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New alkali metal osmium- and ruthenium hydrides

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Abstract

Previously unknown ternary metal hydrides A_xOsH_z and A_xRuH_z (A = alkali metal) were synthesized by the reaction of alkali metal hydrides with osmium or ruthenium under a hydrogen pressure up to 6000 bar. The crystal structures of the hydrides were determined using a combination of X-ray and neutron diffraction experiments with deuterated compounds on powdered samples. Na_3OsH_7 and Na_3RuH_7 crystallize at room temperature in a tetragonal structure type (space group: $P4_2/mnm$), which is characterized by isolated $[OsH_7]$- or $[RuH_7]$ anions. The coordination polyhedron formed by the seven hydrogen (deuterium) ligands can be described as a distorted pentagonal bipyramide. Magnetic susceptibility measurements on Na_3OsH_7 in the temperature range between 3.5 K and room temperature revealed a weak temperature independent paramagnetism. Quantum mechanical calculations confirm these facts and show in detail that the large value of the spin–orbit coupling constant is responsible for the magnetic behaviour of these compounds with the oxidation state +4 for the transition metal atoms. With the heavier alkali metals transition metal(IV) hydrides $A_{3-\delta}OsH_{7-\delta}$ and $A_{3-\delta}RuH_{7-\delta}$ could be synthesized. They crystallize with isotypic atomic arrangements related to the cryolite structure type. Highest hydrogen pressure during the reaction leads to the osmium(VI) hydrides Cs_3OsH_9 and Rb_3OsH_9. The atomic arrangement is characterized by $[OsH_8]$ polyhedra intercalated in a cubic HA_3 framework which corresponds to the ReO_3 structure type. Within these polyhedra the hydrogen ligands occupy two 24-fold positions with a statistical distribution.

Keywords: Metal hydrides; High pressure synthesis; Crystal structure; Neutron diffraction; Magnetic properties

1. Introduction

In the ternary systems A/Os/H and A/Ru/H (A = alkali metal) only the hydrides Li_4OsH_6 [1], Li_4RuH_6 [1,2] and Na_4RuH_6 [1] are known up to now. The compounds were synthesized by the reaction of alkali metal hydrides with osmium or ruthenium under a hydrogen pressure up to 100 bar and a temperature around 750 K. The atomic arrangement of the three hydrides mentioned is characterized by isolated $[MH_6]$ anions in which the transition metals M are in the oxidation state +2.

Our experience that an increased hydrogen pressure during the reaction stabilizes the higher oxidation states of transition metal atoms gave rise to the development of a high pressure apparatus [3]. At present our in-house built autoclaves enable reaction conditions to be attained in which hydrogen pressures up to 6000 bar and temperatures up to 970 K can be achieved.

With the new technique we were able to synthesize ternary alkali metal osmium- and ruthenium hydrides which contain the transition metals with oxidation states higher than +2.

2. General remarks on the synthesis and structure determination

The previously unknown metal hydrides A_xOsH_z and A_xRuH_z (A = alkali metal) were synthesized by the reaction of alkali metal hydrides with osmium or ruthenium under a hydrogen pressure up to 6000 bar via the reaction scheme $xAH + yM + (z - x)/2H_2 \rightarrow A_xM_yH_z$ (M = osmium or ruthenium). The respective temperature of reaction varied between 770 and 870 K. The reaction time was about 8 h. Further details are given in Refs. [3,4].

The crystal structures of the hydrides were determined using a combination of X-ray and neutron diffraction experiments with the deuterated compounds on powdered samples.

