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Electronic Properties of Ternary Hydrides A_2PdH_2 (A = Li, Na)

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That Na_2PdH_2 is a metal was shown by measuring its electrical resistivity as a function of temperature down to 4.2 K. First principles pseudofunction self-consistent-field (PSF–SCF) band electronic structure calculations were performed for the ternary hydrides A_2PdH_2 (A = Li, Na) to find that these hydrides are semimetals. The orbital nature of the partially filled bands of Na_2PdH_2 were analyzed on the basis of extended Hückel tight-binding band calculations. Analysis of the Fermi surfaces of A_2PdH_2 (A = Li, Na) predicts that these hydrides are primarily two-dimensional metals with good conductivity in the *ab* plane.

Recently, a number of ternary transition metal hydrides $A_xM_yH_z$ (A = alkali or alkaline earth metal) have been synthesized and characterized.[1,2] These hydrides consist of anionic M_yH_z complexes in an alkali metal atom framework. Except for Li_2PdH_2 and Na_2PdH_2,[2] all ternary hydrides are not metals. The hydrides A_2PdH_2 (A = Li, Na) are isomorphous in structure with Na_2HgO_2[3] and contain linear H–Pd–H complexes as illustrated in Figure 1. The crystal structure of A_2PdH_2 (A = Li, Na) results when Na^+H^- double rock salt layers are joined by Pd atoms to form linear H–Pd–H bridges. Given the usual oxidation states of Li^+, Na^+, and H^-, the palladium in A_2PdH_2 (A = Li, Na) is in the oxidation state of Pd^0 so that the transition metal d electron count is d^{10}. Thus one might have expected a band gap between the palladium d-block bands and the alkali metal s- and p-block bands and hence nonmetallic properties for A_2PdH_2 (A = Li, Na). Recently, Gupta and Temmerman[4] carried out first principles band structure calculations on Na_2PdH_2 based upon the linear muffin-tin orbital method in the atomic sphere approximation to show that Na_2PdH_2 is a metal, in agreement with experiment. However, this work did not address either the question of the metallic origin or the question about the dimensionality of the metallic character of A_2PdH_2. In the present work, we probe these questions by performing first principles pseudofunction self-consistent-field (PSF–SCF) band electronic structure calculations[5] on A_2PdH_2 (A = Li, Na) and extended Hückel tight-binding (EHTB)[6] band electronic structure calculations on Na_2PdH_2. We also report the resistivity of Na_2PdH_2 measured as a function of temperature.

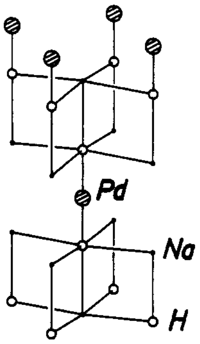

Figure 1. Schematic representation of the coordinate environments of the crystal structure of A_2PdH_2 (A = Li, Na).

Synthesis and Characterization of Na_2PdH_2

A sample of Na_2PdH_2 (2.19 g) was made by reacting a 2:1 molar mixture of NaH and Pd powder according to ref 2c. No weight change (>0.01 g) was observed after the completion of the reaction. The resulting hydride ingot had a metallic luster. This ingot was crushed under argon and then checked with Guinier-Hägg X-ray powder diffraction to find that it is single phased with no traces of Na, NaH, or Pd. The crushed ingot consisted of rectangular plate-like crystallites with metallic luster. The same morphology has earlier been reported for isostructural

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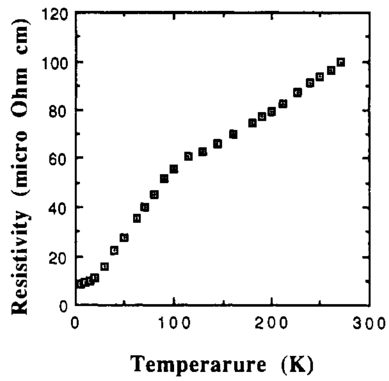

Figure 2. Electrical resistivity of Na_2PdH_2 measured as function of temperature.

oxomercurate and oxonickelate compounds.[3,7] This indicates that the synthetic method of ref 2c is a convenient route to single phase samples of ternary transition metal hydrides.

