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The interaction of oxygen (nitrogen) with hydrogen in Ti, V and Ta

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Abstract

The interaction of oxygen (nitrogen) with hydrogen in transition metals of Groups IV and V was studied. This interaction suppresses hydride precipitation in Nb and Ta down to 10 K. In V, oxygen delays the forming of the hydride until 50 K. In Ti, only 7% H for oxygen and 20% H for nitrogen stay in solid solution at low temperatures.

Keywords: Transition metals; Hydrogen; Capture; Inelastic neutron scattering; O and N effects on solid solutions

1. Introduction

Fast ion channelling (FIC) shows that hydrogen moves from tetrahedral (T) to octahedral (O) positions in V–O–H solid solutions (SS), or to low symmetrical positions in Ta–N SS, due to O(N)–H interaction [1]. Thus for oxygen or nitrogen located in the O positions, the FIC method cannot determine the hydrogen location exactly. In this work the FIC data was checked by inelastic neutron scattering (INS).

2. Experimental

2.1. Sample preparation

Vanadium metal was oxidized to the phase limit of the α-phase (6 at.%) oxygen. The sample was charged with hydrogen at 800 °C and water quenched. A tantalum sample was first alloyed by 3 at.% of vanadium and then saturated with nitrogen and hydrogen from the gas phase and water quenched from 800 °C. Vanadium and nitrogen in Ta form additional defect complexes that capture hydrogen. The titanium sample was prepared by melting Ti with TiN to obtain a concentration of $TiN_{0.05}$ and charged with H. All samples were single phase as determined by neutronography.

3. Results

3.1. V–O–H system

In this system, the formation of β-V_2H hydride was studied by INS. Due to the high luminosity of the neutron spectrometer KDSOG-M at the pulsed reactor IBR-2 (Dubna, Russia), the local mode of hydrogen in the

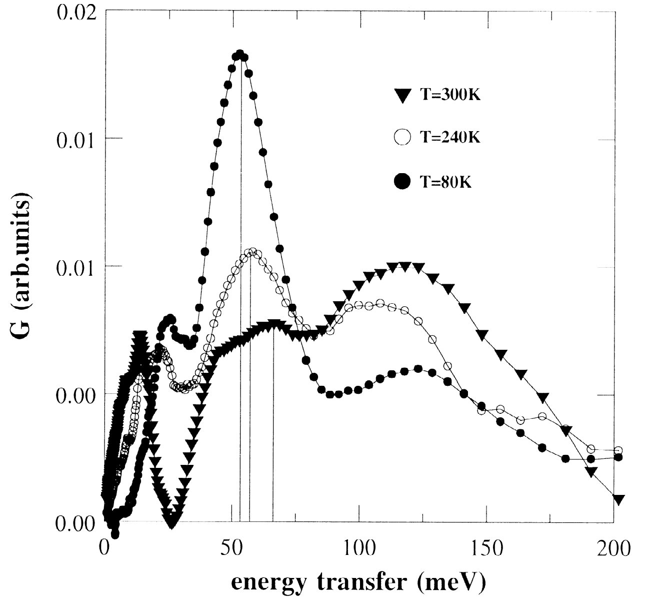

Fig. 1. The partial hydrogen state function (PHSF) in $VO_{0.06}H_{0.03}$ at 300 K, 240 K and 80 K.

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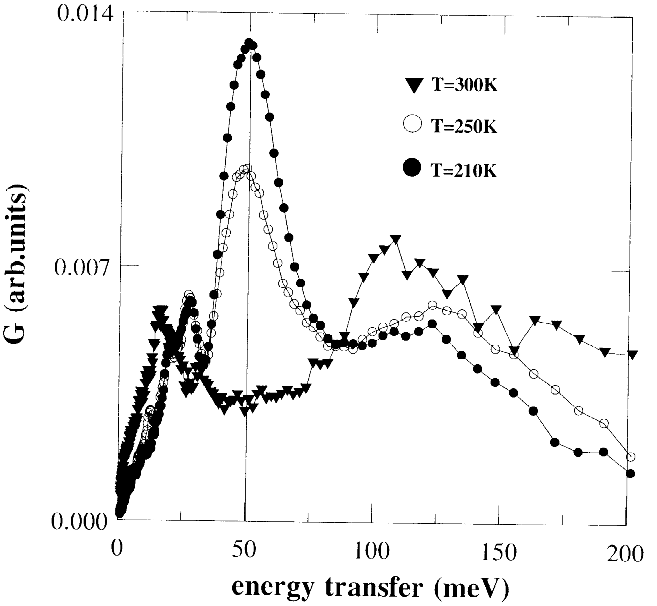

Fig. 2. The PHSF in $VH_{0.01}$ at 300 K, 250 K and 210 K.