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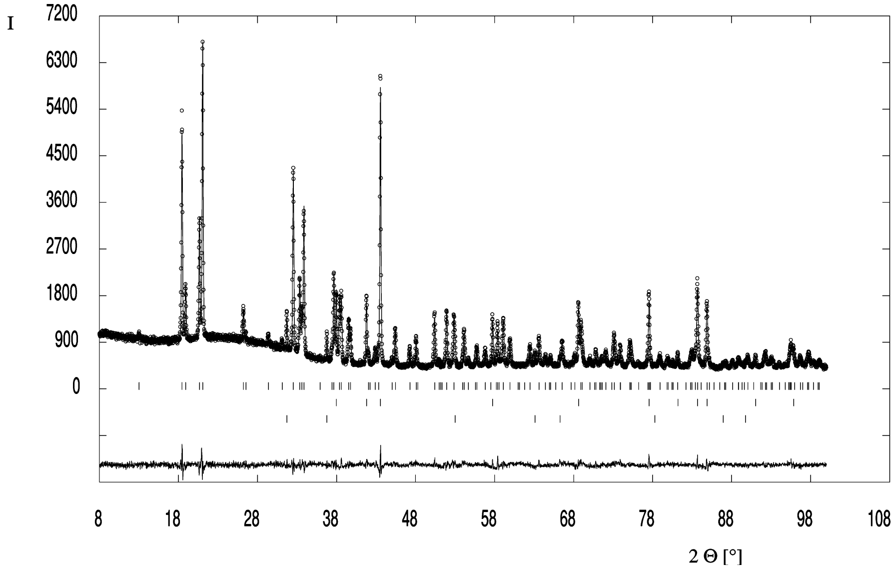

Fig. 1. X-ray diffraction diagram of Na_3OsH_7 (powder diffractometer, Stoe, STADI P2) at room temperature. The observed (○) and calculated (—) profile as well as the difference profile (bottom) are shown. The ticks mark the positions of the Bragg reflections (Na_3OsH_7, Os, NaH (top to bottom)).

3. Na_3OsH_7 and Na_3RuH_7

The ternary osmium hydride Na_3OsH_7 was synthesized by a reaction of sodium hydride with osmium powder under a hydrogen pressure of 1500 bar at 870 K. The corresponding deuterium compound was prepared under analogous conditions. To synthesize the ternary ruthenium hydride it was necessary to increase the hydrogen pressure during the reaction up to 5000 bar.

X-ray investigations on powdered samples led to the atomic arrangement of the metal atoms (Fig. 1, Table 1). Elastic neutron diffraction on Na_3OsD_7 yielded the complete crystal structure (Fig. 2, Table 2). In Fig. 3 the tetragonal atomic arrangement of Na_3OsD_7 is depicted. It is characterized by isolated $[OsD_7]$ anions separated by the sodium cations. The coordination polyhedron around the osmium atom formed by the seven deuterium ligands can be described as a distorted pentagonal bipyramide. The osmium–deuterium distances vary from 1.621(2) to 1.702(2) Å, deuterium–deuterium distances from 1.843(3) to 2.453(3) Å.

Magnetic susceptibility measurements on Na_3OsD_7 in the temperature range between 3.5 K and room temperature revealed a weak temperature independent paramagnetism (Fig. 4). Quantum mechanical calculations confirm these facts and show in detail that the large value of the

Table 1
Na_3OsH_7 and Na_3RuH_7, atomic parameters x, y, z and $B_{iso.}$ ($Å^2$) received from X-ray data (space group: $P4_2/mnm$)

			Na_3OsH_7	Na_3RuH_7
Lattice parameters (Å)			$a=9.604(2)$	$a=9.589(1)$
			$c=5.368(1)$	$c=5.365(2)$
R_{Bragg}			0.060	0.038
Os, Ru	4*f*	$x\ x\ 0$	$x=0.2021(1)$	$x=0.2026(1)$
$B_{iso.}$			0.15(3)	0.05(2)
Na1	8*i*	$x\ y\ 0$	$x=0.2060(1)$	$x=0.2084(3)$
			$y=0.535(1)$	$y=0.5328(3)$
$B_{iso.}$			2.0(2)	1.80(7)
Na2	4*g*	$x\ -x\ 0$	$x=0.8836(9)$	$x=0.8843(3)$
$B_{iso.}$			2.0(2)	1.80(7)

Table 2
Na_3OsD_7, positional parameters and anisotropic displacement factors ($Å^2 \times 10^{-2}$) refined from the HRPD data (compare Fig. 2) and $B_{eq.}$ values ($Å^2$) [$R_{Prof.}=0.047$; space group: $P4_2/mnm$; lattice parameters (Å): $a=9.5836(1)$, $c=5.3541(1)$]

