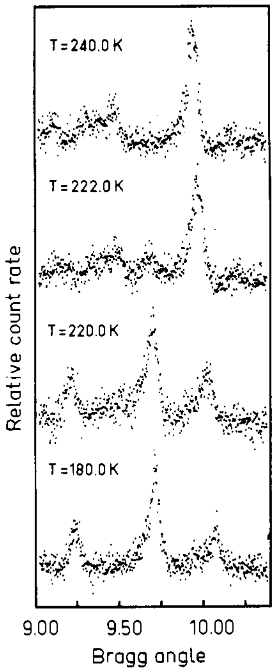

Figure 4. X-ray powder diffraction peak profiles of $[Fe(bt)_2(NCSe)_2]$ for Bragg angles between 9.00 and 10.40° at 240.0, 222.0, 220.0, and 180.0 K. The data are for decreasing temperature.

decreasing temperatures encompass the transition temperature $T_c^{\downarrow} \simeq 221.3$ K quite well (see Figures 3 and 4), those of 225.0 and 227.0 K for increasing temperatures (not displayed here) being only slightly offset from the value $T_c^{\uparrow} \simeq 224.9$ K derived from the Mössbauer spectra. It is obvious, on the basis of previous studies,[7,8] that the X-ray powder diffraction at T_c will comprise the patterns of both the HS and LS phases in equal proportion. Due to the very sharp nature of the transition in the present substance, the construction of such a diffraction pattern is, however, difficult to accomplish. First of all, the observed hysteresis requires that, in approaching T_c, the direction of temperature variation should not be reversed. Second, differences of temperature calibration will result in slightly different T_c values for Mössbauer effect and X-ray diffraction measurements.

In more general terms, the observation of two different diffraction patterns for a discontinuous spin-state transition indicates that the two phases involved are characterized by different unit cell parameters.[7] These unit cells correspond to the discrete molecular structures associated with the HS and LS states of the $[Fe(bt)_2(NCSe)_2]$ complex that are participating in the transition.

The findings are well in line with the results found for a number of first-order spin-state transitions in compounds of iron(II).[8] In particular, the transition seems to be closely related to that observed for the compound $[Fe(bt)_2(NCS)_2]$ containing the same ligand.[3,4] As indicated by the change of the effective magnetic moment,[3] the transition in $[Fe(bt)_2(NCSe)_2]$ is almost as abrupt as that observed for the thiocyanato complex, whereas the hysteresis width is considerably lower, $\Delta T_c = 3.6$ vs 9.5 K for $[Fe(bt)_2(NCS)_2]$.[4]

In order to investigate a possible trapping of the HS species, the effect of rapid cooling of a sample of $[Fe(bt)_2(NCSe)_2]$ has been investigated by the Mössbauer effect. However, no unusual behavior has been observed. Apparently, the transition in this compound is reversible and fast, at least under the conditions imposed by the experiment.

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The Ternary System Mg–Co–H

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In the scope of a research program for preparing and characterizing new hydrogen storage materials containing Mg and 3d metal elements, two ternary hydrides, Mg_2FeH_6[1,2] and Mg_2CoH_5,[3] have been detected recently. Zolliker et al.[3] have prepared Mg_2CoH_5 and its deuteride by a sintering technique at temperatures between 620 and 770 K and under a hydrogen (or deuterium) pressure of 4–6 MPa. These compounds are black crystalline solids. X-ray and neutron powder diffraction data recorded at room temperature suggested, according to the authors, a tetragonally distorted CaF_2-type metal atom structure. They specified that the structure transforms at 488 (5) K into a disordered cubic-symmetry modification. They pointed out the existence of another ternary hydride as well, which, however, was not further investigated. In the present paper we report new results that we have obtained in studying the ternary system Mg–Co–H.

Experimental Procedure

Several samples were prepared as follows. Magnesium and cobalt powders in a 2:1 atomic ratio were mixed for 2–3 days in a ball mill. These mixtures were pressed into pellets under 500-MPa pressure and placed in a steel autoclave. They were hydrided for several days at temperatures and pressures selected with reference to the phase diagram. Other samples were prepared by mechanical alloying in a high-energy planetary ball mill (600 m/s^2) as described elsewhere.[4] Mechanically alloyed samples were not pressed into pellets before reaction with hydrogen under the chosen conditions. The reaction products consisted of small amounts of MgH_2, Mg, and Co in addition to a ternary hydride. The Mg and MgH_2 impurities were removed by treatment in 1,2-dibromoethane in a way described elsewhere.[3] The Co content was checked by magnetic susceptibility measurements.

