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Neutron diffraction study of deuterium ordering in C15 type TaV_2D_x ($x>1$) in the temperature range of 1.5–295 K

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Abstract

Neutron diffraction investigations on the C15-type Laves phase deuterides TaV_2D_x with nominal compositions $1.3 \leq x \leq 1.65$ have shown that at T>150 K deuterium atoms (D) occupy 96g sites of space group $Fd\bar{3}m$, i.e. tetrahedral interstices with $[Ta_2V_2]$ coordination. However, the D positions are found to be considerably displaced from the geometrical centres of these sites. Below 150 K deuterium ordering is revealed by the appearance of superlattice peaks. Their intensities are found to increase substantially with increasing D content.

Keywords: Neutron powder diffraction; Transition metal deuterides; Order–disorder transitions; Laves phases

1. Introduction

The cubic C15-type Laves phase compound TaV_2 (space group $Fd\bar{3}m$) can absorb considerable amounts of hydrogen or deuterium, forming homogeneous solid solutions $TaV_2H(D)_x$ with $x<1.7$ [1]. For all x a single-phase state with C15 host-metal lattice is retained at least for temperatures down to about 80 K. However, recent measurements of heat capacity C of $TaV_2H_x(D_x)$ [2] have revealed distinct $C(T)$ peaks for samples with $x>1.1$ at temperatures below 120 K. The observed behaviour of $C(T)$ suggests H(D) ordering at low temperatures.

The aim of the present work was to study the temperature dependence of the crystal structure of TaV_2D_x. In particular the positions of D atoms were determined, and deuterium ordering was investigated. We have performed in the temperature range from 1.5 K to 295 K high-resolution neutron diffraction measurements on five TaV_2D_x samples with nominal D contents x ranging from 1.3 to 1.65. Previously only neutron diffraction results for room temperature were published [3].

2. Experimental

The preparation of the intermetallic compound was made similar to the one described in Ref. [4]. Small pieces of TaV_2 were charged with D_2 gas at pressures of about 1 bar in a Sieverts-type vacuum system. The nominal D content was determined from deuterium pressure change in the calibrated volume of the system. Samples 1 and 2 (both with $x=1.3$) were prepared from different TaV_2 ingots; in both cases D_2 was admitted at 700 °C, and then the system was slowly cooled to room temperature. Samples 3, 4 and 5 with $x=1.4$, 1.48 and 1.65, respectively, were prepared from the same TaV_2 ingot. In these cases D_2 was admitted at room temperature after annealing in vacuum at 700 °C. In order to prepare sample 5 with highest x, the reactor with the sample was additionally cooled down to 200 K.

High-resolution neutron diffraction investigations were performed on powdered TaV_2D_x samples (sealed under helium gas in cylindrical vanadium containers of diameters ≈9 mm and heights of about 25 to 35 mm) on neutron diffractometer DMC at reactor Saphir (Paul Scherrer Institute, Villigen) and on the neutron diffractometers D1A and D1B of Institut Laue-Langevin at Grenoble (for details see Table 1). For cooling of the samples a closed-cycle helium refrigerator (DMC) and ‘‘ILL’’-type cryostats were

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Table 1
Temperature dependencies of structural parameters of TaV_2D_x for space group $Fd\bar{3}m$, Ta (8a): (0.125, 0.125, 0.125), V (16d): (0.5, 0.5, 0.5)

