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# Resistivity changes in Cr/V(0 0 1) superlattices during hydrogen absorption

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## Abstract

The hydrogen induced resistivity changes in Cr/VH$_x$(0 0 1) superlattices where investigated in the concentration range $0 < x < 0.7$. Initially, the resistivity increases with H content, reaching a maximum at H/V $\approx$ 0.5 atomic ratio. At concentration above 0.5, the resistivity decreases with increasing H concentration. These results are in stark contrast to the H induced resistivity changes in Fe/V(0 0 1) superlattices, in which the resistivity increases monotonically up to H/V $\approx$ 1. The results unambiguously prove the importance of the interface scattering, which calls for better theoretical description of the H induces changes in the electronic structure in this type of materials.

*Keywords:* Hydrogen; Resistivity; Crystal structure

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## 1. Introduction

Changes in resistivity can be related to hydrogen (H) content in metals (M) [1–4] and is often used to determine hydrogen uptake. This was first shown by Pryde and Tsong [1] who suggested that the hydrogen acts as a point scatterer and the excess resistivity would therefore increase at low concentrations. As the hydrogen concentration is increased, the excess resistivity reaches a maximum. This maximum is reached when half the available sites for the hydrogen are occupied, e.g. at a hydrogen concentration equal to 0.5 H/M in e.g. V and Nb. When the hydrogen concentration is further increased the empty sites can be viewed to take away: act as point scatterers, explaining the decrease in the excess resistivity with decreasing (H) vacancy density.

The change in excess resistivity has been used to determine the hydrogen concentration for a wide range of thin films and superlattices [2,4,5]. Absolute calibration of the hydrogen content can for example be obtained by using the $^{1}$H ($^{15}$N, $\alpha\gamma$) $^{12}$C nuclear reaction [6], and the changes in resistivity can be uniquely related to the hydrogen content. The change in excess resistivity does not however show the same behavior for all material combinations. For example, in Mo/V(0 0 1) the excess resistivity increases until a concentration of approximately 0.5 H/M is reached [3]. Thereafter it decreases with hydrogen content, as expected for a random occupation in a classical MH system. The Fe/V(0 0 1) shows a remarkable difference in this context, as there is no maximum at concentration around 0.5 in H/V, the resistivity instead continues to increase [7].

In multilayered structures, the resistivity can be much higher than the weighted contribution from the components. This originates in the presence of interface scattering, which is expected to scale with the interface density. For example, the resistivity of Cu/Cr multilayer is shown to have a strong dependence on the individual layer thickness of the two metals [8]. In superlattices such as Mo/V [3] and Fe/V [4,7,9], the difference of the lattice parameters of the constituents can be used to create different strain states in the V layer. In the Fe/V [10] superlattice, V lattice is under an in-plane tensile strain state while in Mo/V [11] superlattice, V lattice is under a compressive in-plane strain state. Thus, the $c/a$ ratio of V is smaller than 1 in Mo/V(0 0 1) – and larger than 1 in Fe/V(0 0 1) – superlattices. This has a large influence on the hydrogen uptake of V, while the hydrogen content of the iron (Fe) and the molybdenum (Mo) is negligible.

The absence of a maximum was addressed in a theoretical study by Meded et al. [12]. The influence of the $c/a$ ratio and

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the volume change, $\Delta V/V$, in the vanadium lattice during hydrogenation were concluded to be the most important factor with respect to the changes in the resistivity [12]. This was in line with the available experimental findings, as described above.

Here, we will explore the influence from the $c/a$ ratio on the changes in the resistivity. A Cr/V superlattice was chosen for the experiments since Fe and Cr have similar lattice parameters (0.287 and 0.291 nm, respectively). This gives the possibility to form a similar in-plane strain state in the vanadium, as compared to vanadium in a Fe/V. Thus if the absence of maximum originates solely from the $c/a$ ratio, the resistivity changes in Cr/V(0 0 1) should resemble those of Fe/V(0 0 1).

## 2. Experimental

The samples used for the experiments were Cr/V(0 0 1) superlattices grown on a MgO substrate at 620 K using dc magnetron sputtering. The thickness of the layers were $[14\,\mathrm{ML\ Cr}/14\,\mathrm{ML\ V}]_{40}$ and $[7\,\mathrm{ML\ Cr}/14\,\mathrm{ML\ V}]_{54}$ where ML stands for monolayer. The layer repetitions are chosen to give a total thickness of 166 nm. To catalyze the hydrogen uptake and prevent oxidation of the sample, the surface of the samples were covered with a 5 nm layer of Pd. X-ray reflectivity (XRR) and high angle X-ray diffraction (XRD) measurement were performed, before and after hydrogen loading in a Siemens D-5000 in a Bragg–Brentano (focusing) geometry, to obtain information about the chemical modulation and the crystalline structure. The XRD scans of the Cr/V 14/14 sample is shown in Fig. 1.

