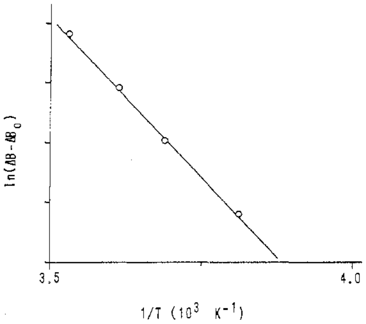

Figure 8. Temperature dependence of the width at half-height of the absorptions labeled Y in Figure 2.

From measurements of the static susceptibility, we estimate that the percentage of "dimers" in the triplet state increases from 0.1 to 0.3% over the temperature range 194–214 K. In this concentration range, spin exchange between "dimers" would be negligible if the triplet "excitations" were localized. However, a measurable decrease of the splitting between the absorptions labeled Y in Figure 2 is observed over this concentration range; this is taken as evidence that the triplet "excitations" of I are excitons.[20] Two further experimental observations support this idea.

(i) A small single crystal, large enough to observe EPR spectra, was obtained on one occasion; no splitting of the resonance lines due to hyperfine interaction with the ^{14}N nuclei (even at temperatures at which the spin exchange interaction was assumed to be negligible) was observed, as is expected in the EPR spectrum of triplet exciton salts.[24]

(ii) At triplet concentrations of greater than ca. 0.1%, a continuous broadening of the absorption lines and an enhancement of the intensity of the EPR signal ascribed to $S = {}^1/_2$ monomeric $[ON(SO_3)_2]^{2-}$ ions was observed. A similar broadening effect has been observed in an X-irradiated single crystal of $[(C_6H_5)_3PCH_3]^+[TCNQ]_2^-$ and was interpreted as arising from spin exchange between triplet excitons and free radicals.[25]

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Contribution from the Department of Chemistry and Materials Science Institute,
University of Connecticut, Storrs, Connecticut 06268, and the Departments of Physics and
Chemistry, Trinity College, Hartford, Connecticut 06106

Ternary Hydrides of Calcium with Silver

MARSHALL H. MENDELSOHN,[1a] JOHN TANAKA,*[1a] ROBERT LINDSAY,[1b] and RALPH O. MOYER, Jr.[1b]

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A new ternary hydride, $CaAg_2H$, can be prepared either by hydriding the alloy $CaAg_2$ or by a solid state reaction of calcium hydride and silver in a hydrogen atmosphere. The hydride is a black, nonvolatile, diamagnetic solid. The X-ray powder pattern can be indexed orthorhombic. No other hydrides could be isolated from the calcium–silver system except the one which was related to the alloy phase. The correlation of alkali and alkaline earth ternary hydrides with model systems such as complex halides and alloy phases is discussed.

Introduction

Previous work at the University of Connecticut has shown the existence of the following alkaline earth–noble metal hydrides: Ca_2IrH_5,[2a] Sr_2IrH_5,[2a] Ca_2RhH_5,[2a] Ca_2RuH_6,[2a] Sr_2RhH_5,[2a] Sr_2RuH_6,[2a] $SrPd_2H$,[2b] Sr_2PdH_4,[2b] and $Ca_3Pd_2H_4$.[2b] In general, these compounds were prepared by the solid state reaction of the alkaline earth metal hydride and the group 8 metal. One of the compounds, $SrPd_2H$, was also prepared by hydriding the intermetallic phase $SrPd_2$. In order to develop the systematic chemistry of the alkaline earth–transition metal hydrides, we have been interested in exploring the stoichiometries and properties of the hydrides of the neighboring elements of the compounds listed above. In this paper we report the preparation and characterization of a new ternary hydride in the calcium–silver system, $CaAg_2H_{1.0}$.

Experimental Section

Calcium was purified by distillation under vacuum in a steel apparatus. Hydrogen was Matheson extra dry or prepurified grade further purified by passage through a palladium tube in a Bishop hydrogen diffusion cell Model No. A-1-D. Calcium hydride was synthesized by direct combination of the elements at 450–500°. The binary hydride thus produced was checked by X-ray diffraction and by hydrolysis of the hydridic hydrogen. Silver metal was 99.99% purity obtained from Cerac, Inc. and was used without further purification. Argon was Matheson high purity grade.