Os	4*f*	$x\ x\ 0$	$x=0.2023(1)$			$B_{eq.}=0.32$
	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
	0.3(2)	0.3(2)	0.6(3)	−0.6(2)	0	0
Na1	8*i*	$x\ y\ 0$	$x=0.2066(4)$, $y=0.5344(3)$			$B_{eq.}=1.82$
	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
	0.4(4)	0.8(4)	5.7(6)	−2.6(4)	0	0
Na2	4*g*	$x\ -x\ 0$	$x=0.8849(3)$			$B_{eq.}=2.58$
	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
	2.5(5)	2.5(5)	4.8(8)	−1.8(6)	0	0
D1	8*j*	$x\ x\ z$	$x=0.1058(1)$, $z=0.8004(1)$			$B_{eq.}=1.74$
	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
	3.1(2)	3.1(2)	0.4(2)	−0.3(3)	0.5(2)	0.5(2)
D2	8*j*	$x\ x\ z$	$x=0.2468(2)$, $z=0.2811(1)$			$B_{eq.}=6.87$
	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
	10.8(4)	10.8(4)	4.5(4)	−1.0(3)	−2.4(3)	−2.4(3)
D3	8*i*	$x\ y\ 0$	$x=0.0691(2)$, $y=0.3198(2)$			$B_{eq.}=2.92$
	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
	3.5(4)	1.2(4)	6.4(3)	1.8(3)	0	0
D4	4*f*	$x\ x\ 0$	$x=0.3253(2)$			$B_{eq.}=5.90$
	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
	3.8(4)	3.8(4)	14.8(8)	−6.1(4)	0	0

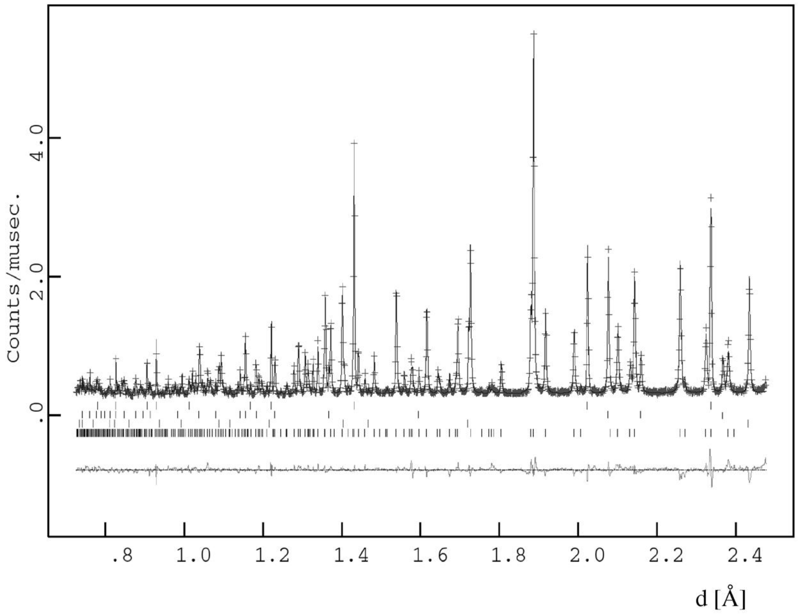

Fig. 2. Neutron diffraction diagram of Na_3OsD_7 (time-of-flight spectrometer HRPD, Rutherford Appleton Laboratory, UK) at room temperature. The observed (+) and calculated (—) profile as well as the difference profile (bottom) are shown. The ticks mark the positions of the Bragg reflections (Al, Os, NaD, Na_3OsD_7 (top to bottom)).

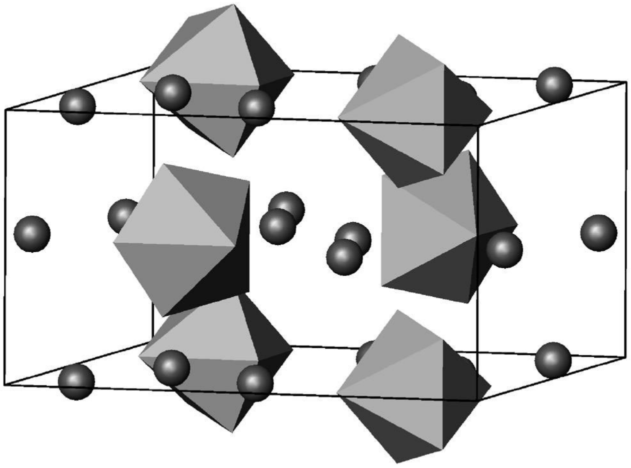

Fig. 3. Crystal structure of Na_3OsD_7 at room temperature showing the positions of the $[OsD_7]$ pentagonal bipyramids and the sodium atoms.