The hydrogen loading system contains a four point measurement probe controlled by a Keithley 199 multimeter. The pressure is obtained by three capacitance pressure gauges in the range of 0–10, 0–100 and 0–1000 mbar. Hydrogen gas of 99.999% purity is led through a NuPure3 cleaner before entering the system. The evacuation is performed by a turbomolecular pump and a residual gas analyzer (RGA) is used to determine the composition of the residual gas. The base pressure is below $10^{-8}$ mbar where the dominating residual gas is hydrogen. Before exposing the sample to hydrogen, the sample is heated to the desired temperature. The temperature is controlled using a Eurotherm 94C temperature controller with accuracy ±1 °C. The temperature is measured directly beneath the sample, giving reliable measurement of the actual temperature. As the desired temperature is reached, the system is flushed four times with hydrogen gas prior to the start of the measurement. During the measurement, the hydrogen pressure is increased, stepwise from vacuum to 1 bar while the resistivity is measured. The waiting time is determined by the time required to reach equilibrium. The time required to reach equilibrium ranged from between 10 and 120 min depending on the temperature and pressure used. To determine the hydrogen concentration in the sample corresponding to the maximum resistivity, a Cr/V 7/14 ML sample was grown without a Pd capping. This sample was hydrogenated at 523 K under a hydrogen pressure of 22 mbar, which corresponds to a maximum in the resistivity for the Pd-caped Cr/V 7/14 sample. The sample was kept under hydrogen pressure until the resistance over the sample was stabilized. At that point the sample was rapidly cooled ensuring conservation of the hydrogen content. Thereafter, the $^{1}\mathrm{H}(^{15}\mathrm{N},\ \alpha\gamma)\,^{12}\mathrm{C}$ (NRA) method was used to determine the hydrogen content in the film [6] at the Tandem Accelerator at the University of Uppsala. The average hydrogen content in the vanadium layers was determined to be $\langle c_\mathrm{V}\rangle = 0.35 \pm 0.05$ using a $\mathrm{TaH_2}$ calibration sample [13].

In Mo/V and Fe/V superlattices, hydrogen does not occupy the vanadium layers closest to the interfaces [14]. Assuming the presence of a corresponding depletion zone at the Cr/V interfaces, the hydrogen concentration in the interior region would correspond to 0.45 ± 0.05 H/V. In the remainder of the article, we refer to the average concentration $\langle c_\mathrm{V}\rangle$ if not otherwise stated.

## 3. Results and discussion

The hydrogen induced resistivity changes in Mo/V and Fe/V superlattices are shown in Fig. 2. The excess resistivity increases initially in both samples until a hydrogen concentration of 0.5 H/M (interior region) is reached where the excess resistivity reaches a maximum in the Mo/V superlattice. A corresponding maximum is not observed in the Fe/V superlattice, as mentioned above, where the excess resistivity continues to increases slowly and it is still increasing as a hydrogen concentration is approaching 1 in H/V ratio (interior region).

The measured excess resistivity in samples Cr/V 14/14 and 7/14 is shown in Fig. 3. The change in resistance with applied hydrogen pressure was reversible, returning to within 1% of its original value. At low applied hydrogen pressures, the excess resistivity increases and at a certain pressure both the samples exhibit a maximum in the excess resistivity. This occurs at a pressure of 5.3 ± 0.1 and 7.5 ± 0.1 mbar in the Cr/V 14/14 and Cr/V 7/14 samples, respectively. Further increasing the applied hydrogen pressure decreases the excess resistivity. This behavior resembles the results for Mo/V(0 0 1), although for a given hydrogen load, a different $c/a$ ratio would be expected. To verify this, it is necessary to determine the hydrogen induced expansion in the Cr/V(0 0 1) is needed. Both XRR and XRS measurements

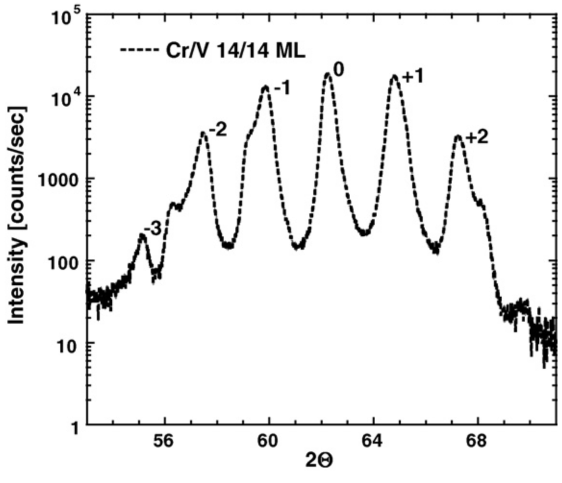

Fig. 1. The high angle XRD spectra of the Cr/V 14/14 superlattice.

