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$MgRhD_{1-x}$, a new interstitial deuteride containing square planar $[Rh_4D_4]$ rings with nearly linear Rh–D–Rh bridges

F. Bonhomme and K. Yvon
Laboratoire de Cristallographie, Université de Genève, 24, Quai E. Ansermet, CH-1211 Geneva (Switzerland)

P. Fischer
Labor für Neutronenstreuung, ETH Zürich, CH-5232 Villigen PSI (Switzerland)

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Abstract

The title compound was investigated by neutron powder diffraction at various deuterium pressures. It has metallic character and crystallizes with a tetragonally deformed CsCl-type metal arrangement ($MgRhD_{0.94(2)}$: space group $P4/mmm$; $Z=4$, $a=6.395(1)$ Å, $c=3.2368(7)$ Å at $p=39$ bar and $T=298$ K). The rhodium atoms are connected to four-membered planar rings via deuterium atoms with bond distances [Rh–D] = 1.708(4) Å and bond angles [D–Rh–D] = 87.5(7)° and [Rh–D–Rh] = 177.5(9)°. Two-thirds of the magnesium atoms are bonded to deuterium at distances in the range [Mg–D] = 2.23–2.33 Å.

1. Introduction

During our previous investigation of the ternary hydride system Mg–Rh–H, the binary compound MgRh was found [1] to absorb significant amounts of hydrogen. In this communication we report on the structural characterization of the deuteride, $MgRhD_{1-x}$. The compound is relatively unstable, has a large homogeneity range and crystallizes with a tetragonally distorted CsCl-type metal arrangement and shows a novel type of linkage between deuterium atoms and transition metal atoms.

2. Experimental details

2.1. Synthesis

The binary alloy MgRh was prepared by sintering elemental powders (magnesium CERAC, −400 mesh, 99.6% purity; rhodium Johnson Matthey 99.9% purity) mixed at the molar ratio Mg/Rh = 1.05 and pressed into pellets of a total mass of 4 g. The pellets were wrapped into tantalum foils, placed with zirconium getters into quartz tubes filled with 250 mbar of argon, and heated to 793 K for one week. After reaction the pellets were reground,

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repressed and annealed again for two weeks at 873 K. The final product was essentially single phase, containing MgRh with $a=3.0992(1)$ Å plus a small amount of unreacted rhodium.

Hydrogenation was initially performed in an autoclave at 748 K and 130 bar pressure for one week. Upon opening the reactor, the samples were found to partially lose hydrogen and thus had to be transferred rapidly to the diffraction equipment. The powders were of dark grey colour and of metallic appearance.

2.2. *X-ray diffraction*

Preliminary diffraction experiments on the alloy hydrogenated *in situ* were carried out in a high-pressure Debye–Scherrer camera ($p=25$ bar). In view of the poor angular resolution of these patterns, further experiments were performed at ambient conditions on samples hydrogenated both at 298 K and at 748 K by using a Guinier–Nonius film camera (Cu $K\alpha_1$ radiation, internal standard cubic $Mg_2RhH_{1.1}$ with $a=12.1962$ Å [1]) and a Bragg–Brentano Philips diffractometer (Cu $K\alpha$ radiation, external standard silicon powder, $a=5.4308$ Å). The diffraction patterns of the partially desorbed samples confirmed the presence of a hydrogen containing $MgRhH_{1-x}$ phase with slightly distorted CsCl-type metal host structure. The observed line splitting and the presence of superstructure reflections indicated tetragonal symmetry with the probable space group $P4/mmm$ [2] and cell parameters $a_t=2a_c=6.387(1)$, and $c_t=a_c=3.226(1)$ Å, and lattice distortion $2c_t/a_t=1.010$ as refined from the Guinier data. A structure model based on three independent magnesium sites with fixed coordinates, and one rhodium site with one free positional parameter was refined from diffractometer data by the Rietveld method, and converged at $R_B=0.059$. Refinements of other structure models gave significantly poorer fits.