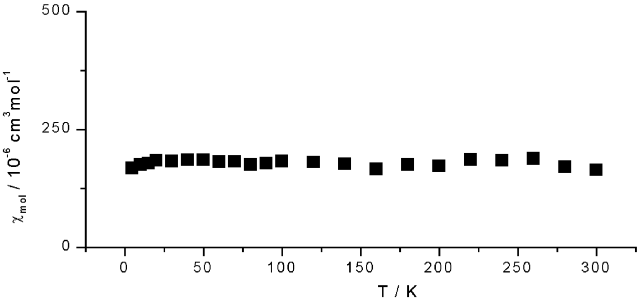

Fig. 4. Temperature dependence of the molar susceptibilities of Na_3OsD_7.

spin–orbit coupling constant is responsible for the magnetic behaviour of the osmium(IV) compound (d^4-configuration) [5–7]. The X-ray investigations (Table 1) showed that Na_3RuH_7 obviously crystallizes in an atomic arrangement isotypic to that of the osmium compound.

4. $A_{3-\delta}OsH_{7-\delta}$ (A=K or Rb) and $A_{3-\delta}RuH_{7-\delta}$ (A=K, Rb or Cs)

With the alkali metals potassium, rubidium and cesium ternary transition metal(IV) hydrides $A_{3-\delta}MH_{7-\delta}$ (M=Os or Ru) could be synthesized. Details are given in Ref. [4]. X-ray investigations led to cubic unit cells (Table 3) and atomic arrangements of the metal atoms related to the cryolite structure type. Illustrating this group of compounds the results for the potassium ruthenium hydride are summarized in Table 4 and Fig. 5. For the potassium atoms in the position 4*b* an occupation factor <1 was found. This result is valid for each of the hydrides $A_{3-\delta}MH_{7-\delta}$ whereby in all cases the δ-values of the

Table 3
Lattice parameters of the ternary hydrides $A_{3-\delta}MH_{7-\delta}$ (A=alkali metal, M=Ru or Os) [space group: $Fm\bar{3}m$]

Compound	Lattice parameter (Å)
$K_{3-\delta}RuH_{7-\delta}$	$a=8.502(1)$
$K_{3-\delta}OsH_{7-\delta}$	$a=8.484(1)$
$Rb_{3-\delta}RuH_{7-\delta}$	$a=8.848(1)$
$Rb_{3-\delta}OsH_{7-\delta}$	$a=8.822(1)$
$Cs_{3-\delta}RuH_{7-\delta}$	$a=9.199(1)$

Table 4
$K_{3-\delta}RuH_{7-\delta}$, atomic parameters *x*, *y*, *z* and $B_{\text{iso.}}$ (Å^2) received from X-ray data (compare Fig. 5) [space group: *Fm*3*m*, $a=8.502(1)$ Å]

Ru	4*a* $B_{\text{iso.}}=1.52(8)$	0 0 0	K1	4*b* $B_{\text{iso.}}=3.7(2)$ $\delta=0.10(2)$	$\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}$
K2	8*c* $B_{\text{iso.}}=3.3(2)$	$\frac{1}{4}\ \frac{1}{4}\ \frac{1}{4}$		$R_{\text{Bragg}}=0.044$	

osmium compounds are larger than those of the analogous ruthenium compounds which is in agreement with the smaller values of the lattice constants of the osmium hydrides (see Table 3). Neutron diffraction experiments on the corresponding deuterides confirm these results. Again the findings obtained for the potassium ruthenium deuteride are given as an example in Table 5 and Fig. 6. Within the [$RuD_{7-\delta}$] polyhedra the arrangement of the deuterium ligands can be described by an occupation of the 192-fold position (space group *Fm*3*m*) in a statistical distribution [8,9]. The correlation of the alkali metal and the deuterium content in the formula $A_{3-\delta}MD_{7-\delta}$ via the δ-value was proved by measurements of the magnetic susceptibilities. As for the sodium compounds mentioned above a weak temperature independent paramagnetism was found indicating a d^4-configuraton of the M atoms.