The composition of the purified samples has been determined chemically by complexometric titration with EDTA and by electron microprobe analysis ("Camebax Micro", Cameca).

The pressure–composition isotherms were determined on unpurified and purified samples by hydrogen desorption.

X-ray powder diffraction data were recorded by using Cu Kα radiation. The electrical conductivity was measured for the pressed pellets under 500-MPa pressure in a stainless steel reactor under hydrogen pressure. The reactor design allows us to use only a dc two-electrode cell. A Model DSC-111 "Setaram" instrument was used for the thermal analysis experiments.

Results and Discussion

The magnesium–cobalt mechanical alloys begin to absorb hydrogen at pressures below the equilibrium pressure of MgH_2. In other words the ternary hydrides of magnesium and cobalt form by direct combination of Mg, Co, and H_2.

Figure 1 shows several desorption isotherms corresponding to unpurified samples that had been previously hydrided at 660 K under $P_{H_2} = 4$ MPa. They exhibit three plateau pressures. The upper one corresponds to the decomposition of MgH_2. This result is confirmed by the calculated enthalpy and entropy values

$$\Delta H^\circ = -75 \pm 1 \text{ kJ (mol of H}_2)^{-1}$$

$$\Delta S^\circ = -135 \pm 2 \text{ J K}^{-1} \text{ (mol of H}_2)^{-1}$$

which are very close to those found by Stampfer for MgH_2[5] ($\Delta H^\circ = -74.3$ kJ (mol of $H_2)^{-1}$ and $\Delta S^\circ = -134.9$ J K^{-1} (mol of $H_2)^{-1}$).

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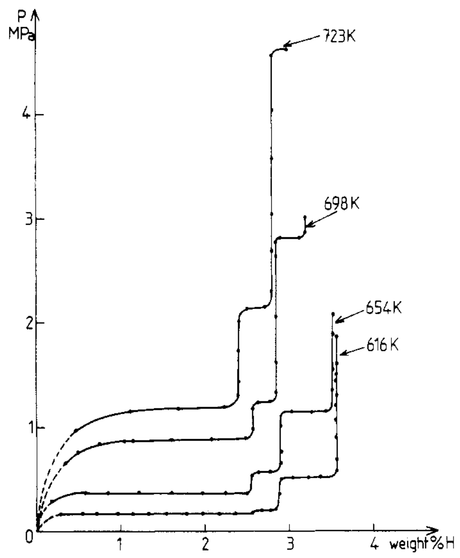

Figure 1. Pressure vs composition plot for the Mg–Co–H system.

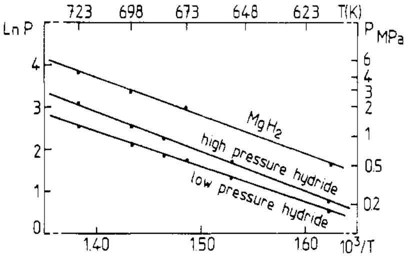

Figure 2. ln P_{eq}–$1/T$ dependency for MgH_2 and the two detected magnesium–cobalt hydrides.

The two lower plateau pressures (Figure 1), respectively called A and B, show the existence of two ternary hydrides. Figure 2 gives ln P_{eq} vs $1/T$ curves deduced from the obtained data. They are linear. The values of the thermodynamic functions for the two ternary hydrides result from the drawn straight lines:

low-pressure hydride (A)

$$\Delta H_A = -70 \pm 4 \text{ kJ (mol of } H_2)^{-1}$$

$$\Delta S_A = -118 \pm 4 \text{ J K}^{-1} \text{ (mol of } H_2)^{-1}$$

high-pressure hydride (B)

$$\Delta H_B = -79 \pm 4 \text{ kJ (mol of } H_2)^{-1}$$

$$\Delta S_B = -134 \pm 4 \text{ J K}^{-1} \text{ (mol of } H_2)^{-1}$$

The ln P_{eq} vs $1/T$ dependencies given in Figure 2 allow us to select for each hydride the experimental synthesis conditions. Zolliker et al.[3] had previously reported the existence of the ternary hydride Mg_2CoH_5, which exhibits an allotropic transformation. By heating at 488 K the tetragonal variety transforms into the cubic one. The enthalpy of formation of the tetragonal phase determined by these authors, $\Delta H = -86 \pm 5$ kJ (mol of H_2)$^{-1}$, agrees with the H_B value corresponding to the high-pressure hydride curve in Figure 2.

