Ion beam analysis of metallic vanadium superlattices
Advanced Physics Project

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23.06.2017

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Abstract

Studying interstitial hydrogen inside metallic vanadium superlattices gives reasons to hope for new insights on finite size and boundary effects. Performing for the first time systematic Rutherford Backscattering Spectrometry (RBS) on a series of different epitaxial lattices, we estimate the applicability of ion beam analysis to the monitoring of sample growth. In addition, first hydrogen profiles measured with $^{15}$N Nuclear Resonance Analysis (NRA) indicate non-homogeneous H concentrations over the superlattice, thus raising new questions on present theory. In the end we show that NRA measurements along crystal channel axes enable direct identification of the interstitial site’s geometry.
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1 Introduction

Finite size and boundary effects on physical properties as magnetic ordering, are not very well understood. Seemingly hypothetical and artificial at first glance, we encounter these nanoscale conditions even in everyday life, for instance in the form of water layers on top of ice in conditions well below phase transition from liquid to ice.

It has been discovered that interstitial hydrogen inside bulk vanadium possesses topologically similar phase diagrams as a liquid, therefore one hopes to deduce new answers from experiments on hydrogen inside metallic vanadium superlattices.

The samples consist of a $10 \times 10 \times 1 \text{ mm}^3$ MgO single crystal on which alternating vanadium and metallic layers were grown by magnetron sputtering. In the two different kind of samples, either iron or chromium is used as the metal.

A relative iron / vanadium, respectively chromium / vanadium concentration of 1/7 has been observed as being ideal for minimizing internal stress. Vanadium has a lattice parameter of 3.024 Å and Iron 2.866 Å. By using several alternating thin layers of V(001) and Fe(001) (Cr(001)) with thicknesses below the theoretical critical thickness, structured epitaxial growth of the vanadium on top of the MgO(001) has been achieved as shown by Droulias et al. The superlattice’s inplane lattice parameter of $\approx 3$ Å fits well on the 45 degrees rotated MgO(001) surface with lattice parameter ($2.98 \AA = \frac{4\sqrt{2}}{\sqrt{3}} \AA$). Several samples of likewise composition have been produced and in this project we performed the measurement on Fe$_1$V$_7$, Fe$_2$V$_{14}$, Fe$_3$V$_{21}$, Fe$_4$V$_{28}$ and Cr$_2$V$_{14}$. Note: The subscripts behind the elements refer to the number of monolayers of each individual layer. On top of the last bilayer another layer of vanadium is grown and a layer of palladium is added for reasons of sealing and catalyzing hydrogen uptake. Inside the vanadium layers, hydrogen can occupy 2 different vacancies, either an octahedral or a tetrahedral site. They are visualized in figure 1.

Figure 1: Schema of metallic vanadium sample with indicated interstitial sites occupied by hydrogen (red dots)


In bulk vanadium, the two phases disordered (α phase; low H concentration) and ordered (β phase; high H concentration) differ in favored site occupancy: in α phase, hydrogen settles more likely in tetrahedral, respectively in β phase in octahedral sites. In the metallic vanadium superlattices, however, one expects octahedral sites to be more favorable due to biaxial
compressive strain [Ref. [2]].

In the scope of this project, absolute composition measurements of the unloaded metallic vanadium samples (section 3.4) as well as the detection of hydrogen in loaded samples (section 3.7) were undertaken. The use of ion beam analysis (IBA) inhibits the advantage that it enables direct real space measurement, thus avoiding problems of reciprocal methods (e.g. phase problem) one faces in X-ray spectroscopies.