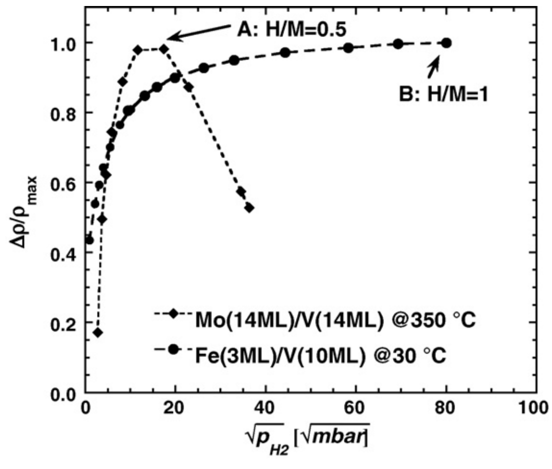

Fig. 2. Excess resistivity changes in a Fe/V 3/10 ML and a Mo/V 14/14 ML superlattice at temperatures 30 and 350 °C, respectively, Fe/V from [7] and Mo/V from [3].

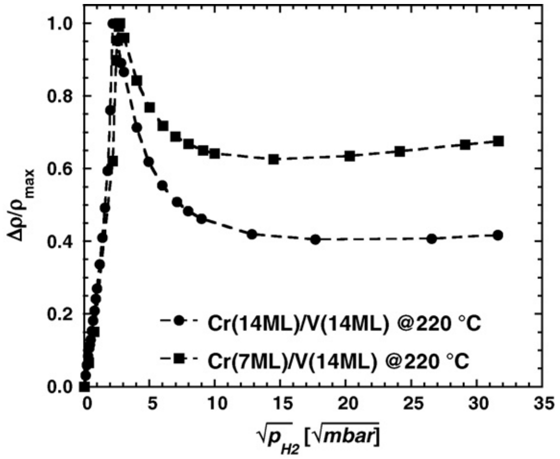

Fig. 3. Excess resistivity changes in a Cr/V 7/14 ML and a Cr/V 14/14 ML superlattices at 220 °C.

were performed on both samples before and after hydrogenation runs. No structural changes in the sample could be observed. To investigate the lattice expansion induced by the hydrogen, XRD measurements on the Cr/V 7/14 superlattice at a hydrogen concentration of $H/V = 0.35 \pm 0.05$ were performed. The measurement yields an average out-of-plane lattice parameter of $0.312 \pm 0.001$ nm for the superlattice. The out-of-plane lattice parameter of the hydrogenated vanadium layer is therefore calculated to be $0.325 \pm 0.001$ nm. Since the hydrogen absorption in the Cr layer is negligible, the Cr lattice parameter can be assumed to be unchanged. The in-plane strain can be calculated by linear elasticity theory. It depends on the lattice mismatch, which is 4% between Cr ($a = 0.291$ nm) and V ($a = 0.303$ nm), as well as the thicknesses of both layers. As stated above, the V – with its larger unit cell – is in a compressive strain state. The in-plane strain of the as-grown V in Cr/V 14/14 and 7/14 ML superlattices is in this way determined to be −2.6% and −2.0%, respectively. Similar strain states have been reported for Fe/V superlattices: there the lattice mismatch is 5.5% and the compressive strain varies from −3.0% [7,15] for Fe/V 10/12 to −2.1% [16] for Fe/V 2/12. The value for the Fe/V(0 0 1) 10/12 superlattice has been obtained by the following relation [10]:

$$a_{\parallel} = a_0 - 0.011\frac{L_{\mathrm{Fe}}}{L_{\mathrm{V}}} \tag{1}$$

where $a_{\parallel}$ is the in-plane lattice parameter, $a_0$ the bulk lattice parameter and $L_{\mathrm{V}}$, $L_{\mathrm{Fe}}$ are the number of monolayers of vanadium and iron, respectively.

