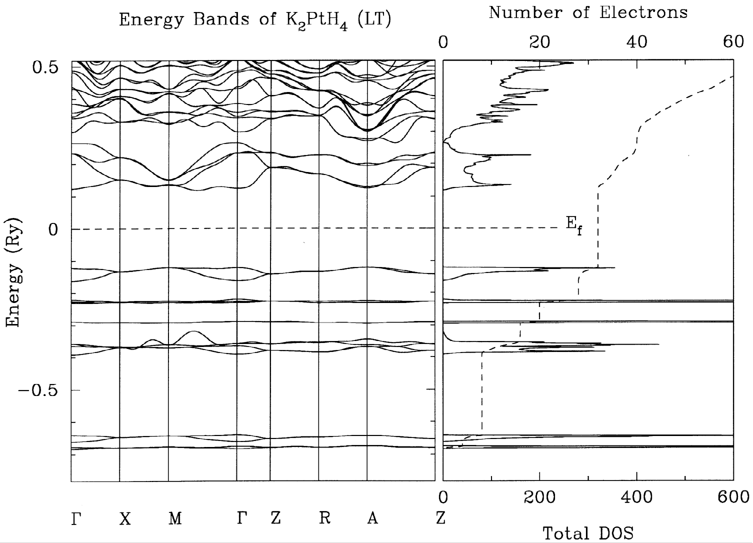

Fig. 2. Energy bands (in Ry) and total density of states (in states of both spins/Ry-unit cell) of K_2PtH_4 (low temperature phase).

Table 2
Symmetry analysis of the wave function coefficients at Γ-$\vec{k}$ point for K_2PtH_4 and Na_2PtH_4 hydrides

State	K_2PtH_4 (Low Temperature)	Na_2PtH_4
1	Pt-d_{z^2},-d_{xy}/H_1-s	Pt-d_{z^2},-s/H-s
2	Pt-d_{z^2},-d_{xy}/H_1-s	Pt-d_{xy}/H-s
3	Pt-d_{xy}/H_2-s	Pt-d_{z^2},-s/H-s
4	Pt-d_{xy}/H_2-s	Pt-d_{xy}/H-s
5	H_1-s/(Pt-p_z)	H-s/(Pt-p_x,-p_y)
6	H_1-s/(Pt-p_z)	H-s/(Pt-p_x,-p_y)
7	H_2-s/(Pt-p_x,-p_y)	H-s/(Pt-p_x,-p_y)
8	H_2-s/(Pt-p_x,-p_y)	H-s/(Pt-p_x,-p_y)
9	Pt-d_{xz},-d_{yz}	Pt-$d_{x^2-y^2}$/(Na-s)
10	Pt-d_{xz},-d_{yz}	Pt-$d_{x^2-y^2}$/(Na-p)
11	Pt-$d_{x^2-y^2}$	Pt-d_{xz},-d_{yz}
12	Pt-d_{xz},-d_{yz}	Pt-d_{xz},-d_{yz}
13	Pt-d_{xz},-d_{yz}	Pt-d_{xz},-d_{yz}
14	Pt-$d_{x^2-y^2}$	Pt-d_{xz},-d_{yz}
15	Pt-d_{xy},-d_{z^2},-s/K-s	Pt-d_{z^2},-s/Na-s
16	Pt-d_{xy},-d_{z^2},-s	Pt-d_{z^2},-s/H-s
17	Pt-d_{z^2},-d_{xy}/K-$d_{x^2-y^2}$,-d_{xy}/H_1-s/H_2-s	Na-s/Pt-p