The ternary hydride was prepared either by the reaction of calcium hydride with silver or by hydrogenation of the intermetallic alloy $CaAg_2$. To prepare the alloy, a stoichiometric mixture of 1Ca–2Ag was compressed into a dense pellet with a hydraulic press. The pellet was placed in a Mo or Ta boat, which was then inserted in a reaction tube. The reaction tube was attached to a vacuum system, evacuated, and filled with argon. The pellet was heated at 700° for 18 hr and the product, $CaAg_2$, was checked by X-ray powder diffraction. The alloy was then heated in either a pellet or powder form in a hydrogen atmosphere at 575–600° for 16–18 hr to form $CaAg_2H$. In the preparation from the binary hydride and the metal, a mixture of $1CaH_2$–$2Ag$ was pressed into a pellet and reacted at 600–650° in a hydrogen atmosphere for 16 hr.

The X-ray powder diffraction data were obtained with a Philips Debye-Scherrer camera using nickel-filtered copper radiation. Hydrogen analyses were obtained by pyrolytic decomposition of the products. The sample was placed in a molybdenum sleeve and placed in a quartz tube which was then evacuated with a standard vacuum system. The sample was then heated to 900° until no more gas was evolved. The gas was transferred to a calibrated volume using a Toepler pump and the amount of gas collected was determined by *PVT* measurements. The evolved gas was finally identified as hydrogen by mass spectrometry.

Differential thermal analyses were performed on a Du Pont 990 with a 1200° furnace. The apparatus was modified to allow operation at a 225 ml/min flow rate of hydrogen gas at 1 atm of pressure. Scans were carried out at a 20°/min heating rate over a temperature range of room temperature to 900°. Molybdenum cup sample holders were used with alumina as the reference standard.

Densities were calculated by the liquid buoyancy method using reagent grade carbon tetrachloride previously dried over calcium hydride. For these determinations, the powder was compressed at 5000 psi into a pellet and submerged in the carbon tetrachloride, and the weight was determined.

The magnetic susceptibilities were measured by means of the Faraday body force method using an automatic analytical balance enclosed in a controlled atmosphere.[3,4] The inhomogeneous magnetic field volume was calibrated with powdered recrystallized reagent grade $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ (Mohr's salt) using susceptibility data reported by Jackson.[5] A cylindrical Teflon boat with a predetermined force correction was used to hold the samples which occupied a volume of about 0.30 cm^3. The susceptibilities of the powdered Ag_2Ca and Ag_2CaH samples were measured at temperatures of 77 and 296 K and at several field strengths between 3000 and 9000 oersteds.

Results and Discussion

The ternary hydride is a black, crystalline, nonvolatile solid reactive to water and acids. The compound decomposes slowly in air, the powder pattern eventually showing metallic silver. Pyrolytic hydrogen analyses on three independent preparations gave 0.98, 1.00, and 0.96 mmol of H_2/mmol of compound confirming the composition $CaAg_2H$. Although the hydride phase can be obtained either by heating calcium hydride with silver or by heating the calcium silver alloy under hydrogen, the preferred method was to heat the alloy under hydrogen at temperatures between 550 and 590°. The hydride phase formed by heating calcium hydride and silver at temperatures below 650° was generally found to be contaminated with starting materials. When the calcium hydride and silver reaction was carried out at temperatures above 650°, a material which gave essentially the same powder pattern as the alloy but which contained 0.22 to 0.26 mmol of H_2/mmol of alloy was obtained. Interestingly enough, when the hydride was first prepared and heated above 700°, this same material was not formed. On heating the hydride at temperatures above 650°, both calcium and hydrogen were lost and the residue eventually formed was silver.

