Hydrogen vibrations and hydrogen trapping in TaN$_{0.006}$H$_{0.003}$

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Abstract. We studied, by neutron spectroscopy, local vibrations of hydrogen interstitials and hydrogen trapping by nitrogen interstitials in TaN$_{0.006}$H$_{0.003}$ and in a nitrogen-free TaH$_{0.086}$ reference sample between 1.4 and 295 K. The measurements on TaH$_{0.086}$ yielded vibrational energies $E_1 = (113 \pm 1)$ meV and (doubly degenerate) $E_{2,3} \simeq 163$ meV at 295 K where hydrogen is in solid solution, together with a higher energy $E_1 = (120 \pm 1)$ meV and essentially unchanged energies $E_{2,3}$ at low temperatures (1.4 to 4.2 K) where hydrogen precipitates in a hydride phase. The energies agree with previous studies. The measurements on TaN$_{0.006}$H$_{0.003}$ yielded, at 295 K and at low temperatures, vibrational energies identical to those of the nitrogen-free sample at 295 K. The results show that the hydrogen interstitials are trapped by the nitrogen at low temperatures and do not precipitate. They show further that the trapped hydrogen interstitials occupy tetrahedral sites, i.e. the same type of site as occupied in the absence of traps.

1. Introduction

Hydrogen interstitials in metals can be trapped by lattice defects like grain boundaries, dislocations, vacancies and substitutional and interstitial defect atoms ([1–7] and references therein). The trapping of the hydrogen influences, in some cases decisively, a number of physical properties—e.g., the solubility and diffusion of the hydrogen, the mechanical behaviour of the host metal (hydrogen embrittlement) and details of the metal–hydrogen phase diagram, in particular the solubility limit of the hydrogen. A further important aspect is the high diffusive mobility of the light hydrogen interstitials [3, 6, 7] which allows trapping and detrapping processes to take place far below room temperature. Hydrogen interstitials differ in this respect from heavier impurity atoms whose smaller diffusivity generally does not permit any low-temperature trapping or detrapping.

A leading and widely studied example is hydrogen trapping in niobium by small amounts (up to ∼2 at.%) of nitrogen and oxygen interstitial atoms that are in solid solution [1, 3–11]. These studies were partly motivated by the fact that the trapped hydrogen interstitials exhibit, below ∼150 K, the complete temperature-dependent tunnelling behaviour of a particle in a double-well potential [6–12]. However, hydrogen-induced low-temperature anomalies in specific heat and thermal conductivity are reported for both niobium and tantalum [13, 14], which suggests that tunnelling of trapped hydrogen interstitials may similarly be found in tantalum.

The present paper reports results of a neutron spectroscopy study in which we determined the energies of the local vibrations of hydrogen interstitials in a $TaN_{0.006}H_{0.003}$ sample that was doped with nitrogen and hydrogen, and in a nitrogen-free $TaH_{0.086}$ reference sample doped solely with hydrogen. The energies of the local vibrations, measured at low temperatures (1.4 to 4.2 K) and 295 K, demonstrate that the nitrogen atoms in the $TaN_{0.006}H_{0.003}$ sample trap all the hydrogen interstitials at low temperatures, and that no hydrogen precipitation takes place as in the nitrogen-free reference sample. Comparison of the local hydrogen vibrations in the two samples shows further that the trapped hydrogen atoms occupy tetrahedral interstitial sites, i.e. the same type of site as hydrogen interstitials occupy in tantalum in the absence of traps.

2. Background and previous studies

This section briefly summarizes the present understanding of hydrogen trapping by nitrogen atoms in niobium and tantalum. For sufficiently small concentrations (up to the at.% range), nitrogen (and oxygen) atoms in niobium and tantalum can exist in solid solution, occupying octahedral interstitial sites in the bcc host-metal lattices [15–17] (this holds also at room temperature and below where the true solubility limit of these atoms is vanishingly small [18]). Hydrogen interstitials in otherwise pure niobium and tantalum are, on the other hand, located in tetrahedral sites within the respective solid-solution α-phases, i.e., for concentrations up to the solubility limit [1, 2, 19]. At room temperature (and in the absence of oxygen or nitrogen traps), the solubility limit is 3.5 and 13 at.% for niobium and tantalum, respectively, and it decreases exponentially with falling temperatures so that hydrogen precipitates completely in the low-temperature limit.