Sample	1	2	3	4	5
$x_{nom.}$	1.3	1.3	1.4	1.48	1.65
T [K]	160	295	290	290	290*
	130	150	150	170	165
	9	1.5	100	100	1.5
			1.5	1.5	
n diffrm.	DMC	D1A	D1A	D1A	D1A
λ [Å]	1.7037	1.9080	2.4783	2.4783	2.4783
$2\theta_{max}$ [°]	83	150	160	160	160
a_X [Å]	7.29	7.29	7.301	7.310	7.328
a_n [Å]	7.2922(5)	7.2932(4)	7.3026(5)	7.3047(3)	7.3272(4)
	7.2913(5)	7.2855(6)	7.2939(5)	7.2973(3)	7.3227(4)
	7.2888(6)	7.2822(6)	7.2926(5)	7.2951(4)	7.3190(6)
			7.2913(5)	7.2934(3)	
$x_{D1\ (96g)}$	0.055(1)	0.0580(5)	0.0560(5)	0.0541(4)	0.0547(3)
	0.055(1)	0.0572(5)	0.0556(5)	0.0555(4)	0.0524(4)
	0.053(1)	0.0573(5)	0.0553(5)	0.0551(5)	0.0527(5)
			0.0543(5)	0.0549(4)	
z_{D1}	0.894(3)	0.8895(6)	0.888(2)	0.886(1)	0.8876(4)
	0.896(3)	0.8879(7)	0.895(2)	0.897(1)	0.886(1)
	0.893(3)	0.8879(6)	0.900(1)	0.901(1)	0.898(1)
			0.901(1)	0.903(1)	
$x_n = n_{D1}$	1.12(1)	1.08(1)	1.19(1)	1.25(1)	1.42(1)
	1.10(2)	1.09(1)	1.02(1)	1.07(1)	1.32(1)
	1.16(2)	1.04(1)	1.04(1)	1.03(1)	1.19(1)
			1.07(1)	1.00(1)	
B [Å^2]	0.4(1)	0.45(4)	1.73(9)	1.33(6)	1.19(3)
	0.3(2)	0.60(5)	1.03(8)	0.74(6)	1.12(7)
	0.6(2)	0.46(5)	0.95(8)	0.54(7)	0.56(8)
			0.62(7)	0.32(6)	
χ^2	4.51	2.43	1.44	1.23	2.43
	6.29	4.51	2.09	1.71	1.82
	9.36	5.96	1.94	1.80	0.79
			1.84	0.41	
R_{wp}	0.026	0.045	0.055	0.041	0.037
	0.026	0.053	0.051	0.044	0.044
	0.030	0.056	0.052	0.045	0.061
			0.053	0.045	
R_{exp}	0.012	0.029	0.046	0.037	0.024
	0.010	0.025	0.035	0.034	0.033
	0.010	0.023	0.038	0.034	0.068
			0.039	0.070	
R_B	0.019	0.052	0.041	0.024	0.078
	0.023	0.064	0.062	0.031	0.028
	0.026	0.067	0.032	0.031	0.061
			0.054	0.041	

Estimated standard deviations are given within parentheses and refer to the last relevant digit. λ = neutron wavelength, a_X = X-ray lattice parameter at room temperature, B = overall temperature factor; R_{wp}, R_B = agreement values concerning weighted profile and integrated intensities, respectively; R_{exp} = expected value from counting statistics.
* $\lambda = 1.9079$ Å

used. Profile refinements were made with program FullProf [5], based on the neutron scattering lengths published by Sears [6].

3. Results and discussion

As examples of the measured neutron diffraction patterns, Figs. 1 and 2 show the experimental data for $TaV_2D_{1.65}$ at T≈165 K and 1.5 K. In the high-temperature region (T>150 K) for all samples studied the structure of the dominant phase is identified as C15-type. In agreement with conclusions published in Ref. [4,7] the profile refinements show that the D atoms occupy only 96g $\{x, x, z\}$ positions of the space group $Fd\bar{3}m$, i.e. tetrahedral interstitial sites with $[Ta_2V_2]$ coordination. In addition the neutron diffraction patterns indicate small fractions of V_2D (space group Cm) or Ta_2D (space group C222) phases (only

