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Hydrogen distribution in Nb/Ta superlattices

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Abstract

The distribution of hydrogen in Nb/Ta superlattices has been investigated by combined neutron reflectivity and x-ray scattering. We provide evidence to support that strain modulations determined with x-ray diffraction can be interpreted as modulations in hydrogen content. We show that the hydrogen concentration is modulated and favors Nb, in agreement with previous studies. We measure the concentration directly using neutron reflectivity and demonstrate no detectable change in the distribution of hydrogen with temperature, in stark contrast to previous studies.

(Some figures may appear in colour only in the online journal)

1. Introduction

The investigation of hydrogen in metals is of great interest, mainly motivated by the prospective use of hydrogen as an energy carrier [1]. Another important aspect of introducing hydrogen into a metal structure is the possibility to alter the magnetic [2, 3], electronic and optical [4, 5] properties of materials. This has led, for instance, to the development of switchable mirrors, switchable solar collectors and optical gas sensors [6, 7].

Nanomaterials have received considerable attention, owing to new properties such as finite size, electronic proximity and change of volume/area ratio. In this context, thin metal films and superlattices offer an ideal route to explore the thermodynamics of hydrogen in metals in the nanorange. This results from the possibility to control important structural parameters such as roughness, thickness or epitaxy, allowing physical properties to be tailored to answer specific scientific questions [8]. Since the hydrogen interaction in a metal is mediated by long range elastic deformations, these systems are highly sensitive to finite size and boundary effects. For example, the phase boundaries of the hydride formation are shifted with the size of the absorbing material, as demonstrated in thin V films [9, 10].

Hydrogen absorbed into superlattices composed of Fe/V and Mo/V exhibits a hydrogen–hydrogen interaction that can be tuned by the strain state, even changing the sign of the interaction [11, 12]. These superlattices are classified as strongly modulated in the chemical potential of hydrogen owing to the large positive enthalpy of formation of Fe and Mo. As a result, the hydrogen is exclusively confined in the V layers. Alternatively, when a metal superlattice is composed of two materials where both absorb hydrogen, a weakly modulated chemical potential can be constructed. The only studied example of a weakly modulated, single-crystal superlattice that we are aware of is Nb/Ta [110], which was investigated by Miceli and co-workers [13, 14]. Nb and Ta constitute an ideal combination of elements for growing high quality superlattices: both are bcc and have close to identical lattice parameters. Nb/Ta superlattices are therefore ideal for exploring the effect of weak modulation in the hydrogen absorption potential on the interaction and the changes in phase boundaries/formation.

Miceli investigated Nb/Ta [110] superlattices of different thicknesses, thickness ratios and hydrogen concentrations with x-ray diffraction. From the relative intensities of the $\pm$ satellites of the (110) Bragg reflection the strain inside the film was determined. The strain field exhibited a Curie–Weiss

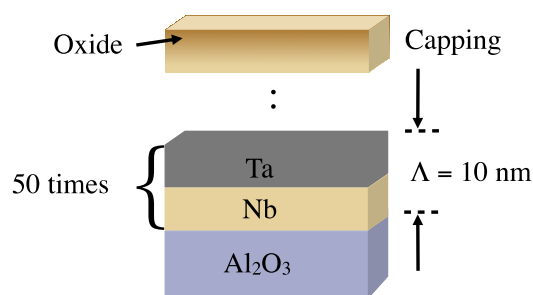


Figure 1. Schematic illustration of the Nb/Ta superlattice used in this study. The sample is capped with a final layer of Nb which was allowed to oxidize upon exposure to the ambient atmosphere.

behavior (linear in $1/T$, with T the temperature) and the stress was attributed to a redistribution of hydrogen with temperature. Nb has a larger binding energy for hydrogen and it can be shown that at low temperatures the maximum of a strain wave is in the niobium layers. This has been attributed to a lower hydrogen concentration in the tantalum. However, this was never proven unambiguously.