The $c/a$ ratio in the Cr/V(0 0 1) 14/14 superlattice is 1.04, in the Cr/V(0 0 1) 7/14 sample 1.03. For comparison, Olsson et al. [16] determined $c/a$ in Fe/V 10/12 and Fe/V 2/12 to be 1.04. So, the V layer shows a similar tetragonal distortion both in Cr/V and Fe/V superlattices. In the Mo/V superlattices, however, the lattice mismatch between V and Mo is 4%. Here the V, having a smaller unit cell than Mo, is under tensile strain, which amounts for Mo/V 14/14 superlattice to 1.7%. This results in a $c/a$ ratio of 0.98 [17].

For the hydrogenated Cr/V 7/14 sample the $c/a$ ratio of the vanadium layers becomes 1.09. The relative volume change is $\Delta V/V = 0.067 \pm 0.002\%$. Comparing again with the Fe/V values of Andersson et al. [15] the Fe/V 10/12 the volume change is $\Delta V/V = 0.067 \pm 0.001\%$ at a hydrogen concentration approximately 0.35 H/M. Again similarities were observed between the lattice expansion in Cr/V and that in Fe/V, whereas in the Mo/V 14/14 superlattice the volume change at the same hydrogen concentration is $\Delta V/V = 0.019 \pm 0.002\%$ and a $c/a = 1.00$ [17,3].

So, the strain state of the V in Cr/V and Fe/V is strikingly similar, in contrast to the excess resistivity–pressure curve, where the two systems behave entirely differently. This strongly indicates, that the strain state of the V does not give a dominat contribution to the presence or absence of a resistivity maximum. This may instead originate from an interface scattering increasing with increasing hydrogen content, but which only seems to have a strong effect in the Fe/V superlattice. This can be seen by writing the hydrogen induced resistivity change as a sum of three terms:

$$\rho(x) = \rho_{\mathrm{sup}} + \rho_{\mathrm{interface}}(x) + \rho_{\mathrm{H}}(x) \tag{2}$$

where $x$ is the hydrogen concentration, $\rho_{\mathrm{sup}}$ the superlattice resistivity, $\rho_{\mathrm{H}}(x)$ the resistance induced by the hydrogen and the term $\rho_{\mathrm{interface}}(x)$ is the contribution from the interface scattering, which may be affected by the hydrogen absorption. The resistivity values, at room temperature without hydrogen in a Fe/V superlattice are around 56 and $23 \pm 1$ μΩ cm in Cr/V. During hydrogenation the change in excess resistivity in Fe/V is measured to be around $\Delta\rho_{\mathrm{Fe/V}} = 11$ μΩ cm at a hydrogen concentration of $x = 0.5$ (interior region) and $\Delta\rho_{\mathrm{Mo/V}} = 2$ μΩ cm in the Mo/V. This agrees well with what Meded et al. calculated, that the Fe/V superlattices would have higher excessive resistivity changes upon loading than that of Mo/V superlattice due to stronger changes in the coherent structure in the Fe/V superlattice. In the Cr/V superlattice the increase in excessive resistivity is determined to be $\Delta\rho_{\mathrm{Cr/V}} = 5$ μΩ cm for the same hydrogen concentration. From Eq. (2) the change in the excess resistivity during hydrogenation can then be expressed as:

$$\Delta\rho(x) = \Delta\rho_{\mathrm{interface}}(x) + \Delta\rho_{\mathrm{H}}(x) \tag{3}$$

By this argument, we see that the relative increase of the $\Delta\rho_{\mathrm{interface}}(x)$ term has to be larger upon hydrogenation in Fe/V superlattice as compared to Mo/V and Cr/V where the $\Delta\rho_{\mathrm{H}}(x)$ term is much stronger than the interface term. From this we can conclude that the interface scattering must have a much stronger influence in the Fe/V superlattice during hydrogenation. The increased interface scattering is also greatly affected by the presence of the layers in vanadium closest to the interface of Mo and Fe upon hydrogen loading. This region is referred to as a "dead" layer since it is not usually occupied by hydrogen and with an extension of 2 ML Mo/V [14] compared to that of 3 ML in Fe/V[4]. The difference in the extension of the depletion zone and change in hydrogen occupancy during loading can thereby influence the interface scattering strength in the different superlattices.

## 4. Summary and conclusion

The excess resistivity due to hydrogen loading in Cr/V superlattices was measured. The excess resistivity exhibits a maximum in the Cr/V superlattice comparable to the one observed in Mo/V. The vanadium layers exhibit a compressive in-plane strain state comparable to that of Fe/V, as determined by X-ray analysis. The results unambiguously show that the $c/a$ ratio and the volume change in the vanadium lattice during hydrogenation cannot be the main contribution to the monotonic increase in the resistivity in Fe/V(0 0 1) superlattices. Instead, the contribution from the interface scattering must be considered, emphasizing the need for theoretical calculations on the electronic states and scattering at interfaces.

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