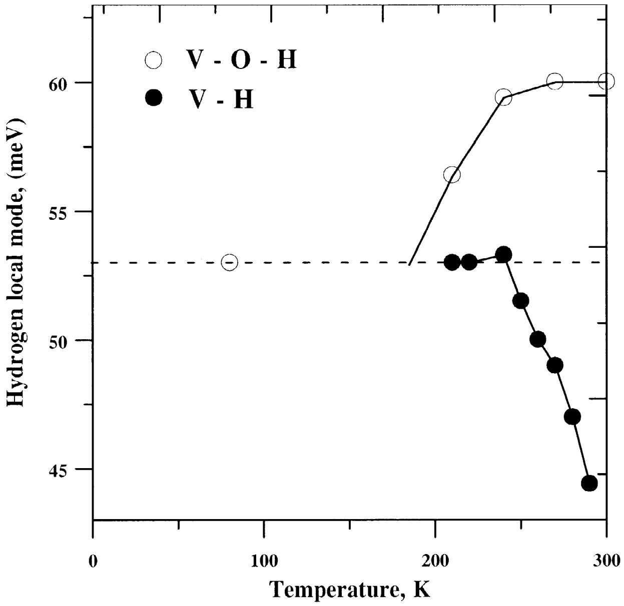

Fig. 3. The dependence of LMP versus temperature for $VO_{0.06}H_{0.03}$ (open circle) and $VH_{0.01}$ (dark circle).

octahedral sites could be measured to within 1 h. The process of β-V_2H formation was studied during a gradual cooling of the samples from room temperature to 210 K (Figs. 1 and 2). Oxygen has a substantial influence on this process, in particular the LM energies which decrease as the temperature is decreased (Fig. 3, Table 1).

In the binary $VH_{0.01}$ system, the hydrogen local mode positions (LMP) increase from 45 meV at room temperature to 53 meV at 240 K, and remain constant at lower temperatures. According to [2], hydrogen precipitates into hydride at 260 K for 1 at.% concentration in V. Above this temperature, LMP changes can be explained by the displacement of hydrogen atoms towards the O-tites in anticipation of the phase transition. This process is accompanied by the increasing tetragonality of VH_x SS [3]. Fukai [3] proposed that the 1T→4T(O) transition is a response to this tetragonality. We confirmed this proposal by INS.

In the case of the ternary $VO_{0.06}H_{0.03}$ system, the LMP decreases from 63 meV to 53 meV (Fig. 3). Oxygen keeps the hydrogen in SS down to 190 K, and this is 50 K lower than for the binary V–H system in spite of the greater H concentration in the ternary SS.

Both for binary and ternary systems, hydrogen participates not only in LM but also in resonance-like lattice vibrations (RLLV) (Figs. 1 and 2). The positions of these RLLV depend on temperature and are close to the predicted value of 16 meV [4].

3.2. $TaN_{0.02}H_{0.045}$ and $TaV_{0.03}N_{0.02}H_{0.02}$ solid solutions

The LMP of the binary $TaH_{0.045}$ SS changes essentially at low temperature due to the formation of β-TaH hydride (Fig. 4). In contradiction to this, the LMP of the nitrogen-containing alloys do not change at low temperatures (Figs.

Table 1
Position ε and halfwidths $\Delta\varepsilon$ of the hydrogen local modes in pure vanadium and vanadium with oxygen depending on the sample's temperatures (in meV)

	$VH_{0.01}$						$VO_{0.06}H_{0.03}$					
T (K)	I		II		III		I		II		III	
	ε	$\Delta\varepsilon$	ε	$\Delta\varepsilon$	ε	$\Delta\varepsilon$	ε	$\Delta\varepsilon$	ε	$\Delta\varepsilon$	ε	$\Delta\varepsilon$
300			108	50	180	57	60	31	117	60	180[a]	
290	44.4	23	121	60								
280	47.0	20	120	55								
270	49.0	28	120	50			60	30	120	60	180[a]	
260	50.0	28	130	60								
250	51.5	28	130	60								
240	53.3	28	130	70	180[a]		59.4	35	112.2	46		
220	53.0	28	130	60								
210	53.0	28	130	50	180[a]		56.4	30	122	69		
80							53.0	26	130	60		

[a] shoulder.