2 Theory

2.1 Rutherford backscattering spectrometry

2.1.1 Principle

The basic principle behind Rutherford backscattering spectrometry is the elastic scattering of light ions by atoms in the sample. Knowing the incident energy \( E_0 \), the mass of the incident particle mass \( M_1 \) and the energy of the ion \( E_1 \) deflected at the scattering angle \( \Theta \), one can calculate the mass of the target atom \( M_2 \) by employing conservation of energy and momentum. Introducing the kinematic factor

\[
K = \frac{(M_2^2 - M_1^2 \sin^2 \Theta)^{1/2} + M_1 \cos \Theta}{M_1 + M_2},
\]

(1)

one finds that the energy of the backscattered ion is

\[ E_1 = K \cdot E_0. \]

(2)

The mass resolution of the experiment is given by

\[ \delta M_2 = \frac{\delta E}{E_0} \left( \frac{dK}{dM_2} \right)^{-1} \]

(3)

where \( \delta E \) denotes the system energy resolution. To increase the \( \delta M_2 \) one can either increase the incident energy or increase the incident ion mass \( M_1 \). Increasing \( M_1 \), however, leads to lesser energy resolution in solid state detectors so that one has to balance both factors.

Building up on this classical mechanic consideration, one can not only obtain information on the mass of the target element (i.e. try to identify the target atom) but furthermore investigate how much of the element is present. To do so we introduce shortly the magnitudes cross sections and stopping powers which are of importance in this context.

2.1.2 Rutherford cross section and stopping power

As a measurement unit for the probability that an elastic scattering of an ion with atomic number \( Z_1 \) by a target atom with atomic number \( Z_2 \) takes place (i.e. the probability that the ion undergoes a large angle scattering at the Coulomb barrier of the target atom), one uses Rutherford cross sections \( \sigma_{Ruth} \). According to theory, these cross section per solid angle \( d\Omega \)
are of the form

\[
\frac{\sigma_{\text{Ruth}}}{d\Omega} \propto \frac{Z_1^2 Z_2^2}{E^2}.
\] (4)

For both high and low energies, however, one has to include correction to this approach.

In reality, \(E_1\), the energy after scattering, deviates from \(E\) due to interaction of the ion with the electrons of the target atoms and low angle scattering. The energy loss in a target with thickness \(d\) is then given by

\[
\int_0^d \frac{dE}{dx} dx
\] (5)

where \(\frac{dE}{dx}\) denotes the stopping power. The stopping power has to be measured for different ion / target pairs as there is no satisfying theoretical model.

As He is the most common ion for RBS experiments, there are many measured stopping powers in the energy region of 2 MeV which are included in the SIMNRA simulation package. The International Atomic Energy Agency provides a database containing all reported stopping powers [Ref [3]]. Stopping powers for compounds as the MgO in our sample substrates, however, are not well known. One way to approximate the stopping power of compounds is by using the weighted sum of the components stopping powers (Bragg’s law, [Ref. [4]]). The downside is that the thereby obtained value is not very accurate for light elements. We chose to measure the stopping power of He in MgO at two different energies 2 MeV and 3 MeV where there is no large energy dependence of \(\frac{dE}{dx}\). The obtained value was furthermore compared to the value of Feng et al. [5].

Interestingly, it turned out that it is reasonable to introduce a correction to the SIMNRA value of the vanadium stopping power in order to make plausible simulations for our samples. Starting with a fixed stopping power for MgO, we varied the thickness and stopping power of the FeV layer in order to simulate the samples.

This procedure seems reasonable because the thicknesses of the samples were estimated with X-ray spectroscopy beforehand [Ref. [1]]. Being able to simulate the RBS signal with virtual samples of thicknesses and stoichiometry close to the expectation values gives indirect proof to this correction for vanadium. Another justification for this is the observation that the stopping power of vanadium in the IAEA database lays about 10% higher than its neighbors in the periodic table, titanium and chromium. Considering the similar crystalline and electronic structure and the lack of datasets for vanadium, discrepancies have to be taken into account in any case. The outcome was a correction factor of 88% to the Bragg value.

### 2.1.3 Measurement with RBS

Combining the basic principle of RBS with cross sections and stopping powers one is able to carry out quantitative measurements.

By regarding the total yield \(Y\) that ions, reflected of a thin target layer, generate over the detector angle \(\Delta\Omega\)

\[
Y(\Omega) = N_I \frac{N_S}{\sin \alpha} \left( \frac{d\sigma(\Omega)}{d\Omega} \right) \Delta\Omega,
\] (6)

one obtains information on the absolute amount of the present element in the layer. Here \(N_I\) is the number of incident ions, \(\sigma\) the cross section of scattering, \(\alpha\) the angle of the incident
Figure 2: Stopping power of vanadium \( b) \), chromium \( c) \), titanium \( a) \)

Source: IAEA [Ref \[3\]]
beam and \( N_S \) the areal density of the target that we are interested in.