Table 5
$K_{3-\delta}RuD_{7-\delta}$, atomic parameters *x*, *y*, *z* and $B_{\text{iso.}}$(Å^2) received from TAS1 data (compare Fig. 6) [space group: *Fm*3*m*, $a=8.4539(9)$ Å]

Ru	4*a* $B_{\text{iso.}}=2.0$ (fixed)	0 0 0	D	192*l* $x=0.1924(3)$ $y=0.03(2)$ $z=0.96(8)$ $B_{\text{iso.}}=4.6(2)$ $\delta=0.12(2)$	*x y z*
K1	4*b* $B_{\text{iso.}}=2.0$ (fixed) $\delta=0.12(2)$	$\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}$		$R_{\text{Bragg}}=0.047$ $R_{\text{Prof.}}=0.07$	
K2	8*c* $B_{\text{iso.}}=2.0$ (fixed)	$\frac{1}{4}\ \frac{1}{4}\ \frac{1}{4}$			

5. Cs_3OsH_9 and Rb_3OsH_9

Under a hydrogen pressure >1500 bar the ternary osmium hydride Cs_3OsH_9 could be synthesized. The temperature of reaction was 870 K. To prepare the analogous rubidium compound Rb_3OsH_9 a hydrogen pressure of 6000 bar during the reaction was necessary. X-ray investigations again on powdered samples led to cubic unit cells and atomic arrangements of the metal atoms related to the $AuCu_3$ structure type (Table 6, Fig. 7). Elastic neutron diffraction experiments on Cs_3OsD_9 yielded the complete crystal structure (Table 7 and Fig. 8). The two osmium(VI) hydrides crystallize in an atomic arrangement which is characterized by isolated [OsH_8] polyhedra intercalated in a cubic HA_3 framework which corresponds to the ReO_3 structure type. Within these polyhedra the hydrogen ligands occupy two 24-fold positions with a statistical distribution (Fig. 9). The osmium–deuterium distances vary from 1.59(2) to 1.69(2) Å. The represented crystal structure is related to that of Rb_3ReH_{10} [10].

6. Final remarks

The synthesis of the new alkali metal osmium- and ruthenium hydrides discussed ahead shows again that the

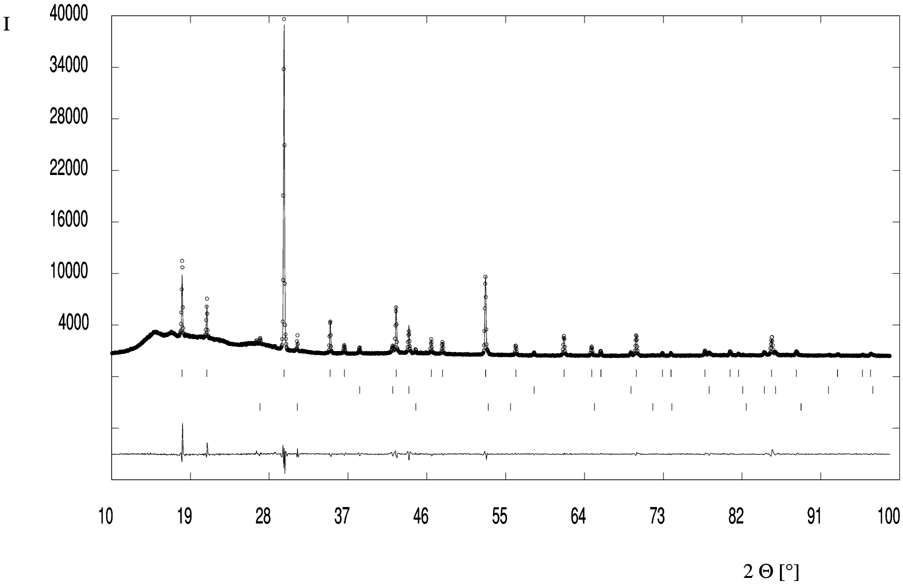

Fig. 5. X-ray diffraction diagram of $K_{3-\delta}RuH_{7-\delta}$ (powder diffractometer, Huber G 645) at room temperature. The observed (○) and calculated (—) profile as well as the difference profile (bottom) are shown. The ticks mark the positions of the Bragg reflections ($K_{3-\delta}RuH_{7-\delta}$, Ru, KH (top to bottom)).

