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Ternary Hydrides of Calcium and Strontium with Palladium

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New ternary hydrides of the stoichiometry $SrPd_2H$, Sr_2PdH_4, and $Ca_3Pd_2H_4$ have been prepared. These compounds were formed by reacting the respective alkaline earth binary hydride with palladium under approximately 625 mm of hydrogen pressure at temperatures ranging from 750 to 850° for 8–10 hr. Differential thermal analyses were used as a guide in evaluating optimum reaction temperatures and decomposition behavior of the reactants and products. The $SrPd_2H$ was also formed by intermetallic hydrogenation. X-Ray diffraction data for each ternary were indexed as cubic. Electrical resistance measurements for each of the ternary hydrides indicated metallic behavior. Magnetic data showed that the ternary systems were diamagnetic or weakly paramagnetic.

Introduction

Sodium borohydride and lithium aluminum hydride were some of the first (*1, 2*) and remain some of the best known of the ternary hydrides. More recently reports have been made on the ternary hydrides K_2ReH_9 (*3*), $KMgH_3$ (*4*), Mg_2NiH_4 (*5*), $ZrNiH_3$ (*6*), Li_4RhH_4, and Li_4RhH_5 (*7*). Information regarding the reactions between lithium hydride and rhodium, iridium, platinum, and palladium is given by Graefe and Robinson (*8*). The identification of $SrLiH_3$, $BaLiH_3$, and $EuLiH_3$ has been made in phase studies by Messer et al. (*9*). In view of the hydride–oxide and hydride–fluoride analogy (*10*), a general study was undertaken in this laboratory of ternary hydrides involving alkaline earth metals and the platinum metals. The investigation led to the preparation of new ternary hydride phases of calcium and strontium with iridium, rhodium, and ruthenium (*11, 12, 13*). This paper reports the preparation and characterization of ternary hydride phases of calcium and strontium with palladium. Parallel to and quite independent from these investigations, Magee and co-workers have reported on ternary hydrides of lithium with palladium (*14*) and other selected metals (*15*). The fact that lithium hydride uniquely melts before dissociation has led to differences between these two groups of investigators in synthesis techniques, the nature of the products formed, and the methods of product characterization used.

Palladium is an interesting reactant since its behavior with hydrogen was first studied by Graham over a century ago (*16*). Intensive investigation since that time shows that the stable product of the reaction deviates extensively from stoichiometric composition (*17, 18*). Hydrogen to palladium ratios may vary in the range of 0.025–0.9 depending upon synthesis mode and conditions. Two methods of synthesis are generally employed, both leading to a maximum hydrogen/palladium ratio of about 0.7 at normal temperatures and pressures. The gas-charged direct combination of the elements gives $PdH_{0.7}$. By making palladium the cathode in the electrolytic dissociation of water or 2 *N* sulfuric acid, a hydrogen/palladium composition approaching 0.7 has been achieved (*19*). A hydrogen/palladium ratio of approximately 0.9 has been reached using a modification of the latter method.

Phase studies have shown that the face-centered cubic palladium lattice ($a_0 = 3.891$ Å) expands upon hydriding. Initially, a single phase (alpha) region develops ($a = 3.984$ Å) and a two-phase region (alpha plus beta) begins at hydrogen to palladium ratios of 0.025–0.03. At ratios of $H/Pd \sim 0.58$, the alpha phase reflections disappear and the beta phase lattice constant increases linearly with continued hydriding to a maximum $a = 4.04$ Å at

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H/Pd ~ 0.7. Neutron diffraction studies show a face-centered cubic metal sublattice with hydrogen in the octahedral interstices (*20*).

Experimental

Materials

Calcium metal (99% from K & K Laboratories, Inc.) and strontium metal (98–99% from A. D. Mackay) were further purified by vacuum distillation at approximately 825° and 1×10^{-5} mm pressure in a stainless steel apparatus. The distilled metal was removed from the steel cold finger in a glove bag and mechanically chipped into small pieces. Strontium hydride and calcium hydride were prepared by the direct combination of the elements at approximately 500° for 12 hr at a hydrogen pressure of approximately 1 atm. Hydrogen and deuterium were Matheson extra dry or prepurified grade further purified by diffusion through a palladium tube heated to 400° in a Bishop hydrogen diffusion cell Model #A-1-D. The palladium powder (–325 mesh and 99.9% from Matthey Bishop) was used as purchased.