The metallic character of Na_2PdH_2 was examined by measuring the electrical resistivity. The ingot immersed in liquid N_2 was found to have the resistivity about 40% of its room temperature value (measured with separate current and voltage leads connected to the sample by springs). To make more detailed resistivity measurements, the hydride was crushed under argon and transferred to a soda glass tube, which had been prepared for the resistivity measurement by insertion of four copper wires through the wall. The inner diameter of the glass tube was 6 mm. The outer current connection were 17 mm apart, and the inner voltage connection were 8 mm apart. The crushed hydride was connected to the copper wire by quickly heating at 409 °C (above the melting point of Na_2PdH_2) under a hydrogen pressure of about 2 bars. Our Gunier-Hägg X-ray powder diffraction measurements of the sample after the melting did not show any impurity lines, so that the single-phase nature of the sample is not altered by the melting under hydrogen pressure.

A wide resistance coil was used to observe the sample during the heating. Some of the intergranular hydrogen remained as bubbles in the liquid Na_2PdH_2, due to the surface tension, and could not be removed. Thus our calculation of the room-temperature resistivity (100 $\mu\Omega$ cm) includes the estimates of hydrogen bubbles remaining in the sample and errors of the geometrical form factor. However, uncertainties in these estimates should not influence the interpretation of the temperature dependence of the resistivity.

The temperature was measured with calibrated carbon and Pt resistors. A low measuring current of 3 mA was used to prevent heating. In order to check the results for reproducibility, data were taken both on heating and cooling. The resistivity vs temperature (ρ vs T) plot, given in Figure 2 between room temperature and 4.2 K, clearly shows that Na_2PdH_2 is a metal. The slope of this plot changes at about 100 K, the cause for which has not yet been investigated. It is interesting to note that the resistivity at room temperature as well as its temperature coefficient of the resistance, about 2.6×10^{-3} K^{-1}, are both similar to the corresponding results obtained for LiPdH.[8]

Electronic Structures of A_2PdH_2 (A = Li, Na)

In our PSF–SCF band calculations on A_2PdH_2 (A = Li, Na), the muffin-tin spheres about all atoms of the unit cell were represented by spherically symmetric potentials (s, p, and d pseudofunctions on Pd; s and p pseudofunctions on Li, Na, and H). The entire unit cell was represented by nonspherical potentials constructed from 25 137 (i.e., 21 × 21 × 57) plane waves.

