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The ZrV_2D_6 crystal structure

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Abstract

We have studied by neutron powder diffraction the crystal structure of the maximum deuteride ZrV_2D_6 based on the cubic Laves phase ZrV_2. The structure is orthorhombic, space group *Pnma* (No. 62), cell parameters: $a=5.5738(3)$ Å, $b=5.6996(3)$ Å, $c=7.9942(3)$ Å. The arrangement of the metal atoms, Zr and V, is the same as in the initial ZrV_2. Three D-atoms are ordered in the tetrahedral interstices Zr+3V, and other three D-atoms are ordered in the tetrahedral interstices 2Zr+2V. Distances between the nearest-neighbour D-atoms are ~2.1 Å. The ZrV_2D_6 structure can be considered as a derivative of the Spinel-type structure found earlier in $ZrTi_2D_4$. Unlike the Spinel-type structure, where four D-atoms ought to be located in Zr+3V interstices, in ZrV_2D_6 one of these atoms is replaced by three atoms located in the nearest 2Zr+2V interstices. The replacement differs for adjacent cells and is directed by the propagation vector $\mathbf{k}=(001)$.

Keywords: Intermetallic hydrides; Crystal structure; Hydrogen ordering; Neutron diffraction

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At present, four types of the hydrogen-ordered phases ZrV_2H_x are known: $ZrV_2H_{1<x<2.2}$ with $\mathbf{k}=(1/2, 1/2, 1/2)$ [1,2], $ZrV_2H_{2.8\leq x<3.5}$ with the variable vector $\mathbf{k}=(0,0,1-\delta)$, $0\leq\delta\leq0.5$ [3], $ZrV_2H_{3.5<x<4}$ with $\mathbf{k}=0$ [3,4] and the saturated hydride $ZrV_2H_{\sim6}$ with $\mathbf{k}=(001)$ [5,6]. The structures of the phases with lower hydrogen content, $x<4$, have been studied in detail, and only the saturated hydride is unexplored. This hydride is known to be thermodynamically stable at low temperatures, at least below 230 K, and has a narrow homogeneity range, $5.6<x<6$. Unlike the phases with the lower hydrogen content, which become disordered with temperature increase, it exists only in the ordered state and releases hydrogen when temperature increases. In this paper we report the crystal structure of the saturated hydride.

For the neutron study, we used the deuterium isotope to decrease the incoherent scattering. In the following, we will speak about hydrogen, whatever isotope (H or D) was used.

The alloy designed for synthesis of the hydride sample contained nearly 93% of the $MgCu_2$-type intermetallic ZrV_2 ($a=7.445$ Å); the rest, about 7%, was the initial b.c.c.-alloy Zr_xV_{1-x} ($x=0.33$, $a=3.19$ Å) surviving the high-temperature annealing at 1100 °C. The powder sample $ZrV_2D_{5.7}$ was synthesized by hydrogen absorption at pressure of about 1 bar in the temperature range 110–210 K, the hydrogen content was deduced from the volume of the absorbed gas and then determined more accurately from the neutron-diffraction data. The preparation method is detailed in [6]. In order to prevent the hydrogen release at higher temperatures, the sample was poisoned, before its evacuation from the reaction chamber, by CO_2–CO mix at ~200 K. (After such treatment, the saturated hydride keeps at standard conditions during half a year and allows repeated grinding without a visible change.) According to X-ray diffraction (see Fig. 1, top), most of the sample was the saturated hydride ZrV_2D_6. In addition, the sample contained a little (~7%) of a secondary phase with f.c.c. lattice ($a=4.27$ Å). As the subsequent neutron-diffraction investigation has shown, it is the CaF_2-type dihydride related to the above b.c.c.-alloy Zr_xV_{1-x}, its composition fitting the stoichiometry, D/Me=2.