In the present study we present a combined x-ray and neutron reflectivity/diffraction study, shedding light on this unresolved question. In contrast to x-rays, which are scattered by electrons, neutrons interact with the nuclei and, as a consequence, the scattering cross section of neutrons does not scale with the atomic number of elements. In particular, neutrons are quite sensitive to light elements such as hydrogen, which makes neutron scattering highly suitable to simultaneously study the changes in volume and concentration [15]. The combination of neutron and x-ray scattering is therefore an excellent approach to investigate the validity of the hypothesis of redistribution of H in Nb/Ta as both the strain and the hydrogen concentration in the individual layers can be determined separately.

2. Experimental details

The samples shown schematically in figure 1 were grown using DC magnetron sputtering. The samples used for the previous studies were grown using molecular beam epitaxy (MBE) [13]. Similarly to the MBE samples, the current samples were grown in ultra-high vacuum (UHV) with a base pressure of 5.0×10^{-10} Torr on an Al_2O_3 (11 $\bar{2}$ 0) substrate. Sputtering was done under an Ar (purity: 99.9999%) pressure of 2 mTorr and at a temperature of 1020 ± 50 K using high purity (99.99%) Nb and Ta targets. The Al_2O_3 (11 $\bar{2}$ 0) substrates had been annealed for 24 h at a temperature of 1200 °C in air to maximize the terrace widths. The growth was done in one go, without intermediate determination of the crystallinity or interface quality. The growth aimed towards a layer thickness of 5 nm for each layer and was chosen in order to provide a Bragg reflection from the superlattice that is sufficiently far away from the critical angle of total reflection but still at relatively small Q , resulting in a stronger signal. The sputtering rate has been determined by reference samples prior to the actual growth of the samples. Four samples, 50 repetitions of the Nb/Ta bilayer each, were grown

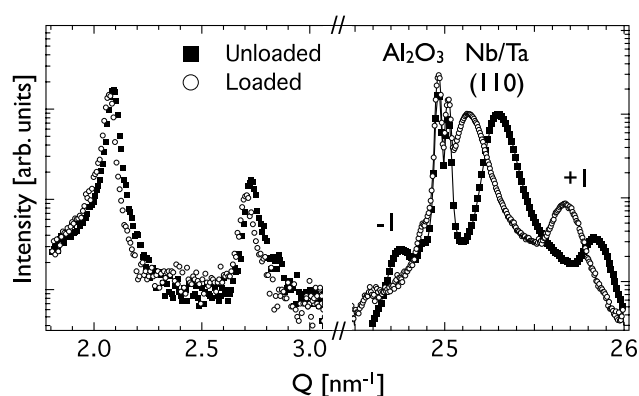


Figure 2. X-ray reflectivity (left) and diffraction (right) of a Nb/Ta superlattice in its unloaded and loaded state. The change in bilayer thickness can be seen by the shift of the reflectivity peaks and the increase in the lattice spacing by the shift of the diffraction peaks.

simultaneously under constant rotation of the sample holder and at the same conditions and can be treated as identical before loading with hydrogen. As the top layer on all samples, additional Nb was sputtered, which oxidizes upon exposure to the ambient atmosphere but protects the sample from further oxidation, since Nb is self-passivating. Additionally, the niobium oxide acts as a diffusion barrier for hydrogen and, after loading the samples once, the total number of hydrogen atoms stored in the sample can be assumed constant, provided the samples are not heated for extended periods of time. This allows the investigation of the hydrogen redistribution throughout the sample in a broad temperature range (up to at least 600 K) and at very low pressures in an UHV sample chamber. At the high temperatures and low pressures during the sputtering process the equilibrium concentration of hydrogen in the sample is expected to be at least an order of magnitude lower than during the subsequent loading conditions. To further minimize the uptake of hydrogen by the sample the chamber was pumped down to UHV prior to cooling.