Preparation of Strontium Palladium Hydride 1:2 Phase

Strontium hydride and palladium powders were combined in a 1:2 molar ratio and tumble mixed in a one dram Opticlear vial by manual rotation in all directions. The powdered mixture was then pelletized at 5000 psi into a cylindrical pellet 0.25 in. in diam and 0.125–0.25 in. in length. The pellet was placed into a preconditioned hydrogen-treated molybdenum boat in a quartz reaction tube and attached to the vacuum line. The system was evacuated to 1×10^{-5} mm. Oxygen-free hydrogen was introduced to a pressure of approximately 600 mm at ambient temperature.

The reaction was carried out by heating the pellets at 750–760° for 10 hr. The strontium hydride to palladium mole ratio of 1:2 gave a single phase free from starting materials as shown by the X-ray powder pattern. All sample handling was done in a dry nitrogen atmosphere.

Strontium was analyzed as the insoluble sulfate following the procedure of Erdy (*21*). Palladium, left as the metal after acid hydrolysis of the ternary compound, was determined gravimetrically. X-Ray analysis of the solid residue confirmed the presence of only palladium metal.

Hydrogen was determined by hydrolytic, pyrolytic, and combustion methods. Hydrolytically, a weighed sample was placed into a reaction tube and placed on the vacuum line. After evacuation, concd hydrochloric acid was condensed under vacuum at –196° into the reaction tube. Upon warming, the acid reacted with the sample. After the reaction was completed as indicated by a constant manometric pressure, the reaction tube was cooled to –196° and the evolved hydrogen was transferred by a Toepler pump through two –196° traps into a calibrated volume. The number of moles of hydrogen generated were calculated assuming ideal gas behavior. Samples for pyrolytic hydrogen determination were pelletized and placed in a 3.5 cm molybdenum tube and slipped into a quartz sleeve 7–8 cm long and 11 mm o.d. This unit was placed into a silica reaction tube, horizontally attached to a vacuum line and a nichrome-wound furnace slipped over the end. After evacuation to better than 1×10^{-4} mm the sample was heated to 925° and held at this temperature until no further gas evolved. The gas was passed through two –196° traps and transferred as it evolved by a Toepler pump into a calibrated volume. Baron Consulting Company of Orange, Connecticut, performed classical combustion analyses for hydrogen on several samples. *Anal.* Calcd for $SrPd_2H$: Sr, 29.1; Pd, 70.6; H, 0.33. Found: Sr, 28.4; Pd, 70.6; H, 0.32 (hydrolysis), 0.33 (pyrolysis), 0.30 (combustion). Density for $SrPd_2H$: Calcd 7.91 g/cm^3; Found 7.82 g/cm^3.

Preparation of Strontium Palladium Hydride 2:1 Phase

The same sample preparation techniques as described for the strontium palladium hydride 1:2 phase were used. The reaction was carried out by heating the pellets at 800–810° for 10 hr under a hydrogen pressure 625 mm. X-Ray evidence showed a single phase free from starting materials at a 2:1 mole ratio of strontium hydride to palladium.

Elemental analyses were performed as discussed above for the 1:2 phase. *Anal.* Calcd for Sr_2PdH_4: Sr, 61.2; Pd, 37.2; H, 1.41. Found: Sr, 60.8; Pd, 37.2; H, 1.34 (hydrolysis), 1.37 (pyrolysis), 1.27 (combustion). Density for Sr_2PdH_4: Calcd 3.83 g/cm^3; Found 3.83 g/cm^3.

Preparation of Calcium Palladium Hydride 3:2 Phase

Similar techniques to those employed in the sample preparations for the strontium palladium hydrides were used for the preparation of the 3:2 calcium palladium hydride phase. The specific conditions in this case were a reaction temperature of 850° for 10 hr under a hydrogen pressure of 625 mm.