Pt-d_{xz},-d_{yz} (doubly degenerate at $\Gamma\vec{k}$-point) and Pt-$d_{x^2-y^2}$ contributions. In our choice of coordinate axis, the Pt-d orbitals pointing towards the H atoms are d_{z^2} and $d_{x^2-y^2}$. In addition, we found marginal contributions of K-d,s states in the partial DOS in this energy region. The remaining four valence electrons fill the last narrow structure consisting of two bands with a band width of 0.56 eV which arises from the Pt-d_{xy},-d_{z^2},-s and K-s interactions. We thus found sixteen bands filled with the 32 valence electrons contained in the tetragonal unit cell. These occupied bands are separated from the conduction bands by an indirect energy gap of 3.30 eV between the M and Γ symmetry $\vec{k}$–points. The energy gap concerns the occupied state at M$\vec{k}$-point of Pt-d,-s character and the unoccupied state at $\Gamma\vec{k}$-point which is the result of Pt-d, K-d and H-s orbital interactions. The first unoccupied bands show a structure slightly separated from the bands of higher energies (band width = 1.98 eV). These bands are essentially the result of Pt-d and K-d interactions with a contribution from H-s orbitals.

In Fig. 3 we show the energy bands and total DOS of Na_2PtH_4. We observe 16 filled bands separated from the unoccupied states by an energy gap of 1.97 eV. The sixteen bands form five well defined structures in the total DOS plot. The first, at the bottom of the energy scale, is 0.84 eV wide and is formed by four bands, two of which result from a strong Pt-d_{xy}/H-s interaction since these d orbitals point towards the H atoms, the other two bands are due to rather weak Pt-d_{z^2},-s/H-s interactions. The next three structures are contiguous in energy, however, we can identify a structure of band width of 0.42 eV,which is obtained from four bands of H-s character with no negligible Pt-p_x,-p_y contributions. In increasing order of energy, a third narrow structure, of 0.82 eV width, appears and concerns two bands essentially formed by no bonding Pt-$d_{x^2-y^2}$ orbitals. The fourth structure is also very narrow (0.34 eV) and it is formed by four bands arising from no bonding Pt-d_{xz},-d_{yz} orbitals.

Finally, the occupied bands are completed by a last structure which is relatively wide (1.09 eV) and is formed by 2 bands which are provided by the Pt-d_{z^2} orbitals with small contributions from H-s states. The first unoccupied state appears at $\Gamma\vec{k}$-point and it is the result of Pt-d,s and H-s interactions with a marginal contribution of Na-p states. The direct energy gap is present at $\Gamma\vec{k}$-point between the Pt-d,-s/H-s state and the unoccupied states which result from the Na-s/Pt-p orbital interaction.

The comparison between the electronic structure results of both hydrogen ordered hydrides can be facilitated by comparing the symmetry analysis of the wave function coefficients at the $\Gamma\vec{k}$-point listed in Table 2. For the K_2PtH_4 hydride a d orbital mixing appears for the orbitals pointing in the hydrogen directions (d_{xy} and d_{z^2} in our

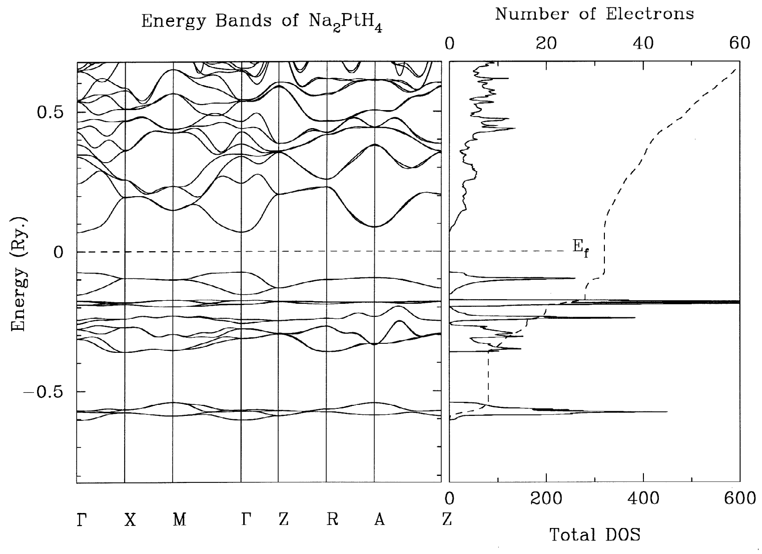

Fig. 3. Energy bands (in Ry) and total density of states (in states of both spins/Ry-unit cell) of Na_2PtH_4.