The X-ray powder pattern for the hydride is given in Table I. Compared to the pattern for $CaAg_2$,[6] the pattern for $CaAg_2H$ is clearly unique and shows the presence of a new phase. It appears to index orthorhombic with cell parameters of $a = 5.45$, $b = 5.19$, and $c = 9.86$. The calculated density for four formula units per unit cell is 6.12 g/cm^3 compared with experimentally determined densities on samples prepared in separate reactions of 6.15 g/cm^3 and 6.04 g/cm^3. These materials gave the same X-ray pattern after the density determinations as before.

Table I. Powder Pattern Data for $CaAg_2H$

I^a	$d_{(obsd)}$	$d_{(calcd)}$	h	k	l
30	4.740	4.769	1	0	1
20	4.550	4.593	0	1	1
30	2.726	2.725	2	0	0
5	2.629	2.626	2	0	1
10	2.411	2.413	2	1	0
100	2.353	2.343	2	1	1
60	2.254	2.246	1	0	4
55	2.122	2.111	1	2	2
20	2.045	2.037	0	2	3
30	1.969	1.972	0	0	5
40	1.797	1.787	0	2	4
45	1.584	1.590	3	0	3
50	1.549	1.564	1	3	2
20	1.512	1.509	1	2	5
5	1.480	1.474	1	3	3
50	1.446	1.445	2	3	1
30	1.415	1.416	0	3	4
80	1.367	1.364	1	0	7
70	1.313	1.313	4	0	2
50	1.234	1.232	0	0	8
50	1.179	1.179	1	4	3
20	1.157	1.162	4	1	4
30	1.015	1.015	5	1	3
30	0.987	0.987	1	3	8
30	0.851	0.849	0	6	2

[a] Estimated visually from film.

Table II. Differential Thermal Analysis

System	Peak Temp	Peak description
$CaAg_2$	~210–360	Broad exotherm
	463	Broad endotherm
	540	Broad endotherm
	656	Sharp endotherm
	671	Sharp endotherm
	692	Sharp endotherm
	720	Sharp endotherm
$CaAg_2H$	365	Broad exotherm
	656	Sharp endotherm
	674	Sharp endotherm
	692	Sharp endotherm
	720	Sharp endotherm
CaH_2 + Ag	662	Sharp endotherm
	676	Weak broad endotherm
	719	Very weak broad endotherm

The differential thermal analysis data were not only valuable in locating the reaction conditions to be tried but were also evidence for the new hydride phase. The data determined in a hydrogen atmosphere are shown in Table II. Specific assignments for the endotherms and exotherms observed were not made. However, it is assumed that the 463 and/or the 540 endotherms observed for the $CaAg_2$ were for the absorption of hydrogen to form the hydride phase. These endotherms were not observed for the hydride phase nor for the reaction of calcium hydride and silver. One would, of course, not expect to see this reaction with these two systems. The set of endotherms observed between 656 and 720° for all three systems indicates a rather complex decomposition process. The processes which are taking place, not necessarily in the order mentioned, are the loss of hydrogen from the hydride phase, the phase transition from hexagonal to orthorhombic, the loss of hydrogen from the alloy–hydrogen system, and the decomposition of the alloy phase.

A noticeable dependence of magnetic susceptibility on field strength was observed in the data which indicated the presence of a ferromagnetic impurity. This impurity was attributed to the diffusion of trace amounts of iron into the calcium while the calcium was being vacuum distilled in a steel distilling column. A plot of the observed susceptibilities against the reciprocal of the field strength gave a straight line at the higher field strengths indicating saturation of the ferromagnetic

Table III. The Specific Susceptibility, χ_g (cgs units/gram)

Temp, °K	Ag$_2$Ca	Ag$_2$CaH
296	2.3×10^{-7}	-1.5×10^{-7}
77	3.0×10^{-7}	-1.0×10^{-7}

inclusion. The extrapolated values of the susceptibility to infinite field strength were then taken as representing the intrinsic alloy and hydride susceptibilities.[7] These values are shown in Table III. χ_g is the specific susceptibility in cgs units/gram.

The estimated accuracy of these values is $\pm 0.5 \times 10^{-7}$ cgs/gram so that the experimental error blurs any apparent significance in the increase in χ_g between 296 and 77°K for each sample. However, the difference between the positive or paramagnetic susceptibility of the Ag$_2$Ca alloy and the negative or diamagnetic susceptibility of the Ag$_2$CaH ternary hydride is considered a valid experimental result.