Calcium was determined by precipitation of the insoluble oxalate (*22*) and by atomic absorption spectroscopy. Atomic absorption was performed on a Techtron/Varian Atomic Absorption Spectrophotometer Type AA4 using a hollow cathode calcium lamp (4226.7 Å) and an air/acetylene flame. Standard solutions were prepared from dried analytical grade calcium carbonate. The ternary hydride was prepared for atomic absorption by HCl hydrolysis and appropriate dilution of the hydrolysis filtrate. Hydrogen and palladium analyses were performed as discussed above for the Sr–Pd–H systems. *Anal.* Calcd for $Ca_3Pd_2H_4$: Ca, 35.7; Pd, 63.1; H, 1.20. Found: Ca, 34.3 (oxalate), 34.5 (atomic absorption); Pd, 64.2; H, 1.29 (hydrolysis), 1.21 (pyrolysis). Density for $Ca_3Pd_2H_4$: Calcd 3.94 g/cm^3; Found 3.90 g/cm^3.

Physical Measurements

Pellet densities were measured by the liquid buoyancy method using carbon tetrachloride previously dried over calcium hydride.

X-Ray data were obtained with a GE XRD-5 diffractometer using Ni-filtered Cu radiation and a proportional counter as well as by Debye–Scherrer techniques, using glass capillaries sealed under nitrogen. For the diffractometer runs, the sample was dispersed in Vaseline on a glass microscope slide.

Differential thermal analyses were carried out on a DuPont 1200 high-temperature apparatus, modified to allow either vacuum operation or a 225 ml/min flow rate of hydrogen gas at 1 atm of pressure. Scans were carried out at either a 10°/min or more generally 20°/min heating rate over a temperature range of room temperature to 900°. Platinum cup sample holders were used with alumina as the reference standard.

Electrical resistivities were roughly measured on pellets between two probes of a Model #260 Simpson voltmeter.

Magnetic susceptibilities were measured by the Faraday method over a temperature range of 77–295°K.

Results and Discussion

Strontium hydride reacts with palladium metal in a hydrogen atmosphere to form two new Sr–Pd–H ternary hydride phases, $SrPd_2H$ and Sr_2PdH_4. They are black, crystalline, nonvolatile solids which react with protonic materials such as water and acids.

The stoichiometry of each new phase was initially indicated by X-ray powder pattern data. When a 1:2 molar ratio of strontium hydride to palladium was used, the resulting product exhibits a characteristic X-ray powder pattern free from the starting materials. These lines were assigned to the $SrPd_2H$ phase. Strontium hydride to palladium molar ratios were varied from 2:1 to 1:10 under reaction conditions similar to those used in the formation of the new 1:2 phase, i.e., ~750° and 625 mm of hydrogen pressure. These results showed that at ratios greater than 1:2, excess strontium hydride appeared along with the new ternary phase. As the palladium content of the reactant mixture increases beyond 1:2, lines characteristic of the new ternary phase disappeared and lines for $PdH_{0.706}$ appeared in the powder pattern. The latter predominates at molar ratios between 1:6 and 1:7.5. Above 1:7.5, X-ray analysis indicates the presence of unreacted palladium metal. The $SrPd_2H$ was also formed by the direct hydrogenation of intermetallic $SrPd_2$. The intermetallic was initially formed by the reaction of stoichiometric amounts of strontium and palladium metals under vacuum. Careful monitoring of hydrogen uptake during the hydrogenation reaction showed the absorption of one mole of hydrogen atoms to two moles of palladium. The X-ray powder pattern for this product was identical to that observed for the 1:2 SrH_2:Pd reaction product.