The neutron-diffraction experiment has been performed in the Laboratoire Léon Brillouin on the high-resolution powder diffractometer 3T2 ($\lambda=1.2252$ Å) at 10 K. In the

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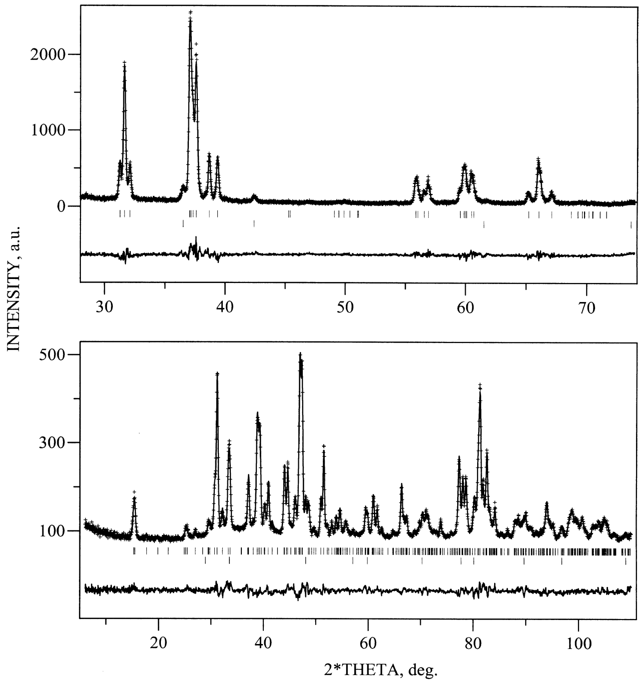

Fig. 1. Powder diffraction patterns of $ZrV_2D_{5.7}$. (Top) X-ray, CuKα, $T=300$ K. (Bottom) Neutron, $\lambda=1.2252$ Å, $T=10$ K. (+) experimental curves, (−) calculated ones, in accordance with Table 1, and, below, the difference between them; vertical bars indicate Bragg positions for the saturated hydride ZrV_2D_6 (above) and for the dihydride $(Zr_xV_{1-x})D_2$ (below).

structure determination we have used the FULLPROF program [7].

The results are summarized in Table 1 and Fig. 1. There are the crystallographic parameters of the saturated hydride ZrV_2D_6 and the experimental diffraction patterns compared with the calculated ones. Figs. 2 and 3 show graphically the ZrV_2D_6 crystal structure.

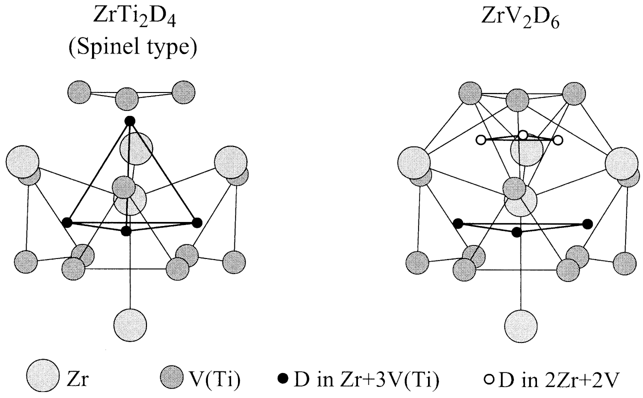

Fig. 2. Hydrogen arrangement in the Spinel-type hydride $ZrTi_2D_4$ (on the left) and in the saturated hydride ZrV_2D_6 (on the right).

The saturated hydride ZrV_2D_6 is actually the hydrogen-ordered solid solution based on the $MgCu_2$-type intermetallic ZrV_2. Its crystal structure has orthorhombic symmetry. The unit cell is oriented in regard to the initial ZrV_2 cubic cell as follows:

$$\begin{pmatrix} a \\ b \\ c \end{pmatrix}_{\text{orth}} = \begin{pmatrix} 1/2 & 1/2 & 0 \\ -1/2 & 1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} a \\ b \\ c \end{pmatrix}_{\text{cub}}$$

The arrangement of the metal atoms, Zr and V, is the same as in the host ZrV_2 (see Table 1). Six hydrogen atoms are ordered in the tetrahedral interstices of two types, Zr+3V and 2Zr+2V. If the phase was *completely* ordered, then three atoms occupied three Zr+3V interstices (D1 and D2 positions in Table 1) and other three atoms occupied three 2Zr+2V interstices (D3 and D4 positions). In reality, the phase is slightly disordered. The hydrogen atoms occupy additionally, with minor probability, other interstices of the same types, Zr+3V and 2Zr+2V, accessible in ZrV_2