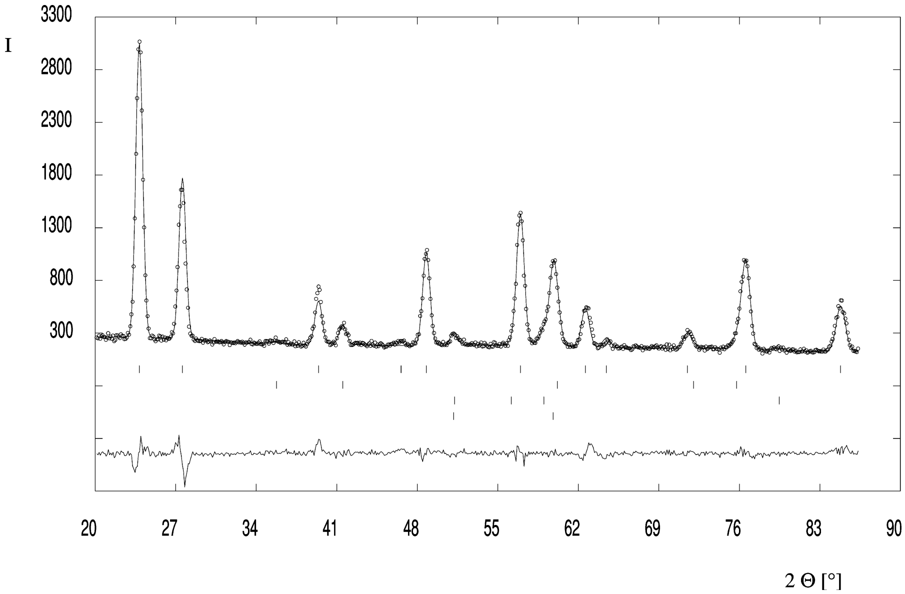

Fig. 6. Neutron diffraction diagram of $K_{3-\delta}RuD_{7-\delta}$ (spectrometer TAS1, Risø National Laboratory, Denmark) at room temperature. The observed (○) and calculated (—) profile as well as the difference profile (bottom) are shown. The ticks mark the positions of the Bragg reflections ($K_{3-\delta}RuD_{7-\delta}$, KD, Ru, Al (top to bottom)).