It is interesting to note the formation of $PdH_{0.706}$ at lower strontium to palladium ratios. The presence of strontium seems to stabilize the beta palladium hydride and allows for its formation and persistence at temperatures in excess of those allowable for its synthesis by direct combination of the elements. Evidence for a similar action by calcium is presented later in this discussion. In effect, the alkaline earth metal is acting as an alloying element under these conditions. In the case of palladium in alloys, X-ray studies of the alpha to beta phase transitions have been reported to date for only the Pd–Ag–H (*23*), Pd–Pt–H (*24*), Pd–Au–H (*25*), and Pd–Cu–H (*26*) systems. These studies have been limited to measurements at or close to ambient room temperature. Hydrogen introduction into these samples has been done either by electrolysis or spontaneous absorption from hydrogen-saturated solutions. In these systems, alloys containing 10–20% of the alloying metal exhibit alpha to beta phase transitions and changes in lattice parameter like those for pure palladium. At higher concentrations of alloying element, the difference between the lattice parameters characteristic of alpha maximum and beta minimum is gradually reduced and thus sharp transformations will no longer occur (*27*). Thus, the high-temperature reaction of palladium and strontium hydride (or calcium hydride) discussed above represents an additional method for the formation of beta palladium hydride.

When a 2:1 molar ratio of strontium hydride to palladium is reacted at the higher temperatures of 800–810°, the formation of another ternary hydride, Sr_2PdH_4, occurs. When strontium hydride is used in amounts greater than indicated by the 2:1 ratio, the X-ray powder pattern indicates unreacted strontium hydride. Reducing the amount of strontium hydride in the reactant mixture to 1:2 favored the formation of an $SrPd_2H$-related phase. This phase is formed at a higher temperature than the synthesis temperature for $SrPd_2H$. Its cell parameter is less than that observed for $SrPd_2H$, but somewhat greater than the value for the intermetallic $SrPd_2$. This decrease could be due to the loss of some hydrogen at this higher temperature and would lead, with complete hydrogen release, to $SrPd_2$. This view is supported by X-ray evidence that $SrPd_2$ is the post-pyrolysis product of $SrPd_2H$.

A variety of reaction conditions were tried for the synthetic procedure. The most favorable conditions for $SrPd_2H$ formation are an 8 hr heating period at 750°; Sr_2PdH_4 formation occurs most readily at an 800–810° heating period for 10 hr.

The synthesis conditions for the Sr–Pd–H system ternary hydrides did not yield the analogous calcium compounds. A new ternary hydride of calcium and palladium was formed by the reaction of a 2:1 molar ratio of calcium hydride to palladium at 850° under 625 mm of hydrogen pressure. Under these conditions, the resulting darkening of the reaction tube and the pellet's loss of structural integrity were taken to indicate a loss of material from the starting mixture. To check material balance, a preweighed quartz sleeve was placed around the molybdenum reaction boat and the sleeve in turn placed into the reaction tube. The weight gained by the sleeve during the reaction equaled the weight via calcium loss from the pellet. This evidence was supported by subsequent analytical work, indicating the new phase to be $Ca_3Pd_2H_4$. Calcium palladium hydride is a dark gray, crystalline, nonvolatile solid susceptible to attack by water and acids. X-Ray diffraction data indicated this new ternary hydride to be free of starting materials.

When the 2:1 molar ratio of CaH_2:Pd is reacted at a lower temperature (800°) than the 850° temperature used in the synthesis of $Ca_3Pd_2H_4$, a new cubic phase forms. However, residual calcium hydride was present in the X-ray powder pattern. A decrease in calcium hydride content by 0.25 mole increments between the range of 1.75:1–1.0:1.0 for the starting mixture failed to produce under similar conditions, either a pure ternary hydride or the new cubic phase observed for the 2:1 molar ratio reaction. As the CaH_2:Pd ratio decreased, the powder patterns for the reaction products displayed a diminution in the intensities of the calcium hydride lines and an increase in the intensities of lines assignable to $CaPd_2$ (*28*). The new 800° 2:1 phase, contaminated with calcium hydride, was indexed as cubic with a cell parameter of 7.03 Å.