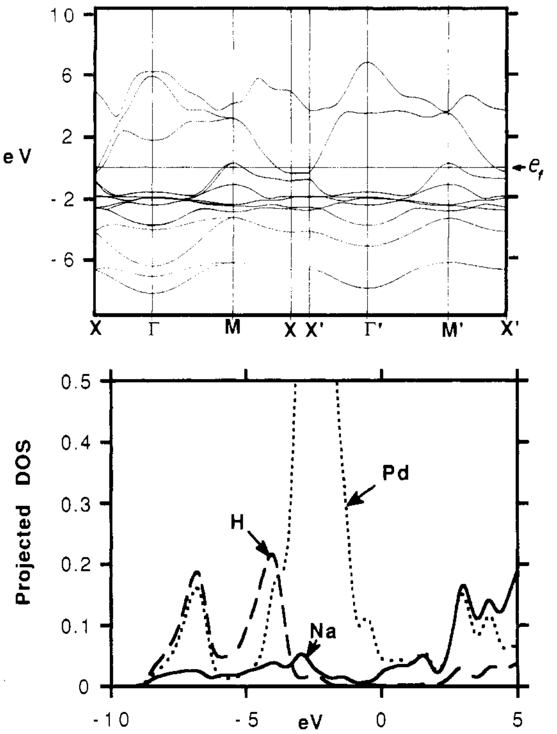

Figure 3. Top: (a) Band dispersion relations calculated for Na_2PdH_2, where the Fermi energy is taken to be zero. In terms of the reciprocal vectors a^*, b^* and c^*, the wave vector points are defined as follows: $\Gamma = (0, 0, 0)$, $X = (a^*/2, 0, 0)$, $M = (a^*/2, b^*/2, 0)$, $\Gamma' = (0, 0, c^*/2)$, $X' = (a^*/2, 0, c^*/2)$, $M' = (a^*/2, b^*/2, c^*/2)$. Bottom: (b) Projected DOS plots calculated for Na_2PdH_2.

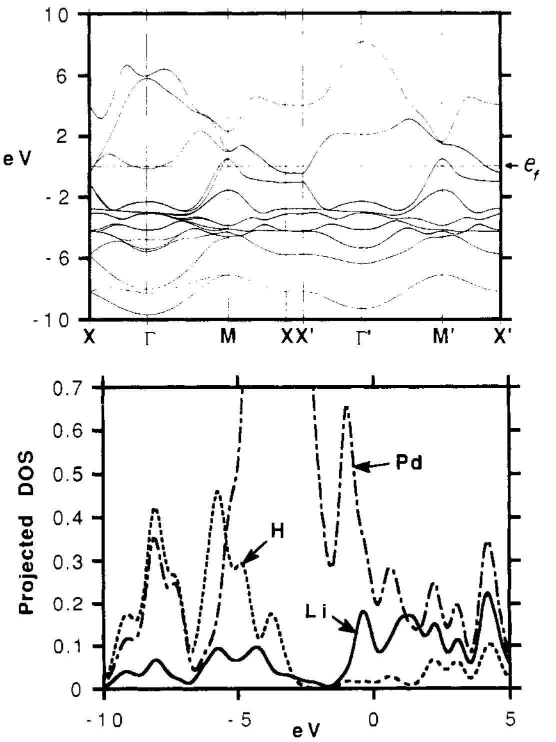

Figure 4. Top: (a) Band dispersion relations calculated for Li_2PdH_2, where the Fermi energy is taken to be zero. $\Gamma = (0, 0, 0)$, $X = (a^*/2, 0, 0)$, $M = (a^*/2, b^*/2, 0)$, $\Gamma' = (0, 0, c^*/2)$, $X' = (a^*/2, 0, c^*/2)$, $M' = (a^*/2, b^*/2, c^*/2)$. Bottom: (b) Projected DOS plots calculated for Li_2PdH_2.

Figure 3a shows the band dispersion relations calculated for Na_2PdH_2, where the energies are given with respect to the Fermi level (taken to be zero). The valence and the conduction bands overlap slightly, so that Na_2PdH_2 is a semimetal. Figure 3b plots the projected densities of states (DOS) calculated for Na_2PdH_2.

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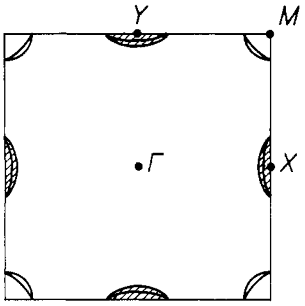
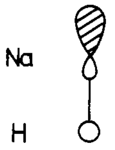


Figure 5. Schematic cross-sectional view of the cylinder-like hole and electron Fermi surfaces expected for A_2PdH_2 (A = Li, Na), where the electron surfaces are indicated by shading. $\Gamma = (0, 0, 0)$, $X = (a^*/2, 0, 0)$, $Y = (0, b^*/2, 0)$, and $M = (a^*/2, b^*/2, 0)$.