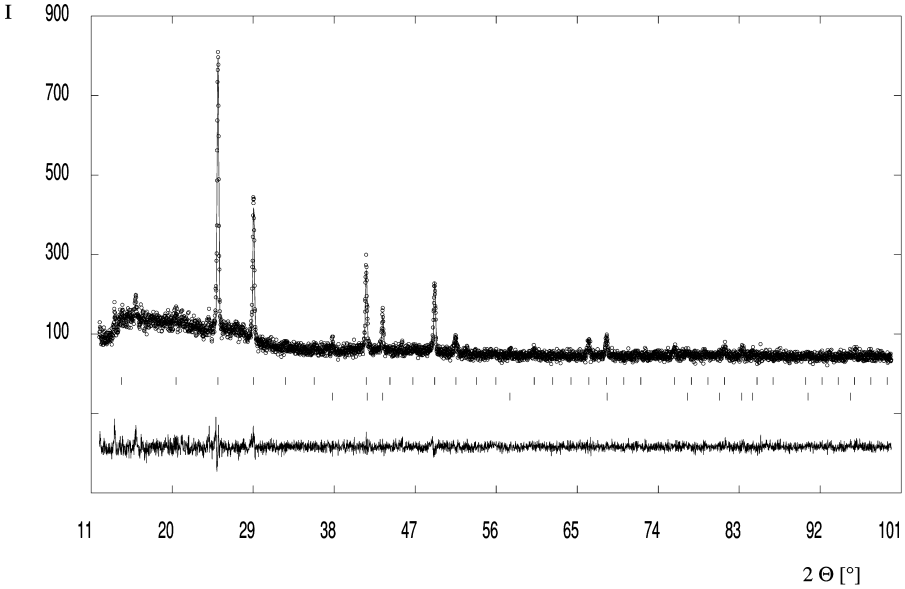

Fig. 7. X-ray diffraction diagram of Cs_3OsD_9 (powder diffractometer, Huber G 645) at room temperature. The observed (○) and calculated (—) profile as well as the difference profile (bottom) are shown. The ticks mark the positions of the Bragg reflections (Cs_3OsD_9, Os (top to bottom)).

Table 6
Cs_3OsD_9 and Rb_3OsH_9, atomic parameters x, y, z and $B_{iso.}$ ($\mathring{A}^2$) received from X-ray data [space group: $Pm\bar{3}m$]

		Cs_3OsD_9	Rb_3OsH_9
Lattice parameters (Å)		$a=6.1315(2)$	$a=5.8599(1)$
R_{Bragg}		0.041	0.082
$R_{Prof.}$		0.104	0.018
Os	1*a*	0 0 0	0 0 0
$B_{iso.}$		2.0 (fixed)[a]	0.72(4)
Cs/Rb	3*c*	$\frac{1}{2}$ $\frac{1}{2}$ 0	$\frac{1}{2}$ $\frac{1}{2}$ 0
$B_{iso.}$		2.0 (fixed)[a]	3.02(5)

[a] The powder pattern contains only few reflections with sufficient high intensities (cf. Fig. 7). Therefore, a refinement of the temperature factors was not possible.

Table 7
Cs_3OsD_9, atomic parameters x, y, z and $B_{iso.}$ ($\mathring{A}^2$) received from TAS1 data (compare Fig. 8) [space group: $Pm\bar{3}m$, $a=6.128(2)$ Å]

Os	1*a* $B_{iso.}=1.2(3)$	0 0 0	D2	24*k* $y=0.088(4)$ $z=0.263(3)$ $B_{iso.}=3.0$ (fixed) Sof[a] $=0.1667$ (fixed)	0 *y* *z*
Cs	3*c* $B_{iso.}=2.3(3)$	$\frac{1}{2}$ $\frac{1}{2}$ 0	D3	24*m* $x=0.103(3)$ $z=0.215(3)$ $B_{iso.}=3.0$ (fixed) Sof[a] $=0.1667$ (fixed)	*x* *x* *z*
D1	1*b* $B_{iso.}=3.2(4)$	$\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$	$R_{Bragg}=0.05$ $R_{Prof.}=0.11$		

[a] Site occupation factor.

high-pressure method has now provided access to metal hydrides with high oxidation states of the transition metals [3].

The investigations of the alkali metal osmium- and ruthenium hydrides presented here aim at their atomic arrangements at room temperature. Concerning the $[MH_z]$ anions in some compounds a statistical distribution of the hydrogen ligands in a higher-fold position of the chosen space groups was found obviously a dynamic behaviour of the hydrogen atoms [11]. In all these cases we observe phase transitions at low temperatures, but up to now the crystal structures of the low temperature modifications are unknown. On the other hand the structure investigations of the ternary sodium hydrides Na_3MH_7 yield no dynamic behaviour of the hydrogen ligands. Here high-temperature phase transitions can be expected. In agreement with this prediction we observed that the hydride Na_3OsH_7 crystallizes in a high temperature form above 459±2 K. The atomic arrangement is unknown and this, of course, raises subsequent questions.