The calcium analog of $SrPd_2H$ did not form under reaction conditions leading to the Sr–Pd–H phase formation, i.e., CaH_2:2Pd reaction under hydrogen or direct hydrogenation of $CaPd_2$. Instead, powder pattern data revealed the initial formation of $PdH_{0.706}$ at temperatures less than or equal to 275°. This was followed by the disappearance of calcium hydride between 420 and 500° with the associated formation of a partially characterized new phase. This phase was indexed to be cubic with a cell parameter of 4.10 Å. It persisted in conjunction with $PdH_{0.706}$ to at least 580°. Variation of reaction hold time from 4–10 hr at 575° neither enhanced nor diminished this composition. Attempts to isolate the product from $PdH_{0.706}$ by increasing the reaction temperature to 755° led to $CaPd_2$ formation. This behavior precluded any further attempts to fully characterize this interesting new product as being either a binary or ternary hydride. Since these experiments failed to form a pure calcium analog of $SrPd_2H$, one of the factors mitigating against its formation might be the greater tendency for $CaPd_2$ formation over that of $SrPd_2$ in these systems.

Densities were measured by the liquid buoyancy method. Good agreement between measured and calculated densities was obtained for each system. Density data show that there are 8 formula units per unit cell for both $SrPd_2H$ and Sr_2PdH_4 and one for $Ca_3Pd_2H_4$. The equation $\rho = (1.6602)(\sum A)/V$ was used where ρ is the density, 1.6602 is a conversion factor, $\sum A$ is the sum of all the atomic weights of the component atoms and V is the cell volume. These data are tabulated in Table I.

X-Ray diffraction powder patterns were indexed on the basis of a cubic unit cell for each of the ternary phases. The indexing data for $SrPd_2H$, Sr_2PdH_4, and $Ca_3Pd_2H_4$ are given in Tables II, III, and IV, respectively. Potassium chloride was used as a reference standard.

The X-ray diffraction pattern of strontium palladium hydride, $SrPd_2H$, appears to be iso-

TABLE I

DENSITY MEASUREMENTS

	Density, g/cm^3	
Compound	Calculated	Measured
$SrPd_2H$	7.91	7.82
Sr_2PdH_4	3.83	3.83
$Ca_3Pd_2H_4$	3.94	3.90

morphous with $SrPd_2$ (*28*). The intermetallic, $SrPd_2$, has the $MgCu_2$ structure. Compounds of this AB_2 type are commonly known as "Laves phases" in reference to F. Laves who pointed out the spatial relationships of A–A, B–B, and A–B (*29*). The space group is *Fd*3*m* with eight formula weights per unit cell. The strontium atoms are located at the diamond structure positions, i.e., 0, 0, 0; 1/4, 1/4, 1/4; face centered. A corner-shared tetrahedral arrangement of palladium at positions 5/8, 5/8, 5/8; 5/8, 7/8, 7/8; 7/8, 5/8, 7/8; 7/8. 7/8, 5/8 completes the unit cell. These five tetrahedra may be viewed as filling the center and the four octants of the cubic cell not occupied by strontium.

A sample of $SrPd_2D$ has been prepared for neutron diffraction analysis. Deuterium is the isotope of choice because of its higher neutron scattering factor and weaker incoherent scattering. We hope to report the results of the neutron diffraction study at a later date.

TABLE II

X-RAY INDEXING DATA
$SrPd_2H$

		$1/d^2$	
h k l	I_{obs}	Observed	Calculated
1 1 1	m+	0.0470	0.0471
2 2 0	m–	0.1248	0.1256
3 1 1	vvs	0.1712	0.1727
2 2 2	vs	0.1870	0.1884
4 0 0	w	0.2490	0.2512
3 3 1	w–	0.2955	0.2964
4 2 2	w–	0.3739	0.3744
5 1 1, 3 3 3	m—s	0.4181	0.4212
4 4 0	m—s	0.4965	0.4960
5 3 1	w–	0.5426	0.5425
5 3 3	w	0.6657	0.6665
6 2 2	m–	0.6823	0.6820
4 4 4	vw	0.7447	0.7440
5 5 1, 7 1 1	vw	0.7900	0.7905
5 5 3, 7 3 1	m—s	0.9145	0.9138
8 0 0	w	0.9918	0.9920

TABLE III

X-RAY INDEXING DATA
Sr_2PdH_4

		$1/d^2$	
h k l	I_{cbs}	Observed	Calculated
2 1 0	w	0.0540	0.0508
2 2 0	vvs	0.0812	0.0812
2 2 2	w	0.1250	0.1218
4 0 0	s	0.1640	0.1625
4 2 2	m	0.2416	0.2436
5 1 1, 3 3 3	m	0.2738	0.2741
4 4 0	w—m	0.3228	0.3248
6 2 0	w	0.4078	0.4060
7 0 0	w	0.4942	0.4939

Unit cell parameters were calculated from the X-ray diffraction powder pattern data and these results are listed in Table V.