Table 2
Position and widths of hydrogen local modes in pure tantalum, tantalum withnitrogen, tantalum with vanadium and nitrogen (in meV)

T (K)	$TaN_{0.02}H_{0.045}$			$TaV_{0.03}N_{0.02}H_{0.02}$			$TaH_{0.04}$		
300	–	117(17)	163(47)	–	115(25)	–	85(50)	116(28)	164(18)
80	100(40)	118(12)	168(20)	101(40)	116(12)	162(60)	–	–	
20	102(50)	118(15)	168(15)	98(12)	116(8)	176(40)	85(10)	125(12)	172(14)

Numbers in brackets shows experimental widths of the hydrogen local modes.

5 and 6; Table 2). From these facts, we conclude that either NoH or V–N–H interactions retain hydrogen in SS.

Moreover, in the $TaV_{0.03}N_{0.02}H_{0.02}$ SS, the hydrogen LM splits into three peaks (Fig. 5) as for ε-V_2H hydride [5].

The calculation of the lattice dynamics for microcrystals showed that such splits can be explained by N–H or H–H interactions that cause the deformation fields. An empirical vanadium–hydrogen potential simultaneously satisfies not only the vibrations of hydrogen in the T-positions (α-V_2H phase) or O-positions (β-V_2H phase), but also H vibrations in the saddle points between the T and O-positions (ε-V_2H phase). The last phase forms due to the elastic H–H interaction in the nearest neighbour hydrogen pairs. The low symmetry of the H atoms in the saddle point splits the fundamental hydrogen vibrations into three peaks. This split was measured for the ε-V_2H phase [5] and for the $TaV_{0.03}N_{0.02}H_{0.02}$ SS (Fig. 5). An empirical potential, satisfied for the H vibrations in Ta, gives three energies: 97, 125 and 172 meV for the nearest H–H pairs in Ta, which is nearly the same as the experimental values (Fig. 5).

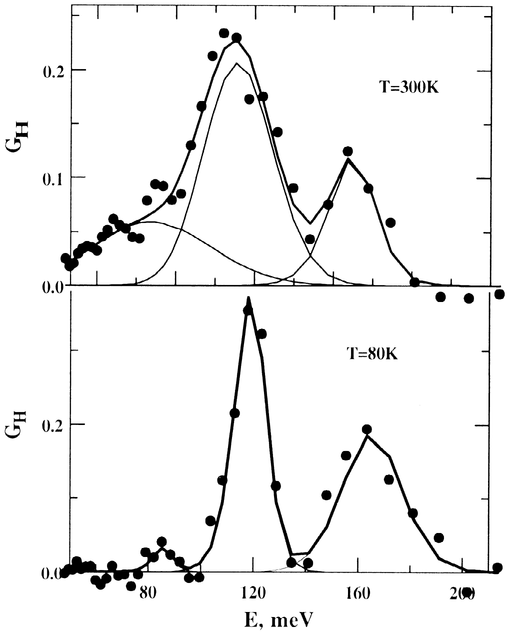

Fig. 4. The PHSF in $TaH_{0.045}$ at 300 K and 80 K.

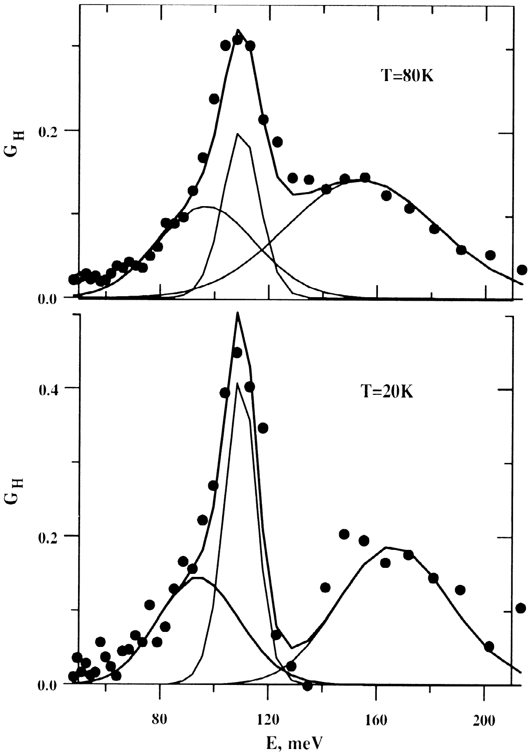

Fig. 5. The PHSF in $TaV_{0.03}N_{0.02}H_{0.02}$ at 80 K and 20 K.