2.3. *Neutron diffraction*

In order to fully characterize the structure, neutron powder diffraction patterns were recorded on a sample which was deuterated *in situ* at various deuterium pressures on the DMC powder diffractometer [3] at the reactor SAPHIR at PSI Villigen (Ge (511) monochromator, $\lambda=1.0864$ Å, angular range 3.0–130.0°, angular step $\Delta 2\theta=0.1°$, $(\sin\theta/\lambda)_{max}=0.83$ Å^{-1}, $T=298$ K, sample weight 4 g, gold coated cylindrical vanadium container of inner diameter 8 mm. (Experimentally determined transmission factor, $\mu R=0.115$; measuring time, up to 18 h per pattern; D_2 gas, Air Liquide, 99.8%; neutron scattering lengths (10^{-12} cm), $b_{Mg}=0.5375$, $b_{Rh}=0.593$, $b_D=0.6674$.) Four consecutive measurements were performed, one on the binary MgRh alloy, two on the deuterated alloy at deuterium pressures of $p=2.5$ and 39 bar respectively, and one on the partially desorbed alloy under a dynamic vacuum of $p=10^{-2}$ mbar. All patterns were analysed by using the profile fitting routine DBW3.2S [4] modified for simultaneous treatment of several phases.

The binary alloy MgRh was used as a reference for the subsequent structure refinements. Its structure (CsCl-type) and cell parameter ($a_c = 3.1008(5)$ Å) agreed with the X-ray results ($a_c = 3.0992(1)$ Å). The 2.5 bar data were analysed on the basis of a tetragonally distorted structure in which deuterium was assumed to be distributed at random over three crystallographic sites representing the centres of the six interstices surrounding rhodium octahedrally. Of these sites only one refined to a population parameter significantly different from zero, $PP(\mathrm{D}) = 86(1)\%$. Thus the occupancies of the other two sites were fixed at zero during the final refinement. The analysis of the 39 bar data gave similar results except that the cell parameters, the lattice distortion, $2c/a$, and the population parameter of the deuterium site, $PP(\mathrm{D}) = 94(2)\%$, had increased with respect to the values of the 2.5 bar data. On the other hand the data on the partially desorbed deuteride ($p = 10^{-2}$ mbar) yielded smaller cell parameters, a smaller cell distortion and a smaller deuterium population, $PP(\mathrm{D}) = 61(1)\%$. All refinements took into account small amounts of impurity phases (Rh metal and MgO, the latter not detected by X-ray due to its poor crystallinity). Refinement results are summarized in Table 1, and bond distances and deuterium–deuterium contact distances are given in Table 2. The observed, calculated and difference neutron patterns are shown in Fig. 1 and a structural drawing of $MgRhD_{1-x}$ is given in Fig. 2.

TABLE 1

Refinement results[a] of $MgRhD_{1-x}$ from neutron data at different deuterium pressures, at 298 K (space group: $P4/mmm$ (123); $Z = 4$, Mg1 in $1a(0, 0, 0)$, Mg2 in $1c(1/2, 1/2, 0)$, Mg3 in $2f(1/2, 0, 0$, etc.), Rh in $4k(x, x, 1/2$, etc.), D in $4m$ (x, 0, 1/2, etc.))

	$MgRhD_{0.94(2)}$	$MgRhD_{0.86(1)}$	$MgRhD_{0.61(1)}$
	$p = 39$ bar	$p = 2.5$ bar	$p = 10^{-2}$ mbar
a	6.395(1) Å	6.3912(7) Å	6.3666(7) Å
c	3.2368(7) Å	3.2322(4) Å	3.1989(7) Å
$2c/a$	1.012	1.011	1.005
x_{Rh}	0.2670(7)	0.2659(4)	0.2598(6)
x_{D}	0.261(2)	0.263(1)	0.261(2)
$PP(\mathrm{D})$	94(2)%	86(1)%	61(1)%
U_{Mg}	0.8(1) 10^{-2} Å^2	0.54(7) 10^{-2} Å^2	0.46(9) 10^{-2} Å^2
U_{Rh}	0.1(1) 10^{-2} Å^2	0.22(5) 10^{-2} Å^2	0.65(9) 10^{-2} Å^2
U_{D}	2.8(3) 10^{-2} Å^2	2.0(1) 10^{-2} Å^2	1.4(1) 10^{-2} Å^2
R_{p}	4.46%	2.51%	2.89%
R_{wp}	5.58%	3.38%	3.70%
R_{exp}	4.28%	2.15%	2.18%
S	1.30	1.57	1.69
R_{Bragg}	11.3%	8.9%	9.2%
	97 reflections	172 reflections	151 reflections

[a] Standard deviations in parentheses.