Data obtained from the differential thermal analyses are summarized in Tables VI and VII. The results were used mainly as a guide in evaluating optimum reaction temperatures and decomposition behavior of the reactants and products. The results for vacuum runs indicated that decomposition with release of hydrogen occurs in several steps. This correlates with the observations that hydrogen is released as a function of time and temperature during pyrolytic hydrogen analyses. Observation of

TABLE IV
X-RAY INDEXING DATA
$Ca_3Pd_2H_4$

		$1/d^2$	
h k l	I_{obs}	Observed	Calculated
1 1 0	m	0.0713	0.0733
2 0 0	vs	0.1484	0.1468
2 1 1	w	0.2225	0.2201
2 2 0	m	0.2955	0.2985
3 1 0	w	0.3672	0.3669
2 2 2	ms	0.4418	0.4403
4 0 0	m–	0.5870	0.5870
4 2 0	w	0.7345	0.7338

TABLE V

UNIT CELL DIMENSIONS

Compound	a, Å
$SrPd_2H$	7.97
Sr_2PdH_4	9.96
$Ca_3Pd_2H_4$	5.22

the 765° endotherm in the Sr–Pd–H system focused attention to this temperature region as a possible fruitful area for synthesis attempts. These attempts then led to the formation of $SrPd_2H$. In a similar fashion, the optimum reaction temperature was evaluated for the synthesis of Sr_2PdH_4. The thermogram for the Ca–Pd–H system was interpreted as indicating $CaPd_2$ formation at 620° and calcium hydride decomposition at 825°. The 440–450° endotherm may be associated with the onset of the new phase contaminated with calcium hydride, which has been previously discussed. Ternary formation in the Ca–Pd–H system above 825° would indicate that the ternary forms only after calcium hydride decomposition occurs. Ternary formation could then proceed through the uptake of hydrogen from the hydrogen atmosphere around the reaction environment. The pellet's loss of structural integrity supports the notion of calcium hydride decomposition.

Complementary results were obtained for hydrogen analyses by pyrolysis and acid hydrolysis techniques. These data in conjunction with analyses for the component metals are consistent with the formulas $SrPd_2H$, Sr_2PdH_4, and $Ca_3Pd_2H_4$ for the ternary hydrides. The analytical results are summarized in Tables VIII and IX.

TABLE VI

DIFFERENTIAL THERMAL ANALYSES
HYDROGEN ATMOSPHERE

System	Temperature, °C
Sr–Pd–H	180 sharp endotherm
	400–445 broad endotherm
	535–575 broad endotherm
	765 sharp endotherm
	790 sharp endotherm
Ca–Pd–H	150 sharp endotherm
	435 broad endotherm
	775 sharp endotherm

TABLE VII

DIFFERENTIAL THERMAL ANALYSES
VACUUM

System	Temperature, °C
Sr–Pd–H	150 sharp endotherm
	340–420 broad exotherm
	650 exotherm
	725 exotherm
	835 exotherm
Ca–Pd–H	220 broad endotherm
	450 broad exotherm
	625 exotherm
	775 exotherm
	830 exotherm

To assess if any hydrogen was being adsorbed *in situ* on the palladium surface, a mixture of the binary alkaline earth metal hydride and palladium metal powder was hydrolyzed. Following completion of the hydrolysis reaction, the reaction tube was cooled to –196° and the hydrogen generated was transferred with a Toepler pump through two –196° cold traps into a calibrated volume. The number of moles of hydrogen generated were calculated, assuming ideal gas behavior. Water was then removed from the reaction vessel by condensing it from the reaction tube into a –196° cold trap. Hydrogen transfer was continued for 1.5 hr while the dried decomposition residue was heated at 108°. The manometric pressure remained invariant during heating from that observed at the end of hydrolysis reaction. The number of moles of hydrogen measured experimentally was equal to that theoretically expected from the hydrolysis of the binary alkaline earth metal hydride alone. This result was interpreted to mean that no *in situ* absorption of hydrogen on the palladium surface occurred which might lead to the formation of a binary palladium hydride under these conditions.