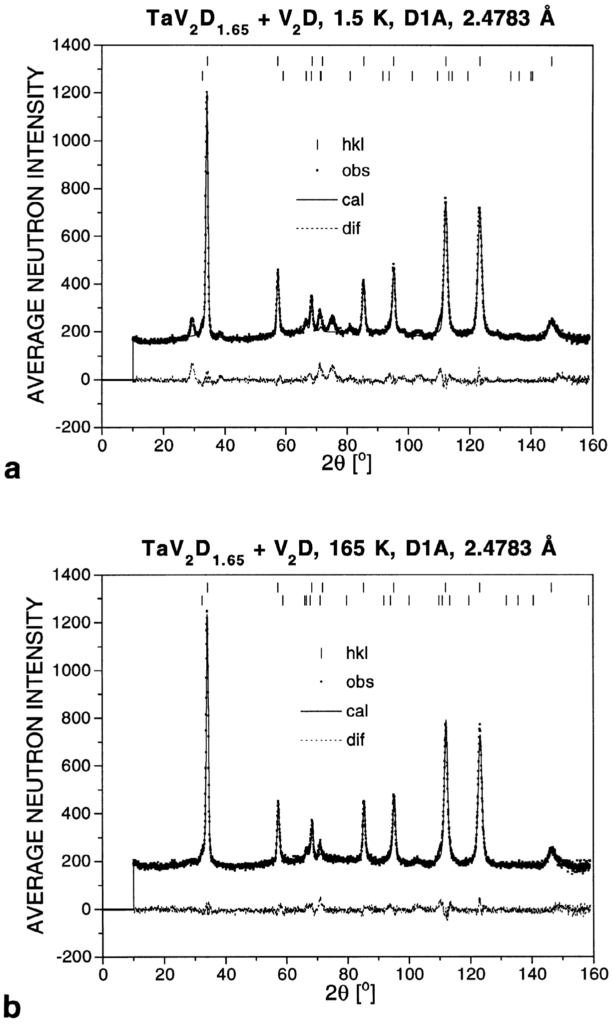

Fig. 1. Observed, calculated and difference neutron diffraction patterns of $TaV_2D_{1.65}$ at (a) 1.5 K and (b) at 165 K (D1A measurements). Vertical bars indicate Bragg peak positions of the dominant C15 phase and of traces of V_2D (lower markers).

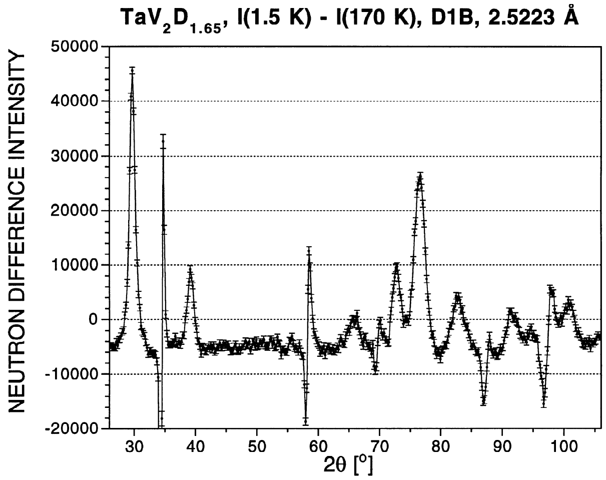

Fig. 2. Difference D1B neutron diffraction pattern of $TaV_2D_{1.65}$ between 1.5 K and 170 K, illustrating clearly the presence of superstructure peaks associated with D atom ordering.

sample 2) which were difficult to avoid completely in the sample preparation due to minor amounts of excess V or Ta in the starting TaV_2 material. Compared to the instrumental resolution considerable line broadening is observed in the case of the dominant deuteride phase.

The structural parameters of the main phase at different temperatures — for space group Fd$\bar{3}$m, i.e. disregarding superstructure peaks at low temperatures — are listed in Table 1. It should be noted that for all samples the positions of D atoms are found to be considerably displaced (by approximately 0.1 Å) from the geometric centres of the 96g sites. For example, for $TaV_2D_{1.65}$ at 165 K the corresponding interatomic distances Ta–D and V–D are ≈1.90 Å and 1.80 Å, respectively, reflecting the smaller metal radius of V. Such displacements also result in the reduction of the distance between the nearest-neighbour g sites. In fact, the sublattice of g sites appears to be split into 6-site rings well separated from each other. For $TaV_2D_{1.65}$ at 165 K the distance between the nearest-neighbour g sites within the ring is 1.00 Å, whereas the minimum distance between g sites at different rings is 1.50 Å. This feature may be related with the occurrence of the unusual localized H(D) motion detected in $TaV_2H_x(D_x)$ by means of nuclear magnetic resonance [4,8] and quasielastic neutron scattering [9].

Comparison of the neutron diffraction patterns at 165 K and at 1.5 K (Fig. 1(a) and (b)) reveals the appearance of a number of weak superlattice peaks in the low-temperature pattern. This is a clear indication of deuterium ordering. Fig. 2 shows a corresponding difference intensity plot obtained on D1B with considerably higher counting statistics. Neighbouring rather narrow minima and maxima originate from shifts of dominant Bragg peaks due to temperature variation and associated lattice parameter changes. All broader positive peaks are expected to represent superlattice lines. Such additional peaks have been observed for all samples except for specimen 2. In agreement with the heat capacity results [2], the order–disorder transition is found to occur between approximately 100 and 150 K. The positions of the superlattice peaks do not depend significantly on the deuterium content. However, their intensities are found to increase rapidly with increasing x. This means that in the studied range of compositions the type of superlattice remains unchanged, but the order parameter increases with increasing D concentration.

Up to now we did not succeed in unambiguously indexing all of the superlattice lines, considering both commensurate and incommensurate cases such as $\vec{K} \approx [0.88, 0.48, 0]$ for a cubic P lattice. Thus the structural parameters given in Table 1 only characterize "average" structures. The differences between the nominal x and x_n values are due to the impurity phases and the fact that V gives practically no contribution to the coherent neutron intensities. The general decrease of the D occupation factor with lowering of the temperature also indicates D ordering at low temperatures.

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