In a more general layer with thickness \( d \), one has to include the energy loss \( \Delta E_{\text{loss}} \) due to the stopping power and the subsequent change of the cross section.

\[
dY = N_I \frac{\Delta E_{\text{loss}}}{|\epsilon| \sin \alpha} \left( \frac{d\sigma(\Omega, E')}{d\Omega} \right) \Delta \Omega
\]

Note that \( |\epsilon| \) includes stopping of incoming and reflected ions.

### 2.1.4 Channeling

Channeling describes the alignment of the ion trajectory with low index crystal axes. It is a phenomena observed in ion beam analysis and can be used for specific analyses. The Coulomb potential of target atoms at the surface casts a *shadow cone* that screens lower laying atoms along the axis (i.e. traps the ion in the crystal channel) (see figure 3). Thus, in deeper layers one observes lower scattering probability due to reduced availability of scattering centers relative to the surface. While this is not desirable for measuring the depth profile of a sample, it can be used to either detect low densities of interstitial atoms, test the crystalline quality or estimate the surface composition.

### 2.2 Nuclear reaction analysis

The applications of RBS for detecting light elements (e.g. C, N, O), especially with low concentration in the target can be difficult and the technique is not adaptive to detect hydrogen. Instead, in these cases one usually makes use of nuclear reactions with large cross sections (NRA).

The basic principle is that the incident ion overcomes the Coulomb potential of the target atom and induces a nuclear reaction. Reaction products as for example \( \gamma \) rays or \( \alpha \) particles can then be detected. Similar to equation 6, the yield is proportional to the areal density of the reaction partner. In contrast to RBS, the cross section is resonant around an ion energy that is characteristic for the reaction. For narrow resonances, there will be very little yield for energies above or below the resonance energy, thereby offering very good depth resolution.

In order to probe at different depth, one has to vary the beam energy. Due to the stopping power of the target, the ion loses energy until it reaches the resonance energy at a certain...
For the detection of hydrogen, we made use of the resonant $^{15}\text{N}(p,\alpha)^{12}\text{C}$ reaction at a nitrogen ion energy of 6.385 MeV. The occurring reaction is

$$^{15}\text{N} + ^{1}\text{H} \rightarrow ^{12}\text{C} + ^{4}\text{He} + \gamma (4.43 \text{ MeV})$$

and we detect the 4.43 MeV $\gamma$ rays. In order to compensate fluctuation of the ion source, one norms the counted gamma ray with the number of incident ions.

For exact quantification of hydrogen content, one can use a reference sample with known content of hydrogen. If the sample is made of the same material, the areal density $N$ is then simply given by

$$N = N_{\text{ref}} \frac{\text{counts}}{\text{counts}_{\text{ref}}}. \quad (9)$$

Using different reference samples, one has to take into account that different volumes get probed by the beam. Due to the finite energy width $\Delta E_{\text{res}}$ of the resonance, the detected gammas result from reactions in the volume

$$V \propto \frac{\Delta E_{\text{res}}}{\epsilon}, \quad (10)$$

where $\epsilon$ denotes the stopping power of the material. Then we obtain the concentration in our sample by

$$c = \frac{\text{counts}}{\text{counts}_{\text{ref}}} \cdot c_{\text{ref}} \cdot \frac{\epsilon}{\epsilon_{\text{ref}}}. \quad (11)$$

It is advisable to use the reference concentration in units of hydrogen per volume instead of atomic concentration and the stopping powers in energy loss over distance. Doing so one is less likely to miscalculate the stopping powers which are highly dependent on the atomic concentrations if given in units energy loss per target atoms.

### 2.3 SIMNRA

SIMNRA is an IBA simulation package offered by the Max Planck Institute of Plasma Physics. In the program one replicates the experiment virtually with similar geometry and defines beam and target. The simulation involves a large amount of parameters so that one needs to perform the fit more or less manually.
3 Measurement and analysis

3.1 Experimental setup

Location of the IBA experiments was the 5 MV pelletron tandem- accelerator from NEC at the Ångström lab at Uppsala University.