We first discuss hydrogen trapping by nitrogen in niobium, which was investigated in detail in resistance measurements [1] and by neutron spectroscopy [5] and is now well understood. The resistance measurements yielded a binding (or trapping) enthalpy of (0.12 ± 0.02) eV. They showed further that a given nitrogen atom traps at most a single hydrogen interstitial at low temperatures (below about 150 K), so that, when the hydrogen concentration exceeds that of nitrogen, the excess hydrogen interstitials that are untrapped precipitate in a hydride phase at sufficiently low temperatures. This behaviour can be explained by two competing enthalpy-gaining reactions of a hydrogen interstitial that is in solid solution and not yet trapped: the hydrogen can be trapped, gaining the binding enthalpy, or it can precipitate, gaining the precipitation enthalpy ($\sim$0.12 eV [1, 19]). In the low-temperature limit, entropy becomes unimportant and the hydrogen interstitials will do what gains the greatest enthalpy. Accordingly, the above low-temperature trapping behaviour shows that the binding enthalpy for the first hydrogen interstitial that is trapped by a given nitrogen atom exceeds (obviously slightly) the precipitation enthalpy, whereas the binding enthalpy for trapping of any additional hydrogen interstitials is smaller than the precipitation enthalpy, so that these interstitials will precipitate rather than become trapped.

In the neutron spectroscopy study [5], which is similar to the present one on the host metal tantalum, the local hydrogen vibrations and the trapping behaviour of the hydrogen were investigated between 4 K and room temperature. The study demonstrated a complete low-temperature trapping of hydrogen interstitials by nitrogen and oxygen atoms whose concentrations exceeded that of the hydrogen, thus confirming the results of the resistance measurements [1]. A further important result of the study was that the trapped hydrogen atoms occupy—as untrapped hydrogen atoms do—tetrahedral interstitial sites in the niobium host lattice.

In the case of the host metal tantalum, the situation is less clear than for niobium. Resistance measurements yielded, for nitrogen traps, a binding enthalpy $\Delta H_b = (0.06 \pm$

0.015) eV [2], which is definitely smaller than the precipitation energy of $\Delta H_p \simeq$ 0.115 eV [2, 19]. According to these enthalpy values, formation of hydrogen precipitates (β-phase [19]) lowers enthalpy more than hydrogen trapping, so that, in the low-temperature limit, all hydrogen atoms should precipitate rather than being trapped. However, the resistance measurements showed further that, at low temperatures, all the hydrogen interstitials either are trapped by the nitrogen or precipitate, depending on whether the nitrogen concentration is larger or smaller than that of the hydrogen. Such a behaviour of either complete trapping or complete precipitation cannot be understood within the concepts of ordinary thermal equilibrium. A plausible explanation involves the enthalpy barrier for nucleation of hydrogen precipitates, together with the assumption that, similarly as for niobium, the binding enthalpy $\Delta H_b = (0.06 \pm 0.015)$ eV between a nitrogen atom and the first trapped hydrogen interstitial is larger than the binding enthalpy between the hydrogen and nitrogen atoms that have already trapped a hydrogen interstitial. In such a situation, the enthalpy gain $\Delta H_p - \Delta H_b \simeq 0.055$ eV for precipitation of hydrogen interstitials that are singly trapped by a nitrogen atom may be too small to overcome the enthalpy barrier for nucleation of precipitates, whereas the large enthalpy gain for additionally trapped hydrogen atoms may be sufficiently large to overcome this barrier. Complete hydrogen precipitation in the case of hydrogen concentrations which exceed those of the nitrogen is then understood by the fact that, once precipitates are formed, the accumulation of additional hydrogen interstitials to these precipitates is no longer seriously impeded by an enthalpy barrier.

3. Sample preparation and experimental details

Our TaN$_{0.006}$H$_{0.003}$ sample was prepared from three tantalum single crystals (length $\sim$80 mm, diameter 10 mm, crystal axes in the $\langle 110 \rangle$ direction, metallic purity 99.99 at.%). To reduce the content of interstitial carbon impurities, the crystals were annealed for 24 h at $\sim$1980 °C in an oxygen atmosphere of 4×10^{-5} mbar [18, 20]. The crystals were then again annealed for 48 h at $\sim$2100 °C in a vacuum better than 4×10^{-10} mbar in order to reduce the oxygen as well as the nitrogen content. For nitrogen doping, the crystals were subsequently annealed for $\sim$150 h at $\sim$1900 °C in a nitrogen atmosphere with pressures between 8×10^{-6} and 5×10^{-5} mbar [18, 20]. The resulting concentrations of nitrogen, oxygen and carbon were determined by fusion analysis of small representative pieces that were cut from the crystals. Table 1 presents the results for the nitrogen content of the three investigated crystals (experimental accuracy is $\sim$20% of the concentration values). The carbon content of the crystals was below the detectable concentration of 80 at ppm, and the oxygen concentrations of the crystals were in all cases 15 times smaller than the nitrogen concentrations given in table 1.