The H contribution is large well below the Fermi level (two peaks representing essentially the in-phase and out-of-phase combinations of the two hydrogen 1s orbitals of each $H–Pd–H^{2-}$ unit), but small in the vicinity of the Fermi level. The palladium d-orbital character extends to above the Fermi level, while the alkali metal s- and p-orbital character extends to below the Fermi level. The latter are consistent with the fact that Na_2PdH_2 is a semimetal. The band dispersion relations and the projected DOS plots calculated for Li_2PdH_2 by our PSF–SCF band calculations are given in parts a and b of Figure 4, respectively. In essence, these results are identical with those calculated for Na_2PdH_2, except for a minor difference that the bottom of the conduction bands at Γ dips slightly below the Fermi level in Li_2PdH_2 while this is not the case for Na_2PdH_2. Thus the present PSF–SCF band calculations show that the metallic properties of A_2PdH_2 (A = Li, Na) originate from a small overlap between the palladium d-block bands and the alkali metal s- and p-block bands.

To analyze the orbital nature of the partially filled bands of A_2PdH_2 (A = Li, Na), we performed EHTB calculations for Na_2PdH_2. Use of the atomic parameters of Na, Pd, and H typically employed for molecular orbital calculations predicts a band gap exceeding 5 eV. Thus in our EHTB calculations, the atomic parameters of Na, Pd, and H were gradually varied until the calculated band dispersion relations become similar to those of Figure 3a. (For the hydrogen s and the palladium d orbitals, the orbital exponents were made less contracted and the valence shell ionization potentials were made smaller. For the sodium s and p orbitals, the orbital exponents were made more contracted and the valence shell ionization potentials were made larger.) Analysis of the resulting EHTB bands show that the bottom of the conduction band at X is represented mainly by the s/p-hybrid orbitals (**1**) of Na atoms, and the top of the valence bands at M mainly by the z^2/s-hybrid orbitals (**2**) of the H–Pd–H complexes. In **2**, the hydrogen 1s orbitals make antibonding interactions with the $4d_{z^2}$ orbital of Pd but bonding interactions with the 5s orbital of Pd. For more detailed discussions of the bonding in the complexes with d^{10} electron count, see ref 9.) In other words, orbital **1** is lower in energy than orbital **2**. In the PSF–SCF band calculations, this feature is obtained as a result of SCF adjustment of the potentials and is responsible for the small amount of electron transfer from the palladium d-block bands to the alkali metal s- and p-block bands in A_2PdH_2 (A = Li, Na).



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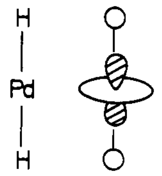

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Figures 3a and 4a reveal that the partially filled bands of A_2PdH_2 (A = Li, Na) are almost dispersionless along the c^* direction. (An exception is the conduction band of Li_2PdH_2 along $\Gamma \rightarrow \Gamma'$, because it is below the Fermi level at Γ but above the Fermi level at Γ′.) Therefore, the Fermi surfaces of Na_2PdH_2 consist of two cylinder-like hole surfaces along $M \rightarrow M'$ (and along its equivalent directions) and two cylinder-like electron surfaces along $X \rightarrow X'$ (and along its equivalent directions), as schematically shown in Figure 5. This means that Na_2PdH_2 is primarily a two-dimensional metal with good conductivity in the *ab* plane, i.e., the plane of the double rock salt layer. The same is true for Li_2PdH_2 except that it has an additional electron Fermi surface given as a small closed pocket centered at Γ. Because of the latter, it is expected that Li_2PdH_2 has a greater metallic character along the c^* direction (i.e., the *c* direction) than does Na_2PdH_2.

Concluding Remarks

The present PSF–SCF and EHTB band electronic structure calculations show that ternary hydrides A_2PdH_2 (A = Li, Na) are semimetals because the top portion of the Pd d-block bands overlaps with the bottom portion of the alkali metal s- and p-block bands. The Fermi surfaces of A_2PdH_2 (A = Li, Na) predict that these hydrides are essentially two-dimensional metals with good conductivity in the *ab* plane, and that Li_2PdH_2 has a greater conductivity along the *c* direction than does Na_2PdH_2.

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Registry No. Li_2PdH_2, 126169-96-8; Na_2PdH_2, 115631-73-7.

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