For the composition and thickness measurements, a RBS chamber with geometry as depicted in fig 4 was used. The scattering angle \( \Theta \) was fixed at 170\(^\circ\) and different incident angles were chosen for the measurements. In all except the channeling measurement, the goniometer was set to cover randomly a \((2^\circ \times 2^\circ)\) angular map to minimize channeling effects. The scattered ions were detected using a Si based solid state detector. The beam energy was set to 2 MeV for \(^4\text{He}\), respectively 12 MeV for \(^{12}\text{C}\) ions.

![Figure 4: Geometry of RBS chamber](image)

Note that the incident and exit angles were defined differently for the goniometer than in equation 6. The difference is 90\(^\circ\), i.e. the \( \sin \) has to be replaced by \( \cos \).

The loading of the samples was performed using a light transmission measurement based setup in which a diode with wavelength 589 nm was employed as the light source. The change of the transmission intensity was monitored by a CCD-camera. Fluctuation of the light source were monitored by a semiconductor detector. Control of the gauges was given by a LabVIEW program.

The goniometer in the NRA setup was capable of translation in 1 dimension and rotation of the azimuth. The \( \gamma \) rays were detected with a solid state detector placed outside the chamber.

3.2 Measurement accuracies

The main factors that are limiting the accuracy are the system energy resolution, residual channeling, statistical fluctuation, uncertainties of stopping powers, calibration of our goniometer and beam energy spread.

The latter is not crucial for our measurements; the beam energy spread of \( \leq 5 \text{ keV} \) is small in comparison to the detector resolution of 20 keV for \(^4\text{He}\), 50 keV for \(^{12}\text{C}\) ions. Furthermore, the detector resolution does not have an influence on the total yield of the metallic vanadium peak and we were not focused on depth profiling the samples. Although it decreases the quality of the fit, it thereby does not affect the total thickness of the layer.
Faulty calibration of the goniometer is relevant for our experiment and may explain discrepancies of the measured thickness at large incident angles (see below). At 70° even a deviation of 1° leads to a change in equation 6 of ≈ 5%.

Statistical fluctuation and residual channeling both contribute ≈ 3% at our count rate.

The stopping power of MgO was assumed to be known within 5%. As the correction to the stopping power of vanadium is not yet measured directly, we assume an uncertainty of 5%.

We estimate the total thickness of the metallic vanadium layer by adjusting the thickness of the virtual target to replicate the signal peak with a certain width $\Delta E$. Hence at small angles, the uncertainty is mainly due to deviation of stopping power of the layer. At large incident angles, the influence of the goniometer is also of importance. The individual contributions add up to an uncertainty of 5% for small incident angles, respectively 7% for large incident angles.

The layer composition is determined by the relative metal and vanadium yield. Thus here statistical fluctuations and residual channeling are of importance. Both add up to an uncertainty of 4%.

For the NRA measurement statistical errors and deviation of stopping powers have to be taken into account. The statistical error is estimated to be 3%. Assuming 3% uncertainty for the stopping powers, the total uncertainty of the hydrogen concentration is 5%.

### 3.3 Stopping power of MgO

The correction to the stopping power of MgO was determined for $^4$He ions at energies 2 MeV and 3 MeV. In intervals of 30 s, the beam focus was altered between a MgO sample and a reference Cu sample of which the stopping power is well known. This procedure minimizes the fluctuation of the incident ion current. The individual measurements were added up and the number of incident ions was determined from the Cu signal. With the known number of incident ions, the correction factor for MgO was fitted, the results are shown in table 1.

<table>
<thead>
<tr>
<th>Beam energy</th>
<th>2 MeV</th>
<th>3 MeV</th>
</tr>
</thead>
<tbody>
<tr>
<td>correction factor to MgO stop. power</td>
<td>0.86</td>
<td>0.90</td>
</tr>
</tbody>
</table>

For the simulation in this project, however, we employed the MgO stopping power correction 0.92 that was obtained by Feng et al. [5].