After the above purification and nitrogen doping process, the three crystals were doped with hydrogen. The doping was performed under ultra-high vacuum conditions at 500 °C in a small calibrated volume, by introducing defined amounts of hydrogen gas that yielded the desired hydrogen concentrations after its (essentially complete) absorption by the metal.

Table 1. Nitrogen and hydrogen concentrations of the three crystals of the TaN$_{0.006}$H$_{0.003}$ sample.

Crystal	Nitrogen concentration (at.%)	Hydrogen concentration (at.%)
1	0.0035	0.0015
2	0.0096	0.0049
3	0.0037	0.0022

After hydrogen doping at 500 °C was completed, the crystals were rapidly cooled to room temperature (about 2 min) in order to suppress precipitation of a tantalum nitride phase (a nitrogen concentration of 0.6 at.% exceeds the solubility limit below about 380 °C [18]). The resulting hydrogen concentrations of the crystals were determined (i) from the amount of the absorbed hydrogen gas during hydrogen absorption, (ii) from the increase of crystal weight after doping and (iii) by vacuum extraction of small pieces that were cut from the crystals. Table 1 presents, for each crystal, the average of the hydrogen concentrations determined by the three experimental methods. The experimental accuracy of the hydrogen concentrations in table 1 is ∼10% of the concentration value (for a given crystal, the concentrations determined by the three methods above deviated from their average in all cases by less than 10%).

As can be seen from table 1, the hydrogen concentrations chosen for the three crystals were about half the respective nitrogen concentrations. This choice guaranteed that, for each crystal, the nitrogen concentration safely exceeded the hydrogen concentration, even under consideration of the experimental accuracy of the concentration values. Therefore, a complete trapping of the hydrogen interstitials could be expected at low temperatures, at least according to the resistance measurements [2] discussed in the previous section.

The nitrogen and hydrogen concentrations, averaged over all the three crystals of the sample, are ∼0.6 and ∼0.3 at.%, respectively. Therefore, we use the stoichiometric formula $TaN_{0.006}H_{0.003}$ for this sample that was doped with both nitrogen and hydrogen.

For a comparison with the results of the $TaN_{0.006}H_{0.003}$ sample, we studied also a $TaH_{0.086}$ reference sample that was prepared from two polycrystalline tantalum plates (dimensions $50 \times 25 \times 1$ mm^3, metallic purity 99.95 at.%) and solely doped with hydrogen. Except for annealing in an oxygen atmosphere (reduction of the carbon content) and nitrogen doping, sample preparation was similar to that of the $TaN_{0.006}H_{0.003}$ sample. The accuracy of the hydrogen concentration (∼5% of the concentration value) was better than that of the $TaN_{0.006}H_{0.003}$ sample because of the higher hydrogen content. The higher hydrogen content means also that the purity of the reference sample was of lesser importance.

The neutron spectroscopy measurements were performed with the beryllium filter option of instrument BT4 at the NIST Center for Neutron Research in Gaithersburg, MD (USA). The copper {220} reflection was used for monochromation, collimation before and after the monochromator was 40′, and the scattering angle was ∼90°. Our neutron spectra were obtained after subtraction of the background from fast neutrons (measured at two different neutron energies), and after subtraction of 3 meV (the average energy of neutrons passing through the beryllium filter) from the energy of the incident neutrons. In the interesting energy range between 100 and 180 meV, full-width-at-half-maximum (FWHM) energy resolution increased from 6 to 12 meV. Neutron spectra were taken at room temperature (295 K), 250 K, 150 K and at very low temperatures (1.4 to 4.2 K).

The measurements on the $TaN_{0.006}H_{0.003}$ sample were difficult because of (i) low scattering intensity (small hydrogen concentration and high neutron absorption by tantalum) and (ii) contamination of the neutron spectra due to strong Bragg scattering of the single crystals that was not completely eliminated by the beryllium filter. In order to reduce the influence of Bragg scattering, the single crystals of the $TaN_{0.006}H_{0.003}$ sample were continuously rotated during the measurements. It was not possible to simply rotate the unwanted Bragg reflections away from the detector since there are many contaminant Bragg-related artefacts for high incident energies and the present difficult sample (three crystals, low signal-to-noise ratio). An attempt to remove unwanted Bragg reflections this way would also lead to the problematic situation that there would most likely be different sample orientations for different energy transfer ranges because of the continuous change of the energy of the incident neutrons in the course of an experimental run.