It is important to note that Nb and Ta have nearly the same scattering length density for neutrons. Since the intensity of a Bragg peak in reflectivity is proportional to the difference squared of the scattering length densities, a very weak Bragg peak is expected from an unloaded Nb/Ta sample. Any measurable change in intensity upon loading with hydrogen can thus be viewed as a redistribution of hydrogen between the layers. Further, the same thickness of the Nb and Ta layers was chosen. This leads to a suppression of the even-order superlattice Bragg peaks and increases the sensitivity to the interfaces between the layers.

After the growth, the sample quality and film thickness were verified by x-ray reflectivity and diffraction on a Philips Pro PW3020, Panalytical and Bruker D8,³ respectively. Figure 2 depicts the result of the x-ray measurements

³ Commercial materials, instruments and equipment are identified in this paper in order to specify the experimental procedure as completely as possible. In no case does such identification imply a recommendation or endorsement nor does it imply that the materials, instruments or equipment identified are necessarily the best available for the purpose.

before and after loading of hydrogen. In the reflectivity region (at momentum transfers, Q , below 3 nm^{-1}) Bragg reflections from the superlattice repetition distance are clearly visible. This confirms good layering of the materials. In the diffraction region (above $Q = 20 \text{ nm}^{-1}$) superlattice satellites, originating from the crystalline coherence of the materials, are visible. From the data a bilayer thickness⁴ of $9.41 \pm 0.03 \text{ nm}$ was extracted by simulations (not shown) with GenX [16] before loading with hydrogen. The thickness of the Nb layer is $4.61 \pm 0.06 \text{ nm}$ and that of the Ta layer is $4.8 \pm 0.06 \text{ nm}$. From the width of the first visible Bragg reflection in diffraction, see figure 2 (right), the coherence of the Nb/Ta [110] crystal was determined to be 33 nm . The change in the satellite intensity will be discussed in detail in section 3. The crystal coherence is almost four times larger than the repeat distance but only 10% of the total thickness of the superlattice as compared to 100% in Miceli's study [13, 14]. The satellites (+ and -1 in the figure) visible to the left and right from the Bragg reflection represent the interference from the bilayer spacing, further confirming the coherence of the superlattice. The width of the rocking curve is narrow, 0.3° , underscoring the quality of the superlattice. This can be compared to Miceli who gave below 0.1° , implying a better crystallinity of samples grown by MBE. Since the energies for sputtering are much higher it is expected that the quality of the interfaces between the Nb and Ta layers between our samples and Miceli's may differ, too.

Three of the four samples were loaded with hydrogen at temperatures up to 650 K and by exposure to a hydrogen atmosphere of different pressures in the mbar range. The high temperatures were chosen in order to overcome the oxide barrier and speed up the kinetics. The electrical resistance was monitored during loading of the superlattice via a four-probe resistance set-up. Changes in resistivity can be attributed to changes in the hydrogen concentration in the metal film [17]. By calibrating the resistivity values with the lattice expansion obtained from x-rays and by knowing the hydrogen expansion coefficient for the material the concentration can be calculated. All samples were continuously loaded up to the desired resistivity/concentration, but not to thermal equilibrium, and then quenched. Table 1 summarizes the loading⁵ of the four samples investigated in this study and calculated from the lattice expansion $c_{\text{cl}} = \frac{1}{k}(\frac{\Delta d}{d})$, where k is the clamped expansion coefficient and $\frac{\Delta d}{d}$ is the measured lattice expansion. For the calculation, clamping was taken into account using the elastic response of the lattice [18] resulting in an expansion coefficient of $k = 0.136$ and 0.131 for Nb and Ta, respectively. This is lower than the bulk expansion coefficient of 0.16 used by Miceli [13], which would translate into a concentration of hydrogen atoms (H) per metal atom (M) of $\frac{H}{M} = c = 0.042$ for sample C, not taking into account the clamping. Sample B was not loaded with hydrogen but left as a reference. In the following discussion we will focus

Table 1. Summary of the average total hydrogen concentrations in the superlattice extracted from x-ray scattering and measured in hydrogen atoms per metal atom. The second column corresponds to the lattice expansion and the third is the volume change determined from reflectivity. The last column shows the calculated concentration after correcting for clamping.