### 3.4 Thickness and composition measurements

Figure 5 shows the measured signal and simulation for a 2 MeV $^4$He ion RBS of the Fe$_3$V$_{21}$ sample. The mass resolution is sufficient to estimate both total thickness and individual Fe and V contribution. In addition, a measurement with 12 MeV $^{12}$C ions was carried out to achieve better mass resolution. At this incident energy, the signal shows two separate peaks for Fe and V, as can
Figure 5: RBS signal of Fe3V21
be seen in figure 6 and better separation of Cr and V (figure 7).

Attempts of RBS with 20 MeV $^{12}$C ions for the CrV sample led to a nuclear reaction, most likely between C and O in the substrate. Detected reaction products superimposed the RBS signal, making the analysis impossible.

![Figure 6: RBS signal of Fe3V21](image)

Figure 6: RBS signal of Fe3V21

![Figure 7: RBS signal of Cr2V14](image)

Figure 7: RBS signal of Cr2V14

The depth resolution of RBS is lower than the individual layer thicknesses so that the targets were simulated by compound layers with a fixed stoichiometry. The samples Fe$_1$V$_7$, Fe$_4$V$_{28}$, Fe$_3$V$_{21}$ and Cr$_2$V$_{14}$ are well simulated by one compound layer with homogeneous metal and vanadium concentration. The thicknesses and stoichiometries that were estimated from the SIMNRA simulation are listed in tables 2 - 5.
Table 2: Thickness and composition of Fe$_3$V$_7$ estimated by RBS

<table>
<thead>
<tr>
<th>Incident angle</th>
<th>Thickness [1E15 atoms/cm$^2$]</th>
<th>Stoichiometry of FeV Layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 MeV He</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5°</td>
<td>46</td>
<td>0.136 0.864</td>
</tr>
<tr>
<td>15°</td>
<td>42.2</td>
<td>0.136 0.864</td>
</tr>
<tr>
<td>25°</td>
<td>48</td>
<td>0.136 0.864</td>
</tr>
<tr>
<td>12 MeV C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5°</td>
<td>44</td>
<td>0.136 0.864</td>
</tr>
<tr>
<td>2 MeV He</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60°</td>
<td>39</td>
<td>0.136 0.864</td>
</tr>
</tbody>
</table>

Table 3: Thickness and composition of Fe$_4$V$_{28}$ estimated by RBS

<table>
<thead>
<tr>
<th>Incident angle</th>
<th>Thickness [1E15 atoms/cm$^2$]</th>
<th>Stoichiometry of FeV Layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 MeV He</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5°</td>
<td>42</td>
<td>0.14 0.86</td>
</tr>
<tr>
<td>15°</td>
<td>41.5</td>
<td>0.14 0.86</td>
</tr>
<tr>
<td>25°</td>
<td>41</td>
<td>0.14 0.86</td>
</tr>
<tr>
<td>12 MeV C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5°</td>
<td>41.25</td>
<td>0.14 0.86</td>
</tr>
<tr>
<td>2 MeV He</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60°</td>
<td>30</td>
<td>0.14 0.86</td>
</tr>
</tbody>
</table>

Table 4: Thickness and composition of Cr$_2$V$_{14}$ estimated by RBS

<table>
<thead>
<tr>
<th>Incident angle</th>
<th>Thickness [1E15 atoms/cm$^2$]</th>
<th>Stoichiometry of CrV Layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 MeV He</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5°</td>
<td>45</td>
<td>0.2 0.8</td>
</tr>
<tr>
<td>15°</td>
<td>44</td>
<td>0.2 0.8</td>
</tr>
<tr>
<td>25°</td>
<td>46.5</td>
<td>0.2 0.8</td>
</tr>
<tr>
<td>12 MeV C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5°</td>
<td>46.5</td>
<td>0.2 0.8</td>
</tr>
</tbody>
</table>

Table 5: Thickness and composition of Fe$_3$V$_{21}$ estimated by RBS

<table>
<thead>
<tr>
<th>Incident angle</th>
<th>Thickness [1E15 atoms/cm$^2$]</th>
<th>Stoichiometry of FeV Layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 MeV He</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5°</td>
<td>43.5</td>
<td>0.12 0.88</td>
</tr>
<tr>
<td>12 MeV C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5°</td>
<td>44.5</td>
<td>0.115 0.885</td>
</tr>
<tr>
<td>2 MeV He</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60°</td>
<td>38.8</td>
<td>0.12 0.88</td>
</tr>
</tbody>
</table>
All except the 60° incident angle measurement showed that the iron concentration grows towards the substrate in the Fe$_2$V$_{14}$ sample. The gradient of Fe concentration is shown in figure 8. The total thickness of the FeV layers is given in the legend.