Table 1
Crystal structure parameters of the saturated hydride ZrV_2D_6, $T=10$ K

Atom	Position type	Occupancy, *p*	Hydrogen surroundings	Coordinates		
				x	*y*	*z*
Zr	4*c*	1	–	0	0.25	0.875
V1	4*b*	1	–	0	0	0.5
V2	4*c*	1	–	0.25	0.25	0.25
D1*	4*c*	0.906(8)	Zr+3V	0.8012(6)	0.25	0.4707(4)
D2*	8*d*	0.860(7)	Zr+3V	0.0219(4)	0.4551(4)	0.2732(3)
D3*	4*c*	0.742(8)	2Zr+2V	0.1238(6)	0.25	0.6319(5)
D4*	8*d*	0.835(7)	2Zr+2V	0.3204(5)	0.0612(4)	0.4411(3)
D5	4*c*	0.106(6)	Zr+3V	0.1875	0.25	0.4688
D6	4*c*	0.096(8)	2Zr+2V	0.8716	0.25	0.6247
D7	8*d*	0.078(5)	2Zr+2V	0.0000	0.3784	0.1253
D8	8*d*	0.098(5)	2Zr+2V	0.8145	0.5639	0.3108
D9	8*d*	0.084(4)	2Zr+2V	0.1855	0.5639	0.3108
D10	8*d*	0.095(5)	2Zr+2V	0.6861	0.4355	0.4392

The dominant hydrogen positions are marked by asterisks. Numbers in parenthesis are standard deviations in the last decimal digit; the parameters without errors are the same as in the disordered hydride $ZrV_2D_{4.5}$ [11]. Space group *Pnma* (No. 62), $a=5.5738(3)$ Å, $b=5.6996(3)$ Å, $c=7.9942(3)$ Å, $B_{Zr}=0.1$ Å^2, $B_V=0.2$ Å^2, $B_D=1.0$ Å^2, $R_{exp}=2.30\%$, $R_{wp}=3.78\%$, $R_F=3.22\%$.