Sample	$10^{-3} \times \frac{\Delta d}{d}$	$10^{-3} \times \frac{\Delta V}{V}$	$10^{-2} \times c_{\text{cl}} [\frac{H}{M}]$
A	5.61 ± 0.04	6.7 ± 2.9	4.19 ± 0.03
B	0.0	0.0	
C	6.69 ± 0.04	6.1 ± 1.8	4.99 ± 0.03
D	12.40 ± 0.07	16.9 ± 3.3	9.25 ± 0.05
SL 18 [14]	10		7.4

on sample C, since this has been most intensively studied with neutrons. The neutron experiments are time-consuming (one reflectivity measurement takes roughly 4 h) and it was not possible to measure all samples at different temperatures. However, the x-ray measurements have been reproduced for all four samples with identical results.

The neutron measurements were done at the reflectometer NG-1 at the **National Institute of Standards and Technology (NIST) Center for Neutron Research, Gaithersburg, MD (USA)**. A constant beam collimation of 4 and 2 mm for the first and second slit, respectively, was used together with an ILL orange cryostat and furnace for the low and high temperature experiments, respectively. Since Nb and Ta have very similar scattering length densities ($\rho_{\text{Nb}} = 3.92 \times 10^{-6} \text{ \AA}^{-2}$ and $\rho_{\text{Ta}} = 3.84 \times 10^{-6} \text{ \AA}^{-2}$) it is expected that a superlattice Bragg reflection becomes intense only if the hydrogen distribution between the layers is very uneven.

3. Results

The volume expansion was determined from the shift in position of the superlattice peaks in the x-ray reflectivity measurement and the relative change in lattice parameter extracted from the x-ray diffraction data as seen in figure 2. Rehm *et al* demonstrated that large differences between volume changes as measured with reflectivity and diffraction can be expected when hydrogen is absorbed irreversibly into Nb-based multilayers [19]. Even in the case of completely reversible loading, as is the case for Nb/Ta at these concentrations, differences are expected [20]. This implies that extracting the volume expansion from the diffraction data only may not result in the correct volume changes, since the contribution from the hydrogen-induced disorder to the lattice planes is not captured by x-ray diffraction. When comparing the uncertainties of the determined d spacings and the superlattice repetition, it becomes clear that, while the accuracy of the volume expansion extracted from the superlattice peaks might be higher, the precision is much lower than the one calculated from the diffraction peaks. Since the volume expansion determined by these techniques is the same to within the error bars determined from the superlattice peaks, we decided to determine the hydrogen concentration in the superlattices from the shift in the diffraction peaks, which yields higher precision. This is justified by the fact that

⁴ Errors have been extracted from the error given by GenX according to a 5% increase in the figure of merit function.

⁵ The uncertainty in peak position was determined based on a statistical analysis (68% confidence) of a Gaussian peak fit. The uncertainty in concentration was obtained by straightforward error propagation.

voids and other irreversible changes are not expected at these low concentrations and, in addition, asymmetries in the strain fields are not present for hydrogen occupying tetrahedral sites in Nb and Ta.

In addition to the shift of the (110) superlattice peak we also notice a relative change in the intensities of the $\pm$ satellites. More specifically the intensity distribution becomes highly asymmetric. Miceli [13, 14] showed that this asymmetry is related to a strain wave inside the superlattice, the Fourier components of which can be calculated as

$$\frac{I_{s\pm}}{I_0} = \left[\eta_s - \epsilon_s \left(1 \pm \frac{\Lambda}{sd} \right) \right]^2 \quad (1)$$

where $I_{\pm}$ denotes the intensity of the satellite with index s , I_0 the intensity of the Bragg peak, ϵ_s the strain wave amplitude, Λ the superlattice bilayer thickness, s the order of the satellite and d the lattice plane distance. η_s is the normalized contrast modulation coefficient:

$$\eta_s = \frac{f_{\text{Ta}} - f_{\text{Nb}}}{a_0 f_{\text{Ta}} + b_0 f_{\text{Nb}}} |a_s|, \quad (2)$$

where a_0 and b_0 are the fractions of the sublattices within a superlattice period ($a_0 + b_0 = 1$). f_i is the atomic form factor for element i and finally a_s are the Fourier coefficients for the composition modulation. In this study $a_0 = 0.49$. Solving for the strain in equation (1) the following expression is obtained:

$$\epsilon_s = \eta_s \frac{\sqrt{\frac{I_{\pm}}{I_0}} - 1}{\sqrt{\frac{I_{\pm}}{I_0} \left(1 - \frac{\Lambda}{sd} \right)} - \left(1 + \frac{\Lambda}{sd} \right)}. \quad (3)$$

By applying this model to the asymmetries observed in the different samples it is concluded that loading with hydrogen results in an increased strain wave in the superlattice. Miceli's interpretation of the induced strain was that the hydrogen does not distribute evenly throughout the superlattice due to the difference in binding energy in Nb and Ta. Therefore a concentration wave develops with the same periodicity as the superlattice. Since the binding energy of hydrogen is higher in Nb this concentration wave has a maximum in the Nb layers and a minimum in the Ta layers. In addition to the strain wave developing as a consequence of a difference in binding energy, the difference between the expansion coefficients (0.136 and 0.131 for Nb and Ta, respectively) adds to the amplitude of the strain wave.

In order to investigate the validity of the hypothesis of a hydrogen concentration wave in the superlattice, we have measured the neutron reflectivity for sample C taken at 20 K (figure 3). The inset at the top right in figure 3 depicts a close-up into the region where the first-order superlattice peak would be expected. In this representation all curves, taken at temperatures of 100, 297 and 473 K, have been normalized to the measurement at 20 K.

The data taken at intermediate temperatures do not differ from the ones shown in the graph. It is evident that, within the experimental error bars, all three curves are identical. No redistribution of hydrogen is therefore seen in the experiments.

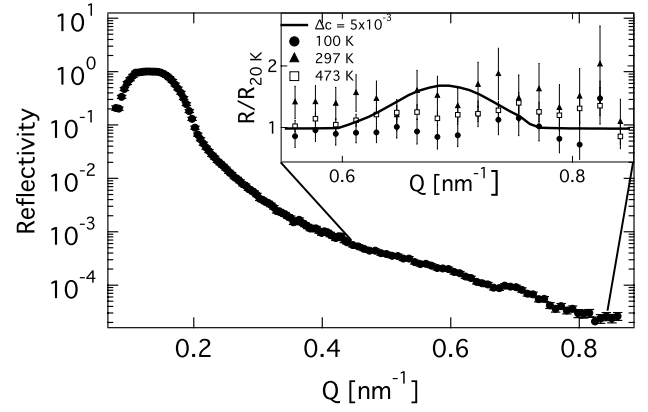


Figure 3. Neutron reflectivity of the hydrogen-loaded sample at different temperatures. The inset (top right) depicts a zoom into the region where the first-order superlattice peak would be expected. The solid line in the inset is a calculation of the change in reflectivity when changing the hydrogen concentration in the respective layers by 0.005 H/M.

The sensitivity of the neutron reflectivity measurements, with respect to the redistribution of hydrogen, was determined by simulations based on the Parratt formalism [21]. The results obtained at 20 K were used as a reference, as described above. The solid line in figure 3 shows a calculation for which it was assumed that the hydrogen concentration in Nb is increased and decreased in Ta by $5 \times 10^{-3} [\frac{\text{H}}{\text{M}}]$ relative to the concentrations that would result in the same scattering length density for the respective layers. The calculated peak is slightly above the experimental error bars in intensity. Accordingly, we estimate that any redistribution of hydrogen in the superlattice that is larger than $5 \times 10^{-3} [\frac{\text{H}}{\text{M}}]$ would have been detected in the experiment and can be excluded. Since no peak is visible in the data, the H concentration in the Nb and Ta layers could not have changed from the values that give identical scattering length density values by more than $0.01 [\frac{\text{H}}{\text{M}}]$. Assuming then that the scattering length density difference between the hydrogenated Nb and Ta layers is 0, and using the definition of the scattering length density