choice of coordinate axis). This can be clearly observed in the first four states concerning the Pt-d/H-s bonding interactions. In the case of Na_2PtH_4, the first and third Pt-d/H-s bonding states involve the hybridation of the Pt-d_{z^2} and Pt-s orbitals. This interaction is possible due to the diffuse character of (small energy difference between) the Pt-5d and Pt-6s orbitals. However, the strongest Pt–H interactions concern the second and fourth states on which the Pt-d_{xy}/H-s contributions are dominant. We recall that in this structure all the H atoms are located in the x–y plane. In the following four states, the H-s/Pt-p interactions are involved. While for K_2PtH_4 both H-s/Pt-p_z and H-s/Pt-p_x,-p_y are present (hydrogen atoms in the x–y plane and z direction), for Na_2PtH_4 only the H-s/Pt-p_x,-p_y are present and are doubly degenerate. The largest differences appear for the occupied states labeled 9 to 14 in Table 2 which show a different ordering of the Pt-d states. This is produced by the stabilizing interaction between Pt-$d_{x^2-y^2}$ and Na-s and Na-p orbitals in Na_2PtH_4. This effect is absent in the K_2PtH_4 hydride. The origin of this weak alkali–transition metal interaction can be attributed to the short Pt–Na (3.125 Å) distance compared to Pt–K (3.446 Å). The two last occupied states (labeled 15 and 16 in Table 2) are of a slightly different nature in both compounds. For K_2PtH_4, we observe two complex hybridized states formed by Pt-d_{xy}, Pt-d_{z^2} and Pt-s orbitals. The state 15 interacts weakly with the K-s orbitals. For Na_2PtH_4, hybridized Pt-d_{z^2},-s orbitals interacts with the Na-s orbital (state 15) and marginally H-s orbital (state 16). Finally, the first unoccupied states (state 17 in Table 2) are very different in nature for each hydride. For K_2PtH_4, the K-d orbital contribution appears as in the high temperature K_2PtH_4 and stoichiometric K_2PtH_6 phases. In the case of Na_2PtH_4, a Na-s state appears at $\Gamma\vec{k}$-point which show a non negligible Pt-p contribution. We observe that the energy gap in both compounds differs by 1.4 eV. This is mainly due to the Na-s unoccupied state appearing at the $\Gamma\vec{k}$-point at lower energies in the Na_2PtH_4 hydride.

3. Conclusion

We have investigated the electronic structure of new ternary platinum based hydrides by means of the ab initio APW method. Structurally, K_2PtH_4 and Na_2PtH_4 differ by the Pt–H (Pt–Pt) distances which are larger (smaller) in the Na-compound. These features are reflected in their electronic structure. The study of the defective ordered phases K_2PtH_4 and Na_2PtH_4 show very similar overall band structures and DOS, (i) the ordering of the energy bands are essentially the same for both hydrides, which is consistent with the electronic states ordering expected for a square planar PtH_4 complex and (ii) these compounds are both insulators with a large energy gap. However, fine differences were observed by the symmetry analysis of the bonding orbitals at $\Gamma\vec{k}$-point. In K_2PtH_4 the shorter Pt–H distances lead to a larger splitting of the bonding versus antibonding metal–hydrogen states while the larger Pt–Pt distances lead to dispersionless bands and to very narrow structures in the DOS. This compound has a strong molecular character. For Na_2PtH_4, in which the Pt–H distances are slightly larger and the Pt–Pt distances shorter compared to K_2PtH_4, we observe that the valence band structures are concentrated in a small energy region with a significant broadening of the energy bands and DOS structures.

An important feature in the electronic structure of Na_2PtH_4 is the effect of the Na-s and Na-p orbitals which interact with Pt-$d_{x^2-y^2}$ orbitals broadening and lowering in energy the corresponding energy bands. The origin of the role of the Na orbitals on the chemical bonding can be understood by comparing the alkali to Pt metal distance, which is lower for the Na_2PtH_4. Finally, the reduction in the energy gap of Na_2PtH_4 with respect to K_2PtH_4 comes from the Na-s states which appear at lower energies at $\Gamma\vec{k}$-point.

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