Figure 8: Gradient of iron concentration in Fe$_2$V$_{14}$
3.5 Channeling

By measuring the signal along a 2D angular map of the incident beam angle, we searched for a crystal axis of the Fe$_1$V$_7$ lattice. Due to the smaller number of scattering centers along the channel, a local minimum of the yield indicates that the beam is orientated along a crystal axis.

Figure 9 shows the signal of the measurement inside the channel that was hit. In comparison to the non-aligned spectrum (the 5° measurement of the previous evaluation in section 3.4), one sees a clear decrease of both the metallic vanadium and the substrate signal. Note that the 5° measurement was normed to the same number of incident particles using the Pd-peak as a reference. The significance of the decrease of both MgO and the FeV signal by a factor $\approx 10$ indicate good epitaxial growth of our sample.

![Figure 9: RBS signal of Fe$_1$V$_7$ by aligned/non-aligned ion beam](image)

In addition, the number of incident particle in the simulation was adjusted to fit to the substrate signals and the slope of the suppressed FeV peak. One observes two peaks in the experimental data (figure 10) where the count rate lays above the simulated signal. These result from the topmost layers of the crystalline structure. Although one has to take into account the small number of channels and low count rates of the iron signal, the peak of the iron atoms indicates that the surface layer of the crystal consists not only of vanadium but also of iron atoms.
Figure 10: RBS signal of FeV layer along a crystal channel
3.6 Sample loading

In order to prevent leakage of hydrogen during the transport to the accelerator and the NRA measurement, the samples were sealed with $\approx 10$ nm AlO$_2$. The processed samples were Fe$_1$V$_7$, Fe$_2$V$_{14}$, Fe$_4$V$_{28}$ and Cr$_2$V$_{14}$. Before loading, the samples were baked several hours at 422 K in vacuum. Afterwards a reference light transmission intensity at $T = 318$ K was measured. Then they were heated to 512 K and exposed to different hydrogen pressures ranging from 3 to 900 mbar. The aim was to establish high hydrogen concentration ($\beta$ phase) in the samples Fe$_2$V$_{14}$, Cr$_2$V$_{14}$ and low hydrogen concentration ($\alpha$ phase) in Fe$_1$V$_7$, Fe$_4$V$_{28}$. Note that the pressure sensor in the loading chamber had a range of 15 Torr, two high pressure sensors were located in the pipes system outside. The control program saved the values of a high pressure sensor (range 1 bar) in a different chamber along the plumbing and the measurements deviate from the second high pressure sensor (range 20 bar) that was used to adjust the hydrogen pressure. Therefore deviations from the pressure in figure 12 have to be taken into account.

The concentration change was estimated by monitoring the light transmission intensity. At constant temperature $T$ we assume Lambert-Beer law, then the concentration $c$ is given by

$$c = A \cdot \ln \left( \frac{I_0}{I_1} \right) \bigg|_{T=\text{const}}$$

(12)

After reaching saturation of hydrogen uptake (constant light transmission rate), the samples were cooled down and a reference transmission rate was measured at temperature equilibrium. In order to ensure low hydrogen concentration, the Fe$_1$V$_7$ sample was cooled down to 318 K before reaching saturation at high temperatures. The expectation was that below a certain temperature, the hydrogen uptake would diminish. Yet figure 11 indicates that the concentration increased until the sample was removed from the hydrogen atmosphere.