TABLE 2

Bond and contact distances (Å) and bond angles (deg) for $MgRhD_{1-x}$ at different deuterium pressures[a]

		$MgRhD_{0.94}$	$MgRhD_{0.86}$	$MgRhD_{0.61}$
		$p=39$ bar	$p=2.5$ bar	$p=10^{-2}$ mbar
Mg_1–	8 D	2.33(1)	2.330(6)	2.31(1)
	8 Rh	2.907(4)	2.896(2)	2.834(3)
	4 Mg^3	3.1975(5)	3.1956(3)	3.1833(4)
	2 Mg^1	3.2368(7)	3.2322(4)	3.1989(7)
Mg_2–	8 Rh	2.657(4)	2.662(2)	2.690(3)
	4 Mg^3	3.1975(5)	3.1956(3)	3.1833(4)
	2 Mg^2	3.2368(7)	3.2322(4)	3.1989(7)
Mg_3–	4 D	2.226(9)	2.216(5)	2.21(1)
	8 Rh	2.785(4)	2.782(2)	2.763(3)
	2 Mg^1	3.1975(5)	3.1956(3)	3.1833(4)
	2 Mg^2	3.1975(5)	3.1956(3)	3.1989(7)
	2 Mg^3	3.2368(7)	3.2322(4)	3.1989(7)
Rh–	2 D	1.708(4)	1.699(3)	1.654(4)
	2 Mg^2	2.657(4)	2.662(2)	2.690(3)
	4 Mg^3	2.785(4)	2.782(2)	2.763(3)
	2 Mg^1	2.907(4)	2.896(2)	2.834(3)
	2 Rh	2.980(6)	2.992(4)	3.058(5)
	2 Rh	3.2368(7)	3.2322(4)	3.1989(7)
	2 Rh	3.415(6)	3.399(4)	3.308(5)
D–	2 Rh	1.708(4)	1.699(3)	1.654(4)
	2 Mg^3	2.226(9)	2.216(5)	2.21(1)
	2 Mg^1	2.33(1)	2.330(6)	2.31(1)
	2 D	2.36(1)	2.374(8)	2.35(2)
D–Rh–D		87.5(7)°	88.7(3)°	90.5(8)°
Rh–D–Rh		177.5(9)°	178.7(5)°	179.5(10)°

[a] Standard deviations in parenthesis.

3. Results and discussion

$MgRhD_{1-x}$ is a relatively unstable deuteride. Its range of existence at 298 K extends from $x=0.39$ at a deuterium pressure of $p=10^{-2}$ mbar to $x=0.06$ at $p=39$ bar. Its tetragonally distorted CsCl-type metal host structure contains only one deuterium site. The deuterium occupancy, the cell volume and the lattice distortion, $2c/a$, increase as the deuterium pressure is increased. At $p=39$ bar the deuterium site is almost fully occupied and $2c/a$ is largest. At these conditions $MgRhD_{1-x}$ is nearly stoichiometric ($1-x=0.94$) and presumably close to its phase limit. Thus $MgRhD_{1-x}$ is likely to have metallic properties.

The most striking structural feature of $MgRhD_{1-x}$ is the arrangement of deuterium with respect to rhodium. As shown in Fig. 2, the D atoms