4. Experimental results and discussion

Inelastic neutron spectra resulting from our measurements are presented in figure 1. The figure shows spectra of the $TaN_{0.006}H_{0.003}$ sample (full circles) and the $TaH_{0.086}$ sample (open triangles), taken at four temperatures between 1.4 and 295 K.
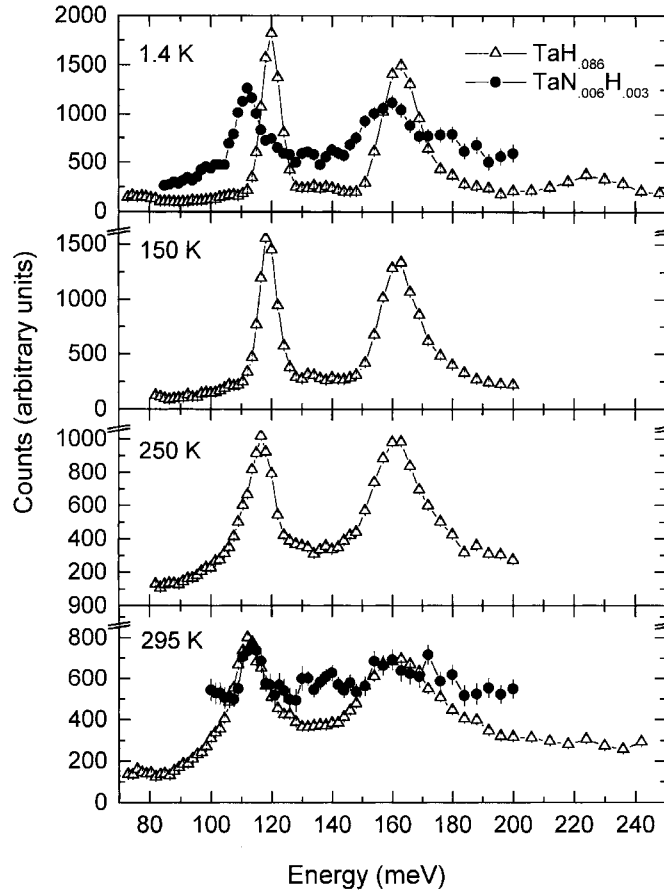

Figure 1. Neutron spectra of $TaN_{0.006}H_{0.003}$ (●) full circles and $TaH_{0.086}$ (△) open triangles measured at low temperatures (1.4 to 4.2 K), 150 K, 250 K and 295 K. The ordinate scale of the six different spectra are completely arbitrary. The solid lines are guides to the eye.

We consider first our results for the $TaH_{0.086}$ reference sample. At 295 K, the hydrogen atoms in this sample are in solid solution (pure α-phase), occupying tetrahedral interstitial sites [19]. The neutron spectrum taken at 295 K shows, above an essentially continuous background, two peaks at energies $E_1 = (113 \pm 1)$ meV and $E_{2,3} \simeq 163$ meV, being distinctly broader than the respective FWHM energy resolutions of 7 and 11.5 meV. The two peaks result from the singlet low-energy and doubly degenerate high-energy local vibrations of the hydrogen interstitials, as already observed and discussed in previous neutron studies [6, 21–23]. Within experimental accuracy, the present peak energies and widths agree with the results of the previous studies. At low temperatures (1.4 to 4.2 K), all the hydrogen interstitials of the reference sample are precipitated in a hydride phase (β-phase) [19].

The corresponding spectra show now two narrower peaks which are only slightly broader than energy resolution. Compared with the 295 K data, the energy $E_1 = (120 \pm 1)$ meV of the low-energy peak has increased, whereas the energy $E_{2,3} \simeq 163$ meV of the high-energy peak remains essentially unchanged. The results are again in quantitative agreement with previous neutron studies [6, 21, 24]. In particular the low-temperature increase of the peak energy E_1 is clearly observable and, thus, a definite sign of hydride formation. Finally, the energy E_1 and the width of the two peaks in the spectra taken at the intermediate temperatures 250 and 150 K demonstrate the continuous formation of the β-phase hydride with decreasing temperature (the solubility limit of the hydrogen is ~ 5.5 and $\sim 1.6 \times 10^{-3}$ at.% at 250 and 150 K, respectively, so that practically all the hydrogen is precipitated already at 150 K [2, 19]).