The X-ray powder diffraction pattern of the high-pressure phase B carried out at room temperature is actually similar to that of the tetragonal phase Mg_2CoH_5 reported by Zolliker et al.[3]

Table I. X-ray Diffraction Data Obtained for the Low-Pressure Hydride Indexed in a Hexagonal System

hkl	d_{calcd}, Å	d_{obs}, Å	I_{obs}
002	5.04	5.04	100
100	4.04	4.04	90
101	3.757	3.750	17
102	3.157	3.155	20
103	2.587	2.589	26
004	2.522	2.525	22
110	2.3377	2.3371	61
014	2.1411	2.1417	42
112	2.1211	2.1222	61
201	1.9849	1.9832	14
202	1.8789	1.8774	8
015	1.8062	1.8054	16
114	1.7147	1.7159	15
204	1.5789	1.5794	13
016	1.5531	1.5536	14

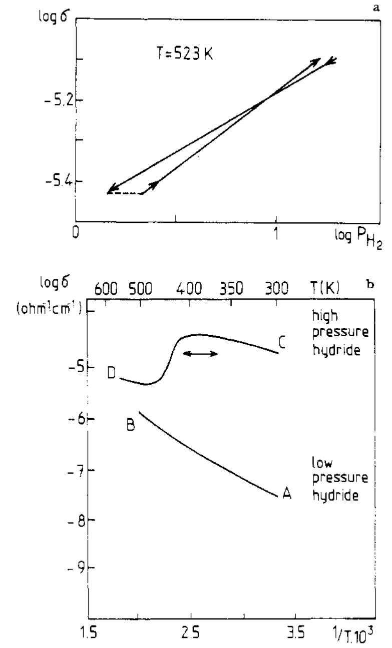

Figure 3. (a) Pressure dependency of the conductivity of the high-pressure hydride. (b) Conductivity measurements on the two magnesium–cobalt hydrides.

The low-pressure phase A has been synthesized at temperatures between 690 and 710 K under 2-MPa hydrogen pressure. The presence of this phase in certain samples sintered above 720 K at P_{H_2} = 4–6 MPa was probably observed by Zolliker et al.,[3] but the authors did not identify it. Table I contains the X-ray diffraction pattern of the A hydride. It has been indexed with a hexagonal cell and the parameters $a = 4.675 \pm 0.001$ Å, $c = 10.09 \pm 0.02$ Å, $Z = 4$, and $\rho_{exptl} = 2.38$ g cm^{-3}.

The X-ray powder diffraction patterns of certain samples sintered above 720 K at P_{H_2} = 4–6 MPa exhibit the presence of this phase. It was probably observed by Zolliker et al.[3] because these authors said "at temperatures above 720 K another ternary hydride phase was found which, however, was not further investigated". They did not identify this phase. The composition of this hydride, which we have estimated by chemical microprobe analysis and hydrogen desorption, is close to the formula "Mg_3CoH_5".

The conductivity measurements of the various phases have been carried out in a modified stainless steel hydriding reactor. For the sake of reproducibility of these measurements it was necessary to treat the samples under a clean hydrogen atmosphere at about 373 K, as the pressure of some CO_2 and H_2O was detected when the samples were heated in a mass spectrometer. This result is related to the conductivity decrease observed upon heating. The relatively high initial conductivity (about 10^{-3} Ω^{-1} cm^{-1}) could be ascribed to the presence of hydroxides and carbonates on the surface sample. These compounds are formed by reaction with

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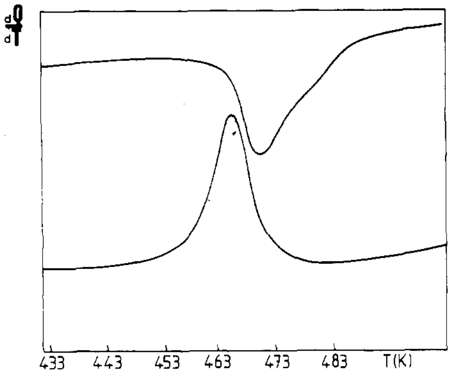

Figure 4. DSC study of the Mg_2CoH_5 phase transformation from the tetragonal to the cubic variety.

trace amounts of air present. Figure 3a shows the conductivity variation of the high-pressure hydride as a function of hydrogen pressure. Such a pressure dependence usually characterizes the hydriding of metals or metallic alloys.

The conductivity of the low-pressure hydride was measured on pellets that did not contain either the high-pressure hydride or any significant amount of impurity, as verified by X-ray diffraction. The measurements were carried out in a temperature range varying from 285 to 500 K (curve AB in Figure 3b). Prior to the measurements the samples were treated under 2-MPa hydrogen pressure at room temperature so as to stabilize the initial conductivity value (point A). The conductivity increases with rising temperature. The same shape for the conductivity curve is obtained in the temperature range considered, whatever the pressure.