TABLE VIII

HYDROGEN ANALYSES

		Hydrolysis, Hydrogen (%)		Pyrolysis, Hydrogen (%)	
System	Analyzed for	Calculated	Found	Calculated	Found
Ca–Pd–H	$Ca_3Pd_2H_4$	1.20	1.29	1.20	1.20
Sr–Pd–H	$SrPd_2H$	0.33	0.32	0.33	0.33
Sr–Pd–H	Sr_2PdH_4	1.41	1.34	1.41	1.37

TABLE IX

CHEMICAL ANALYSES

System	Analyzed for	Alkaline Earth (%)		Palladium (%)	
		Calculated	Found	Calculated	Found
Ca-Pd-H	$Ca_3Pd_2H_4$	35.7	34.3[a] 34.5[b]	63.1	64.2
Sr-Pd-H	$SrPd_2H$	29.1	28.4	70.6	70.6
Sr-Pd-H	Sr_2PdH_4	61.2	60.8	37.2	37.2

[a] By oxalate precipitation.

[b] By atomic absorption spectroscopy.

The electrical resistance was measured for pellets in three conditions: (1) starting mixture of raw materials, (2) ternary hydride, and (3) post-pyrolysis residue. Sample geometry and measurement techniques were similar for all samples. Because of the crudeness of the two-probe method used for the resistance measurements, the experimental values were considered as only relative and not absolute quantities. These values are listed in Table X. The conductivities of the ternary hydrides were less than that observed for the starting materials or the pyrolytic residues. Although the conductivities of the ternary hydrides were less than that for either the starting materials or the pyrolytic residues, the measured conductivities were in the range expected for metallic behavior. It appears that hydrogen in the ternary hydrides is responsible for their lower conductivities. This type of reduced conductivity has been observed for hydrided samples of palladium (*30*).

With the exception of some of the rare earth hydrides, the nonsaline, metallic hydrides are all metallic conductors. The unavailability of single crystals for these materials has limited the gathering of good quantitative measurements of their electrical properties. The data available (*31*) indicate that no simple relationship exists between the resistivity of the hydride and that of the metal. The magnetic evidence of electron donation from hydrogen to the *d*-band of palladium has been offered in experimental support of protonic hydrogen in this system (*32*). This donation of electrons to the *d*-band of the metal should increase the resistivity as pairing of electrons occurs. Alternatively, the presence of hydrogen as hydride ions would lead to removal of *d*-band electrons from palladium and lead to the observed decrease in conductivity. Addition or removal of electrons from the *d*-band could also change the density of states in the Fermi level vicinity. All of these factors indicate that no definite conclusions can be drawn regarding the true mechanism for the resistivities observed for the ternary hydrides.

TABLE X

ELECTRICAL RESISTANCE MEASUREMENTS (Ohms)
0.25 IN SAMPLE LENGTH

Sample	Starting mixture	Ternary hydride	Post-pyrolysis residue
$SrPd_2H$	0.5	2.5	0.8
Sr_2PdH_4	6.0	45	1.0
$Ca_3Pd_2H_4$	5.0	17	1.4

Pure palladium is markedly paramagnetic with a room temperature susceptibility of approximately 600×10^{-6} cgs units and Curie-Weiss Law behavior is observed from 80 to 295°K. In this study, an effective moment of 1.55 Bohr magneton and a theta of −270° were calculated assuming zero diamagnetic correction. Using a diamagnetic correction of -50×10^{-6} estimated from the ternary hydride susceptibility measurements changes the calculated effective moment to 1.66 Bohr magneton and changed theta to −303°. Results of the magnetic susceptibility measurements for calcium palladium hydride indicated diamagnetic behavior from 77°K to room temperature. Both $SrPd_2H$ and Sr_2PdH_4 are diamagnetic at room temperature, but exhibit a slight paramagnetism at temperatures below 150°K. A representative sampling of data points over the range from −196° to room temperature are listed for each of the three ternary hydrides in Table XI.