We discuss now the results for the $TaN_{0.006}H_{0.003}$ sample. The inelastic peaks of the spectrum taken at 295 K from this sample are, within experimental accuracy, identical to those of the $TaH_{0.086}$ reference sample, if we disregard the influence of worse statistics and lower signal to noise due to the 30 times smaller hydrogen concentration. Therefore, the 295 K data demonstrate that the hydrogen interstitials are in solid solution (α-phase), as expected, and that the hydrogen atoms occupy tetrahedral sites. The decisive difference between the two samples becomes evident from the lowest- temperature spectra, taken between 1.4 and 4.2 K. In contrast to the $TaH_{0.086}$ sample, the spectrum of the $TaN_{0.006}H_{0.003}$ sample shows essentially no changes from the 295 K spectrum. In particular, the energy $E_1 = (113 \pm 1)$ meV and the width of the low-energy mode do not change between 295 K and low temperatures (1.4 to 4.2 K). This demonstrates clearly that the hydrogen interstitials in this sample do not precipitate at low temperatures, but become trapped by the nitrogen atoms. Thus, the present neutron results, obtained from a $TaN_{0.006}H_{0.003}$ sample where the nitrogen concentration exceeds that of the hydrogen, confirm the conclusions drawn from the previous resistance measurements [2].

The resistance measurements described offer no insight on the type of interstitial site that is occupied by the trapped hydrogen. However, the fact that the neutron vibration peaks of the $TaN_{0.006}H_{0.003}$ sample show little change (aside from background) on cooling from 295 to low temperatures (1.4 to 4.2 K) indicates that the trapped hydrogen atoms occupy the same type of interstitial sites as hydrogen in solid solution does in the absence of traps (i.e. tetrahedral interstitial sites). This conclusion is similar to that made in the previous neutron spectroscopy study of hydrogen trapping in niobium [5], and it follows from the fact that local hydrogen vibrations are extremely sensitive to the interstitial site and local environment of the hydrogen interstitials [5, 6, 23]. The sensitivity is well demonstrated by the results for the nitrogen-free $TaH_{0.086}$ reference sample, where the low-energy hydrogen vibrations changed clearly in the hydride phase, in spite of the fact that the hydrogen atoms still occupy tetrahedral sites in a slightly distorted and expanded tantalum host lattice [19]. The sensitivity of local vibrations to structural changes becomes even more obvious if we consider, for instance, the vanadium–hydrogen system, where the hydrogen atoms occupy different interstitial sites in two different phases (tetrahedral and octahedral sites in the α- and β-phase, respectively [19]), and where the lowest vibrational bands of the hydrogen in the two phases differ by a factor of two [6, 23]. Thus, the present data do indeed provide strong evidence for the fact that the trapped hydrogen atoms also occupy tetrahedral sites.

The above conclusion is important since the large difference between the binding enthalpies (between nitrogen traps and hydrogen) in the case of the host metals niobium (0.12 eV [1]) and tantalum (0.06 eV [2]) could have been considered an argument for (wrongly) hypothesizing that trapped hydrogen atoms in niobium and tantalum occupy different types of interstitial site. The present results clearly rule out such a possibility.

Finally, the sensitivity of the vibrational energies of the hydrogen to its local environment shows that a trapped hydrogen interstitial cannot be too close to the trapping nitrogen atom since, otherwise, the close nitrogen would, in contrast to the present finding, noticeably modify the vibrational energy of the trapped hydrogen. Therefore, and similarly as in previous discussions of hydrogen trapping in niobium [5–7, 10], we can safely assume that at least the four first-nearest and the eight second-nearest tetrahedral neighbour sites of a nitrogen atom cannot be occupied by a trapped hydrogen interstitial. This conclusion seems indeed reasonable since any occupation of the tetrahedral sites above would meant that the trapped hydrogen has a distance to the trapping nitrogen atom that is at least similar if not smaller than the distance to one of its four nearest tantalum neighbours.

5. Conclusions

The energies of the local vibrations of hydrogen interstitials in tantalum were determined in the presence and absence of nitrogen traps. The measurements demonstrate that the hydrogen interstitials are trapped by the nitrogen at low temperatures, and that formation of β-phase hydride is suppressed at least as long as the nitrogen concentration exceeds that of the hydrogen. The local vibrations of the trapped hydrogen are identical to those of hydrogen interstitials that are not trapped. The latter result shows that the trapped hydrogen atoms occupy tetrahedral interstitial sites, i.e. the same type of site that is occupied by hydrogen in the absence of traps.

Acknowledgments

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