Figure 11: Loading process of Fe$_1$V$_7$

The Cr$_2$V$_{14}$ sample was kept in vacuum for several hours after loading to observe possible leakage of hydrogen. This and the loading process are depicted in figure 12. One observes fluctuation/leakage of the H concentration under vacuum conditions.
3.7 NRA

NRA measurements on the loaded samples Fe₁V₇, Fe₂V₁₄ and Cr₂V₁₄ are shown in the figures 13–15. The Fe₄V₂₈ was not completely loaded on the day of the measurement. In addition we measured the hydrogen profiles of two bulk vanadium samples (≈ 100 nm) (see figures 16–17). The figures show 2 plots. The upper plot shows the number of detected gamma counts divided by the number of incident ions vs. the beam energy. The lower plot shows the corresponding hydrogen concentration throughout the vanadium. Account on how the computation was undertaken is given in the following. The depth scale is given assuming the nitrogen stopping in vanadium at 6.5 MeV. To monitor possible hydrogen leakage due to the ion radiation, we undertook 2 scans of samples Fe₁V₇ and Cr₂V₁₄.

From previous measurements it is known that a Si sample with 17.5 % leads to a norm. counts \( \frac{\text{inc. ions}}{\text{counts}} \) value of 0.07. Taking this as a reference, we can calculate the absolute hydrogen concentration by using equation 11:

\[
c = \frac{\text{norm. counts}}{0.07} \cdot c_{\text{ref}} \cdot \frac{\epsilon_V}{\epsilon_{\text{Si}}}.
\]  

(13)

Here \( \epsilon_V \) and \( \epsilon_{\text{Si}} \) refer to the stopping of nitrogen in vanadium and silicon at the resonance energy 6.4 MeV. The IAEA database does not contain data for nitrogen stopping in vanadium. Therefore we used the program SRIM (version 2013) to calculate our stopping powers. The obtained value is \( \epsilon_V \approx 303 \ \text{eV/Å} \). For nitrogen stopping in silicon we used \( \epsilon_{\text{Si}} \approx 146 \ \text{eV/Å} \) including a 5 % correction due to the hydrogen inside the silicon sample.

The relative height of the count rate from regions inside the metallic lattice (≈ 6.45 - 6.63 MeV) to the signal that results from water at the surface (around the resonance region) in figure 13 shows, that we succeeded in establishing a low hydrogen concentration. Towards the substrate, the concentration increases from ≈ 3 % to ≈ 5 %. The Fe₂V₁₄ and Cr₂V₁₄ samples reveal high hydrogen concentrations with decreasing values towards the substrate. The observed gradients contradict our expectation of a homogeneous hydrogen concentration as can
be seen in the bulk vanadium samples. In addition it attracts attention that the gradients in the samples with high hydrogen concentration are in opposite direction than the one observed in the Fe$_1$V$_7$ measurement.

![Graph showing hydrogen profile in Fe$_1$V$_7$](image13)

Figure 13: Hydrogen profile in Fe$_1$V$_7$

![Graph showing hydrogen profile in Fe$_2$V$_{14}$](image14)

Figure 14: Hydrogen profile in Fe$_2$V$_{14}$

Figure 18 shows a 1 dimensional angular map of the count rate that we obtained for the Fe$_2$V$_{14}$ sample at a incident ion energy of 6.55 MeV. Several measurements indicate a planar channel around 0° azimuth. Inside the channel the count rate decreases significantly indicating lower hydrogen concentration. From the two possible interstitial sites that hydrogen populates in vanadium, the octahedral sites are located in a fashion that would lead to a decreased signal in channeling geometries. Thus we deduce from the plot that octahedral sites were more
Figure 15: Hydrogen profile in Cr$_2$V$_{14}$

Figure 16: Hydrogen profile in 100 nm bulk vanadium sample with high H concentration
Figure 17: Hydrogen profile in 100 nm bulk vanadium sample with low hydrogen concentration favorable in the sample. Similar predictions are made by Xin et al. [[?]].