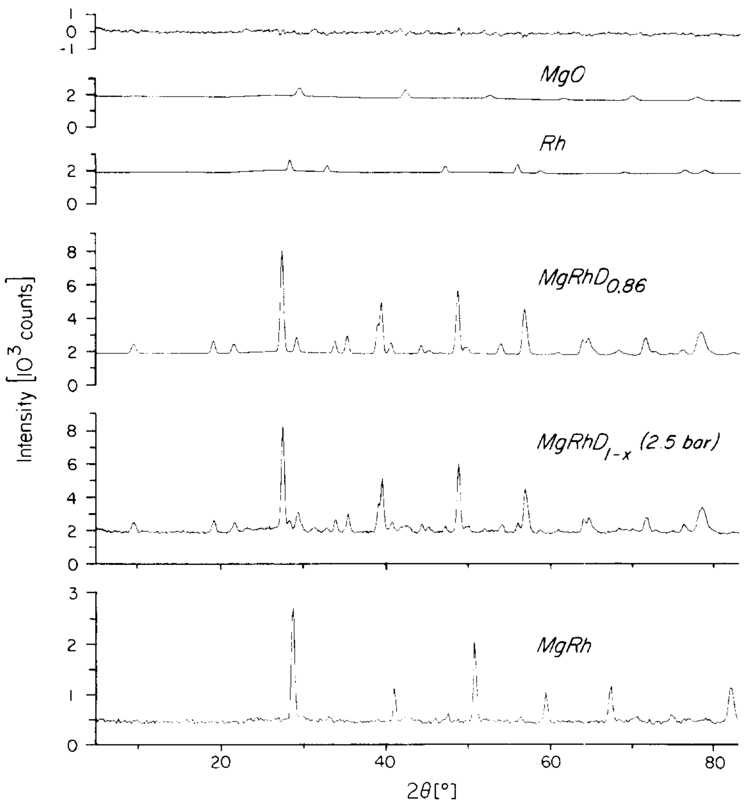

Fig. 1. (a) Observed neutron pattern of MgRh alloy; (b) observed (bottom), calculated (middle) and difference (top) neutron patterns of tetragonal $MgRhD_{0.86(1)}$ at $p = 2.5$ bar, $\lambda = 1.0864$ Å.

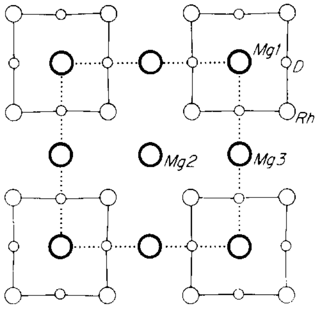

Fig. 2. Structure of $MgRhD_{1-x}$ projected along the tetragonal axis; large circles: magnesium at $z = 0$; small circles: rhodium and deuterium at $z = 1/2$. The occupancy of the deuterium site is 94% ($p = 39$ bar), 86% ($p = 2.5$ bar), 61% ($p = 10^{-2}$ mbar).

connect the Rh atoms to four-membered square planar rings of nominal composition $[Rh_4D_4]$ with Rh–D bond distances that change only slightly as a function of deuterium content: [Rh–D] = 1.708(4) Å, 1.699(3) Å, 1.654(4) Å for $x = 0.06$, 0.14 and 0.39 respectively. The D–Rh–D and Rh–D–Rh bond angles in these rings are nearly 90° and 180° respectively, and they change only slightly within the homogeneity range: [D–Rh–D] = 87.5(7)°, 88.7(3)°, 90.5(8)°; [Rh–D–Rh] = 177.5(9)°, 178.7(5)° and 179.5(10)°. This type of linkage has not yet been observed among ternary transition metal hydrides. In complex (usually non-metallic) hydrides, for example, the deuterium atoms are either connected to one transition metal only, or to none, but never to two as in the present compound (for a recent review on such structures see ref. 5). In metallic hydrides the interstitial hydrogen atoms may be bonded to more than one transition metal atom, such as in structurally related $TiFeH_x$ (for a review see ref. 6). In that compound Fe–H–Fe bridges are interconnected to linear and zigzag chains.

At low deuterium pressures (*i.e.* in deuterium-poor $MgRhD_{1-x}$ samples) the $[Rh_4D_4]$ rings are deuterium deficient. At high deuterium pressures (*i.e.* in nearly stoichiometric samples), however, the great majority of the rings is intact. Their bonding cannot be rationalized in terms of isolated groups, mainly due to the presumably metallic character of the compound and the strong interactions between the metal atoms. Some of these interactions are as strong as in binary MgRh, as can be seen from a comparison of the interatomic distances. In the deuteride $MgRhD_{1-x}$ the shortest [Rh–Rh] and [Mg–Rh] bonds are those within the Mg^2 centred CsCl-type structure block, *i.e.* that containing no interstitial deuterium and linking together the $[Rh_4D_4]$ rings (see Table 2 and Fig. 2). These bond lengths are similar to those in binary MgRh ([Rh–Rh] = 3.10 Å, [Mg–Rh] = 2.68 Å), and they decrease as the deuterium content of $MgRhD_{1-x}$ is increased.

A structurally related and electronically similar compound is the recently reported calcium palladium deuteride, $CaPdD_2$ [7], which also has a CsCl-type metal atom arrangement but has a higher deuterium content and a disordered deuterium distribution. In this compound, palladium tends toward a d^{10} configuration, similar to rhodium in the present nearly stoichiometric deuteride MgRhD. The deuterium distributions, however, differ as deuterium in $CaPdD_2$ has only one transition metal ligand, which is presumably linearly coordinated by two deuterium atoms, whereas deuterium in $MgRhD_{1-x}$ has two transition metal ligands which are coordinated by two deuterium atoms, with [D–Rh–D] bond angles of nearly 90°. The electronic properties of these two hydrides have not yet been investigated. It is likely, however, that they are intermediate between those of interstitial (metallic) and complex (non-metallic) hydrides.

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