$$\rho = \frac{b_{\text{cM}} + c_{\text{H}} b_{\text{cH}}}{(1 + k_{\text{cH}})v}, \quad (4)$$

where b_{c} is the coherent scattering length for neutrons ($b_{\text{cH}} = -3.739$ fm, $b_{\text{cNb}} = 7.054$ fm and $b_{\text{cTa}} = 6.91$ fm), v the volume per atom and the subscripts H and M refer to hydrogen or metal, respectively, the local concentration of hydrogen can be calculated. Since the hydrogen sits in interstitial sites in the Nb and Ta lattice the scattering length of the hydrogen adds to the scattering length of the Nb or Ta as the total number of atoms in the unit cell changes. With the total concentration $\frac{c_{\text{Nb}} + c_{\text{Ta}}}{2} = c$ the hydrogen concentration can be calculated to be $c_{\text{Nb}} = (6.5 \pm 0.5) \times 10^{-2} [\frac{\text{H}}{\text{Nb}}]$ and $c_{\text{Ta}} = (3.5 \pm 0.5) \times 10^{-2} [\frac{\text{H}}{\text{Ta}}]$ in the Nb and Ta layer, respectively. This is in accordance with the larger binding energy of hydrogen in niobium and agrees well with the measured strain wave that was found for the hydrogen-loaded sample measured with x-ray diffraction. However, from the

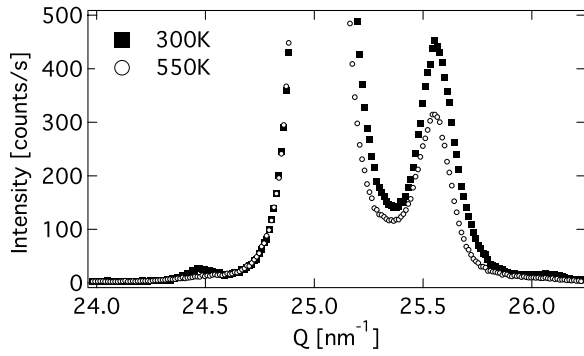


Figure 4. X-ray diffraction data of sample C taken at different temperatures.

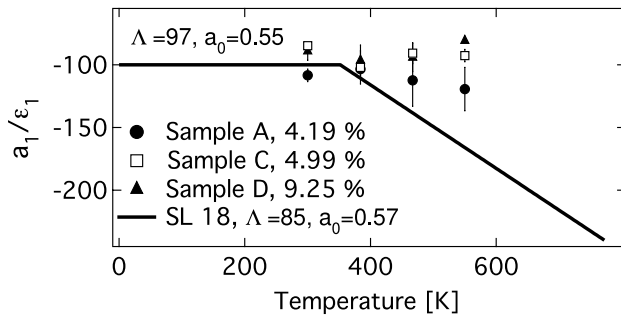


Figure 5. Inverse strain plotted versus temperature as extracted from the x-ray diffraction data and compared to the results of Miceli [13, 14], shown as a solid line.

neutron data it is concluded that the concentration in the respective layers does not change with temperature by more than 5×10^{-3} [$\frac{H}{M}$]. Note that the total amount of hydrogen absorbed in the superlattice cannot be extracted from the position of the critical angle of total reflection, since this is determined by the scattering length density of the substrate.