Figure 18: Channeling for Fe$_2$V$_{14}$ at 6.55 MeV
3.8 Discussion

Assuming an atomic density of the epitaxial Fe and V based on the X-ray measurements of Droulias et al. [1], we can convert the layer thickness $d$ into nm. Iron and vanadium belong to the body centered cubic crystal family. Hence the atomic density is

$$\rho = \frac{2 \text{ atoms}}{V}$$

where $V$ is the volume of the unit cell. The measured lattice parameters are $a \approx 2.98 \text{ Å}$ and $c \approx 3.01 \text{ Å}$, then the atomic density is $\rho \approx 7.5 \cdot 10^{22} \text{ atoms cm}^{-3}$.

$$d = \frac{N_D}{\rho}$$

In table 6 we show the averaged layer thicknesses and compare them to values that were obtained by XRD. Similar lattice parameters were assumed for iron and chromium samples. We excluded the measurements at large incident angles.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total thickness [nm]</th>
<th>Composition (metal:vanadium)</th>
<th>Reference thickness [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_1$V$_7$</td>
<td>53.9 ± 2.7</td>
<td>1:6.35</td>
<td></td>
</tr>
<tr>
<td>Fe$<em>2$V$</em>{14}$</td>
<td>54.8 ± 2.8</td>
<td>1:4.96</td>
<td>54.6</td>
</tr>
<tr>
<td>Cr$<em>2$V$</em>{14}$</td>
<td>59.7 ± 2.9</td>
<td>1:4</td>
<td></td>
</tr>
<tr>
<td>Fe$<em>3$V$</em>{21}$</td>
<td>57.3 ± 2.5</td>
<td>1:7.33</td>
<td>54.7</td>
</tr>
<tr>
<td>Fe$<em>4$V$</em>{28}$</td>
<td>53.2 ± 2.7</td>
<td>1:6.14</td>
<td>54.4</td>
</tr>
</tbody>
</table>

While the thicknesses are in good agreement with the XRD values, Cr$_2$V$_{14}$ and Fe$_2$V$_{14}$ show an increased iron concentration.

Monitoring of the loading process showed indications that hydrogen was leaking under vacuum conditions. It is very advisable for further experiments to quantify the leakage. Doing so, NRA measurements can then be used to estimate the proportionality constant in Lambert Beer law and thus enable more accurate control of the sample loading.

For the interpretation of the gradients that were observed in the NRA measurements, effects of iron concentration gradients have to be taken into account. While only the Fe$_2$V$_{14}$ showed a gradient in Fe concentration in RBS, this can in general not be ruled out for the other samples. This is mainly due to the limited depth resolution and further experiments should focus on optimizing beam energy and geometry to obtain better resolution.

In general, errors of our observations were mainly a result of unknown stopping powers. Here, performing separate measurements of helium stopping in vanadium as well as nitrogen in vanadium at relevant energies may have significant influence on minimizing errors.
4 Summary and outlook

4.1 Summary

The first part of the experiment was dedicated to thickness and composition measurements of our metallic vanadium superlattices, using Rutherford Backscattering Spectrometry. The total thicknesses that were obtained are in good agreement with values that were measured by XRD. Yet some discrepancies from ideal growth have been identified. These include increased / non-homogeneous metal concentrations in the metallic vanadium layer in 2 of the samples. In addition the channeling experiment that was performed for the $\text{Fe}_1\text{V}_7$ indicated presence of iron atoms in the surface layer.

In the second part, Nuclear Resonance Analysis was used to investigate the depth profile of hydrogen concentration in loaded samples. While a homogeneous concentration profile was observed for bulk vanadium, the measurements of the loaded superlattices indicate a gradient of concentration in all 3 samples, thus contradicting our present theory of hydrogen uptake. Running NRA measurements in channeling geometry, a significant lower signal was measured along planar channels. This proofs our expectation that octahedral sites are more favorable in this super lattice.

4.2 Outlook

With regard to the analysis, we conclude that RBS is highly applicable to further experiments on likewise superlattices. Especially the absolute stoichiometry measurements with RBS are of importance to monitor further sample growth.

NRA offers a fast and straight forward way of hydrogen profiling and the results that were obtained in our experiment led to finding of challenging observation to our theory. Here lays a high potential for further, more systematic measurements.

Using NRA and Channeling, we came up with a direct way of probing which interstitial sites are populated by hydrogen. This information is an important element of our theory. Following experiments with this technique offer easy testing of theoretical thoughts.

References