The reasons for the shift from a net paramagnetism in the alloy to a net diamagnetism in the hydride are not clear. It is conceivable there might be some parallels with the palladium hydride binary system in which the normal paramagnetism of the palladium metal is suppressed as hydrogen is added to the metal.[8] This effect has been attributed by some to the filling of holes in the palladium d band by electrons from the hydrogen atoms. It has also been speculated that the addition of hydrogen causes the palladium lattice to expand with an accompanying decrease in the susceptibility.[8] A simple qualitative explanation of the Ag$_2$CaH behavior might therefore be advanced based on the idea that electrons from the hydrogen fill up the conduction band in the alloy responsible for the predominant spin paramagnetism and thereby reduce the available number of empty electron states or holes in the band.

Qualitative resistance measurements on the hydride phase indicated that there was no detectable difference in measuring the resistance of a 2-mm thick pellet and shorting of the leads. Although it is recognized that a crude single temperature measurement on a compressed powder sample does not differentiate between metallic and semiconductor properties, it is of interest to note that the resistances of alkaline earth iridium and ruthenium hydrides indicated they were nonconductors[2a] and that the alkaline earth rhodium[2a] and palladium[2b] hydrides had conductivities at least an order of magnitude less than that observed for the calcium silver hydride.

It should be pointed out that although various ratios of calcium hydride and silver were reacted, the only ternary hydride phase discovered was that related stoichiometrically to the alloy phase. This observation is of interest in that the stoichiometry of new ternary hydride systems is often unpredictable. Some hydrides such as NaBH$_4$, LiAlH$_4$, Li$_2$BeH$_4$, and KMgH$_3$ are stoichiometrically related to the complex halides.[9] Some hydrides such as iron titanium hydride[10,11] are alloy hydrides. Since they result from solubility of hydrogen in metals and alloys,[12] the stoichiometry of the metal atoms of the hydride is that of the alloy phase. The stoichiometries of some ternary hydrides are not predictable on the basis of either analogy. Examples are Sr$_2$IrH$_5$,[2a] Ca$_2$RhH$_5$,[2a] Sr$_2$PdH$_4$,[2b] and Ca$_3$PdH$_4$.[2b] Some pattern for the model a ternary hydride system might be expected to follow is emerging, but reliable predictability of stoichiometry awaits the characterization of other new hydrides.

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Contribution from the Department of Chemistry and Division of Engineering,
Brown University, Providence, Rhode Island 02912

High-Pressure Synthesis and Properties of NiPS[1]

R. HENRY, H. NAHIGIAN, J. STEGER, and A. WOLD*

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NiPS was synthesized at 60 kbars pressure and 1300°C using a high-pressure belt apparatus. The X-ray diffraction patterns obtained from pure NiPS can be indexed assuming a cubic pyrite type structure. The cubic cell dimension was 5.549 (2) Å and a density of 4.75 (2) g/cm^3 was determined by a hydrostatic technique. Magnetic susceptibility and resistivity measurements indicate that the nickel cations can be assigned a low-spin d^7 electronic configuration. No spontaneous magnetism was observed over the temperature range from 100 to 540°K.

Introduction

The electrons of the transition metal chalcogenides have been characterized as ranging from those that are localized and highly correlated in MnS$_2$[2] with strong magnetic ordering and semiconducting behavior to others such as NiSe$_2$[2] in which the d electrons are completely delocalized and uncorrelated. Compounds such as NiSe$_2$ show metallic behavior and Pauli paramagnetism.

Intermediate between these extremes and having characteristics of both localized and delocalized systems are the cobalt dichalocogenides where electrons exist in a periodic field. Consequently, electrons occupy a series of energy bands separated by gaps of forbidden energy. It is the widths of these bands that determine the degree of correlation and transfer energy. With a narrow bandwidth there is a greater degree of electron correlation, thereby increasing the possibility of magnetic ordering.

Interest in the cubic pyrite CoS$_2$ (Figure 1), as a narrow