But at 2-MPa hydrogen pressure and at a temperature of 500 K for 2 days, the low-pressure hydride is transformed into the high-pressure one. This phenomenon corresponds to a slight increase of the conductivity (from the B to the D point). Now the temperature change in the 570–300 K domain leads to the conductivity curve CDEF. The phase transformation from a tetragonal to a cubic symmetry reported earlier[3] resulted in a conductivity jump around 470 K.

The phase transformation was found to be reversible from the conductivity measurements as well as by DSC measurements (Figure 4) with $\Delta H \simeq 0.5$ kcal mol^{-1}.

The conductivity was measured for samples of the tetragonal high-pressure phase synthesized at 4 MPa and 670 K. The conductivity curve obtained exhibits a similar shape.

The conductivity measurements imply a non-metallic character for both high- and low-pressure hydrides. As mentioned above, the low-pressure hydride can be transformed into the high-pressure one at rising temperature in agreement with the phase diagram (Figure 2) at 630 K and under 3–4-MPa hydrogen pressure. The reverse reaction also can take place, but the presence of MgH_2 is necessary.

Thermal decomposition of both hydrides has been carried out under vacuum for 4 days at various temperatures between 698 and 723 K. It always results in the formation of the intermetallic compound Mg_xCo in addition to magnesium and cobalt. It is very difficult to separate the phases present in the mixture after decomposition, so that the exact composition of the alloy could not be determined with sufficient accuracy. However, an electron microprobe analysis gave an atomic ratio corresponding approximately to a Mg_2Co composition. The existence of Mg_2Co has been previously reported[6] but was not confirmed,[7] so that its structure is still unknown. Mg_xCo cannot be obtained either by melting or by mechanical alloying in contrast to Mg_2Ni, which has been recently obtained by both methods.[4,8]

Table II. X-ray Data for Mg_xCo

hkl	d_{obs}, Å	d_{calc}, Å	I_{obs}
111	6.61	6.599	100
220	4.04	4.04	6
400	2.856	2.587	1
422	2.333	2.333	12
511–333	2.198	2.199	70
440	2.020	2.020	23
531	1.932	1.932	5
600–442	1.904	1.905	15
620	1.806	1.807	5
533	1.741	1.743	8
622	1.721	1.723	8
733	1.395	1.396	2
660–822	1.345	1.347	9
751–555	1.319	1.319	4
842	1.248	1.247	3
931	1.1983	1.1982	2

The question is still open whether this intermetallic compound is a metastable phase that is stabilized by the presence of a certain amount of hydrogen or an intermetallic compound thermodynamically stable under our conditions.

Table II presents the X-ray data for Mg_xCo, which has been indexed with a face-centered cubic cell ($a = 11.43 \pm 0.01$ Å).

There is a great difference between the behavior of Mg_xCo and that of a 2 Mg–Fe mixture during hydriding–dehydriding cycling. While the hydrogen storage capacity of the 2 Mg–Fe mixture decreases quickly, that of Mg_xCo remains almost the same after 50 cycles. This could result from the fact that Mg_xCo does not disproportionate while dehydriding of Mg_2FeH_6 leads to a mixture of elemental magnesium and iron. The consequence is a looser contact between Mg and Fe pairs along the absorption–desorption cycles. This phenomenon would account for the observed decrease of the hydrogen storage capacity.

Conclusion

By direct interaction of Mg and Co under hydrogen pressure we could synthesize two different ternary hydrides. We have studied the *P–T* diagram of the Mg–Co–H_2 system. The powder diffraction pattern corresponding to the high-pressure hydride is similar to that of the tetragonal phase reported earlier by Zolliker et al.[3] In addition the existence of a low-pressure hydride has been established. It has been indexed with a hexagonal cell. Thermal decomposition of both hydrides leads to the formation of the new intermetallic compound Mg_xCo. A more detailed study is indeed required to determine the exact composition of this compound and to show how much it contains some residual hydrogen able to stabilize it.

Registry No. Mg, 7439-95-4; Co, 7440-48-4; H_2, 1333-74-0; Mg_2Co, 12139-68-3; Mg_2CoH_5, 98586-77-7.

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Synthesis, Structure, and Physical Properties of Tetrakis(μ-diphenyl phosphato)dimolybdenum(II)

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Scant structural information is available about the coordination of phosphate diesters to two metal centers. Recently the structure of $\{Fe_2O[O_2P(OPh)_2]_2(HB(pz)_3)_2\}$ was described;[1] it contains two diphenyl phosphate ligands bridging the Fe–O–Fe unit. This structure may provide a model for substrate binding pertinent to

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