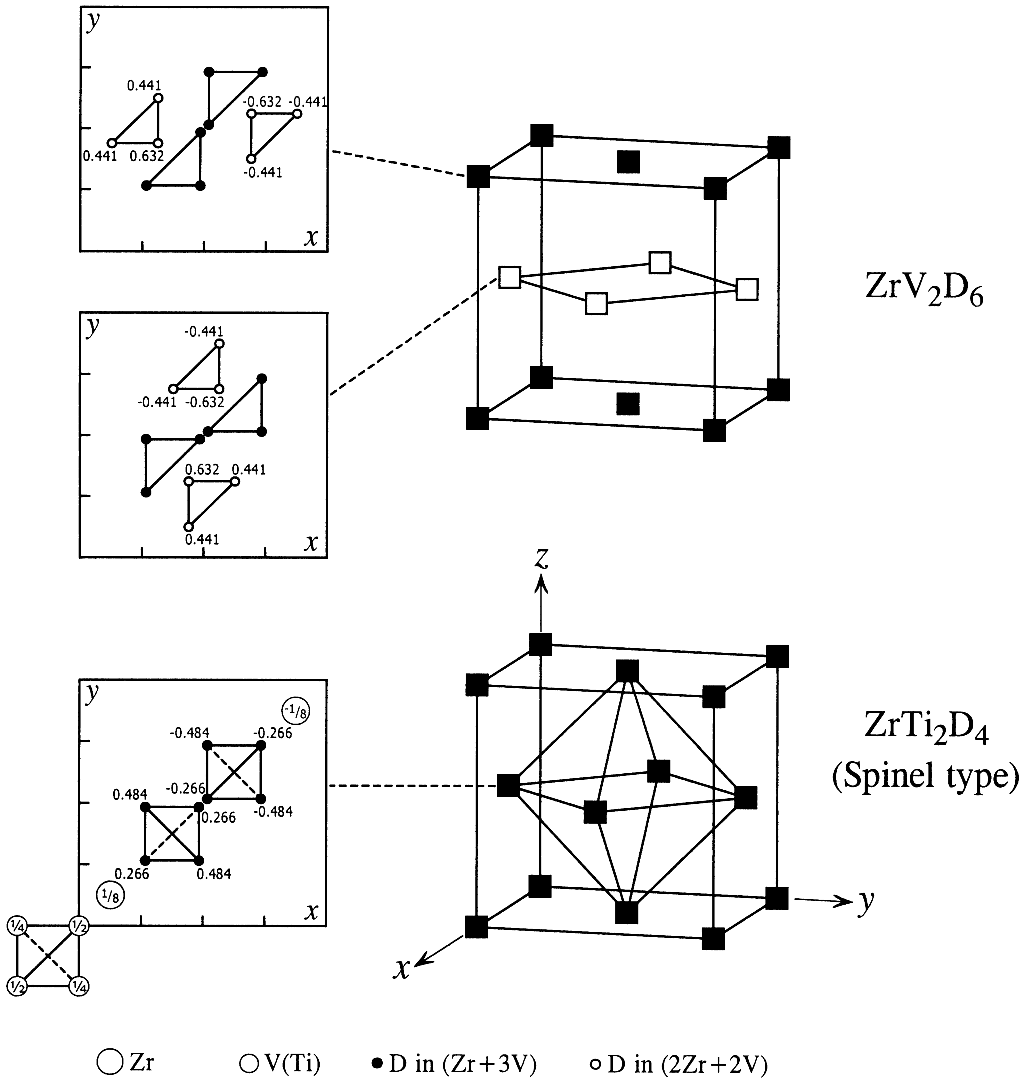

Fig. 3. Scheme of the structures of the Spinel-type hydride $ZrTi_2D_4$ (bottom) and the saturated hydride ZrV_2D_6 (top). On the right, the (super)lattices. On the left, atom arrangement in the (super)lattice sites; numbers correspond to z-coordinates, from Table 1 for ZrV_2D_6 and from Ref. [8] for $ZrTi_2D_4$.

(D5 . . . D10 positions). In the diffraction pattern (Fig. 1, bottom) this disorder reveals itself via weak diffuse peak typical of short-range correlations between hydrogen atoms [5].

The ZrV_2D_6 structure is closely connected with the Spinel-type structure found in $ZrTi_2D_4$ [8] (and, to a certain extent, in $HfTi_2D_4$ [9], where almost 90% of D-atoms are located in the Hf + 3Ti interstices belonging to the Spinel-type structure). It is a derivative of the latter (see Fig. 2). In the Spinel-type structure, four hydrogen atoms ought to be located in the Zr + 3V interstices (Fig. 2, on the left). In the structure under consideration, one of these atoms is replaced by three atoms located in adjacent 2Zr + 2V interstices (Fig. 2, on the right). It is significant to note that if such replacement was the same in all unit cells, then some atoms were situated too close to each other so that distances between them were nearly 1 Å. Such structure, without a change of the translational symmetry, is impossible because in the ZrV_2–D system all distances between hydrogen atoms must exceed the so-called ‘blocking radius’, ~2 Å [5]. The order of replacements, of one Zr + 3V interstice by three 2Zr + 2V, is regulated by the propagation vector **k** = (001) (see Fig. 3). This vector divides the initial f.c.c. lattice into two equivalent superlattices (marked as black and white squares in Fig. 3, top, on the right). On the one hand, the superlattices differ in the replaced interstices Zr + 3V (compare the arrangement of D-atoms in their sites and in the Spinel-type structure, in Fig. 3, on the left). On the other hand, they are fully equivalent physically: they are converted into each other by permutation of the x- and y-axes (compare the ‘black’ and ‘white’ superlattice sites in Fig. 3, top, on the left). With such ordering, the hydrogen atoms are situated at distances exceeding 2 Å and form the closest packing known so far for the RT_2H_x hydrides (for a review, see Ref. [10]).

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