To quantify the amount of strain at different temperatures, the samples were measured in a UHV-compatible scattering chamber, equipped with an internal heater. Figure 4 depicts the result of the x-ray diffraction measurement for sample C for two representative temperatures, the highest and lowest temperature under investigation. It can be seen from the data that the intensity of the + satellite is decreased with increasing temperature. The reason for this might be an increased hydrogen concentration at the interfaces between the Nb and Ta layers. However, when analyzing the ratio of the + and - satellite it turns out that this is hardly affected by temperature and accordingly the strain wave in phase with the superlattice periodicity in the sample does not change significantly. This is clearly seen in figure 5 where the inverse of strain is shown as a function of temperature for the three samples loaded with hydrogen. For comparison the strain obtained by Miceli *et al* [14] is included as a solid line. As seen in the figure, the measurements reproduce the amount of strain reported by Miceli [13, 14], while the change of slope in the inverse of strain for higher temperatures as well as the Curie–Weiss behavior are not reproduced. The temperature was limited due to the fact that hydrogen could diffuse out of the sample for temperatures above 600 K. For sample C one can calculate the amplitude of the strain wave

Table 2. Distribution of the hydrogen concentration in the Nb and Ta layers separately as determined from the intensity of the superlattice peak in neutron reflectometry and the relative first-order Bragg reflection satellite intensities in x-ray diffraction.

Probe	c_{Nb} [$10^{-2} \frac{H}{Nb}$]	c_{Ta} [$10^{-2} \frac{H}{Ta}$]
X-ray diffraction	7.4 ± 0.8	2.5 ± 0.6
Neutron reflectivity	6.5 ± 0.5	3.5 ± 0.5

$\epsilon_1 = (3.4 \pm 0.4) \times 10^{-3}$ using equation (2). Comparing this to $\epsilon_0 = 6.7 \times 10^{-3}$ from table 1 means a $\frac{\Delta d}{d}$ of 3.3×10^{-3} and 10.1×10^{-3} for the Ta and Nb layer, which translates into a hydrogen concentration⁶ of $(2.5 \pm 0.6) \times 10^{-2}$ [$\frac{H}{Ta}$] and $(7.4 \pm 0.8) \times 10^{-2}$ [$\frac{H}{Nb}$], respectively. This result is consistent with the neutron reflectivity data. Note that the concentrations have been extracted from completely independent measurements with no adjustable parameters. The concentrations extracted from the neutron and x-ray measurements are summarized in table 2.

4. Conclusion

In summary, we have studied Nb/Ta superlattices using neutron and x-ray reflectivity and diffraction. We find increasing strain for loading with hydrogen, which is consistent with results presented earlier [14]. We have thus verified the hypothesis that satellite intensity asymmetries as measured with x-ray diffraction and induced by a strain wave yield consistent results with direct measurements of the hydrogen concentration using neutron reflectivity. However, changes in the strain wave with temperature were neither found using x-ray diffraction nor with neutron reflectivity, in contrast to measurements made by Miceli and co-workers. The reason for this might be related to differences between the samples. The mosaicity is 0.3° as compared to below 0.1° for the MBE samples. Additionally, the crystal coherence in our samples is 33 nm, being less than the total thickness but the samples discussed by Miceli have coherence throughout the full thickness. This may result in hydrogen atoms getting pinned at local defects. The Curie–Weiss behavior in the strain wave may also depend sensitively on slight changes in the period and the ratio between the constituents of the superlattice. A third possibility might be related to the quality of the interfaces between the niobium and tantalum layers. It can be seen (figure 4) that the intensity of both satellite peaks decreases with increasing temperature, implying a strain wave with twice the periodicity of the lattice or maxima/minima at the interfaces [14]. A slightly increased hydrogen concentration at the interfaces could be explained by a larger number of defects in this region. The results clearly demonstrate the intricate influence of crystal quality, confinement and boundary effects, which are only rudimentarily known at present and need further systematic investigations.

⁶ The intensities of the satellites were assessed by fitting a Gaussian peak to the data and weighing the data with the experimental errors ($\sqrt{\text{counts}}$). The error of the peak area was obtained by propagating the statistical errors (based on 68% confidence) in the width and the amplitude.

Acknowledgments

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