Lithium hydride is diamagnetic with a molar susceptibility of -4.6×10^{-6} cgs (*33*). Although literature values are lacking for calcium and strontium hydrides, pure samples of these compounds should also be diamagnetic. In this study, a small paramagnetic susceptibility was noted for these binary hydrides. This effect could have arisen from an impurity in these materials. One source of contamination could be the metal distillation column used in the purification of the alkaline earth metals.

Plots of X_m versus current for the binary and ternary hydrides generated a family of similarly shaped curves. This would qualitatively indicate that the material causing the paramagnetism of the binary is also present in the ternary hydrides and

TABLE XI

MAGNETIC SUSCEPTIBILITIES[a]

$HdH/dZ = 14.462 \times 10^6$ Oe

$SrPd_2H$		Sr_2PdH_4		$Ca_3Pd_2H_4$	
Temp., °K	Mag. suscp. $X'm \times 10^6$	Temp., °K	Mag. suscp. $X'm \times 10^6$	Temp., °K	Mag. suscp. $X'm \times 10^6$
78	70	86	77	78	−130
148	9	147	42	147	−122
217	−47	208	−31	237	−113
294	−58	294	−50	295	−104

[a] Corrected for binary hydride experimental susceptibility.

contributing to their residual low-temperature paramagnetic behavior. After accounting for the contribution of the binary hydride to the susceptibility of the ternary, a net slight, low-temperature paramagnetism is observed for Sr_2PdH_4 and $SrPd_2H$. This could arise from an enhancement of the susceptibility for the impurity due to its dilution in the ternary. Alternatively, a very slight amount of unreacted palladium, less than that capable of being detected in the X-ray analyses, could generate the slight magnetic behavior. The fact that the slight residual paramagnetism is not observed for the calcium palladium hydride could be significant. Strontium hydride has a much greater moisture sensitivity than calcium hydride. Although precautions were taken to exclude air and moisture during sample handling, the reaction of strontium hydride with moisture on the walls of containers could have led to a slightly less than stoichiometric amount of strontium hydride in the reaction mixture and, thus, cause a slight excess of unreacted palladium to be present in the ternary product. Neither strontium hydride hydrolysis products nor palladium metal were in evidence in the X-ray powder patterns of the products.

The formal oxidation state of palladium in the ternary hydride sequence Sr_2PdH_4, $SrPd_2H$, and $Ca_3Pd_2H_4$ may be considered as 0, $-1/2$, and -1, respectively. The room-temperature susceptibility value per palladium in $SrPd_2H$ is in the range of what can be expected for a formal charge of $-1/2$ by extrapolation from values for Pd^{2+} and Pd^{4+} (*34*). The formal -1 charge on palladium in $Ca_3Pd_2H_4$ could account for the room-temperature susceptibility per palladium of -52×10^{-6} cgs. This value could result from an increase in the number of electrons about palladium and the resulting increase in size of the palladium atom, both factors would lead to an increase in diamagnetism.

The formation of the new group of alkaline-earth–palladium ternary hydrides discussed here is a basis for inquiring if palladium is unique among its congeners in this ability. As part of this laboratory's study of alkaline-earth–transition-metal–hydrogen systems, preliminary investigations of the Ca–Ni–H system and Sr–Pt–H system have been undertaken.

Calcium hydride and nickel in a 2:1 molar ratio were reacted at a maximum temperature of 800° for 12 hr under 650 mm of hydrogen pressure. The X-ray diffraction patterns of the reactants and post reaction materials were identical. This was taken as evidence that no reaction had occurred leading to ternary hydride formation under these conditions.

Strontium hydride and platinum in a 2:1 molar ratio were reacted at 800° for 12 hr (*35*). The X-ray diffraction pattern indicated a new phase, contaminated with strontium hydride, had formed. Studies are planned to investigate the various experimental conditions which could optimize the opportunity for ternary hydride formation in both systems.

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