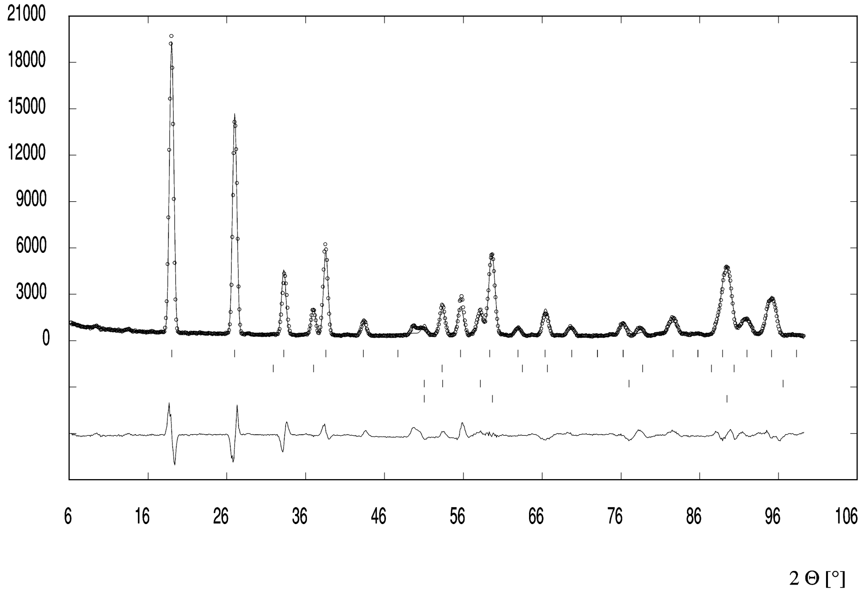

Fig. 8. Neutron diffraction diagram of Cs_3OsD_9 (spectrometer TAS1, Risø National Laboratory, Denmark) at room temperature. The observed (○) and calculated (—) profile as well as the difference profile (bottom) are shown. The ticks mark the positions of the Bragg reflections (Cs_3OsD_9, CsD, Os, Al (top to bottom)).

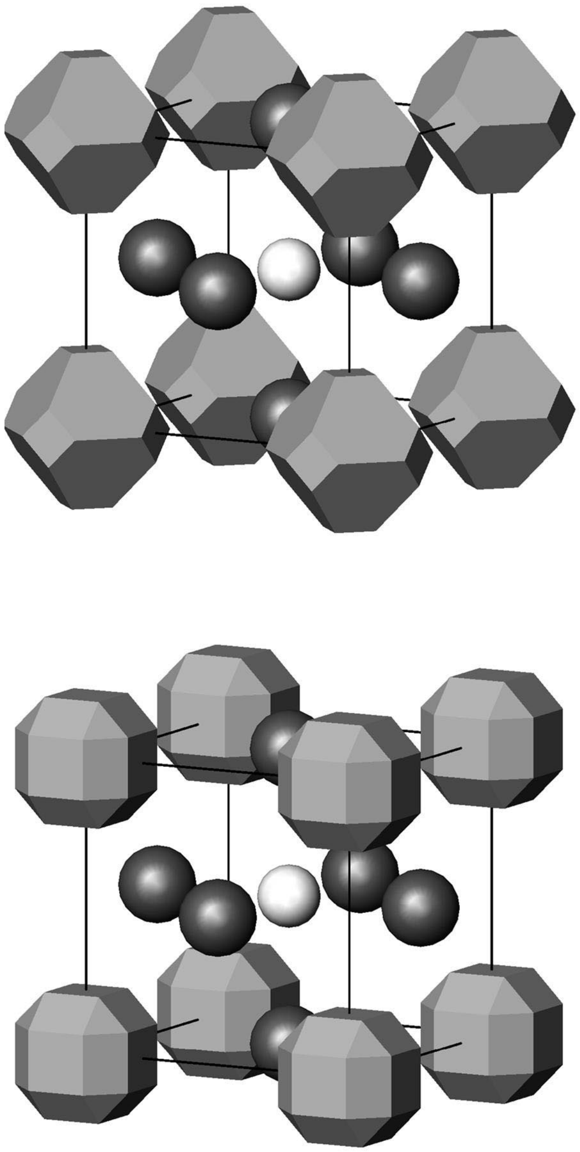

Fig. 9. Crystal structure of Cs_3OsD_9 at room temperature showing the positions of the $[OsD_8]$ polyhedra (two 24-fold positions of the deuterium ligands in a statistical distribution, separated in two pictures, site 24*k* on top and 24*m* at bottom), the cesium atoms and the additional deuterium atom in the position $\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2}$.

Acknowledgements

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