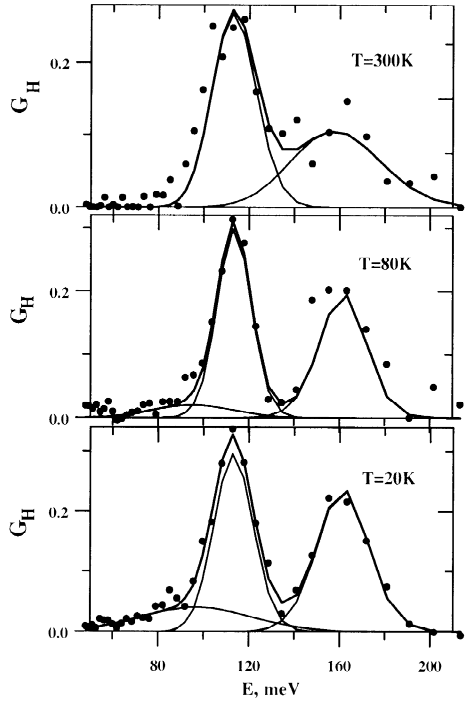

Fig. 6. The PHSF in $TaN_{0.02}H_{0.045}$ at 300 K, 80 K and 20 K.

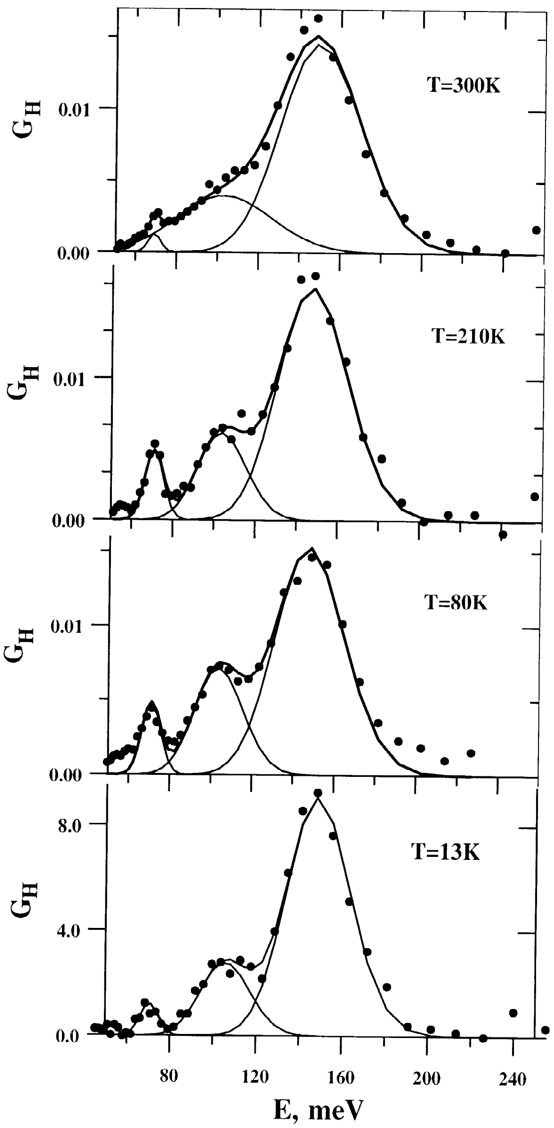

Fig. 7. The PHSF in $TiN_{0.05}H_{0.03}$ SS at 300 K, 210 K, 80 K and 13 K.

Table 3
Position and widths of local modes of the hydrogen and nitrogen in Ti and $TiN_{0.05}$ (in meV)

	Ti	$TiN_{0.05}$		
T (K)	(H)	(N)	(H)	(H)
300	153 (35)	73 (8)	107 (54)	155 (43)
210		73 (8)	108 (25)	153 (36)
80	153 (39)	73 (8)	108 (25)	153 (36)
13		73 (7)	110 (24)	155 (30)

3.3. Ti–N–H system

The greatest part of the hydrogen in both Ti–O SS [6] and in Ti–N SS (Fig. 7, peak at 153 meV; Table 3) are in the hydride phases.

The deformation fields for nitrogen in Ti increase in comparison to the fields for O atoms in Ti–O SS because the effective size of the interstitial nitrogen is greater than that of for oxygen. This causes an increase in the amount of residual hydrogen in the octahedral sites of Ti–N SS (Fig. 7: peak at 110 meV). In Ti–N SS, this amount is nearly 20%, but for the Ti–O SS it is only 7% [6]. In Ti, however, neither N–H nor O–H interactions suppress the formation of hydrides.

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