Phase Transitions and Phase Formation of Hydrogen in Quasi-2D Lattices

BY

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Dissertation at Uppsala University to be publicly examined in Room 80101, Ångström lab, Monday, September 29th, 2003 at 13:15 for the Degree of Doctor of Philosophy. The examination will be conducted in English

Abstract


The role of the dimensionality and strain state of metallic lattices on the phase behavior of dissolved hydrogen was explored. Metallic superlattices with well defined hydrogen absorption potential on the nm scale, were utilized as test systems. The solubility isotherms of hydrogen in Fe/V(001), Mo/V(001), and Nb/W(110) superlattices were measured by a resistometric method, and the hydrogen-induced changes of the structures were measured by in-situ X-ray diffraction. In the V based superlattices, the long-ranged ordered bulk V hydride phase ($\beta$ - V$_2$H) is absent, which is attributed to the finite-size of V lattice. The intrinsic strain-state of the hydrogen dissolving layers was found to have a strong effect on the interaction between metal and hydrogen as well as on the hydrogen-hydrogen (H-H) interaction. For low hydrogen content in the V layers, the compressive strain resulted in a strong enhancement of the H-H interaction, while a tensile strain appeared to diminish the H-H interaction. This is due to different site occupancy of hydrogen for different strain states, which depending on the relation between the symmetries of hydrogen induced global and local strain fields, gives rise to different elastic H-H interaction. Moderately strained V layers exhibited a strong attractive H-H interaction over a broad concentration range. In the concentration ranges where attractive H-H interaction was established, the hydrogen atoms appeared to be strongly correlated on a microscopic length scale. In the Nb based superlattices, the critical temperature for the $\alpha - \alpha'$ transition was found to be suppressed as a result of the clamping of the film plane by the film-substrate coupling. An exception from this could be noticed when the intrinsic compressive strain were reduced.

Keywords: hydrogen, finite-size effects, long-range interactions, superlattices, phase transitions, elastic interaction

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ISBN 91-554-5732-0

ISSN 1104-232X

urn:nbn:se:uu:diva-3571 (http://urn.kb.se/resolve?urn=urn:nbn:se:uu:diva-3571)
List of Papers


Comments on my participation

The hydrogen loading apparatus was to large extent reconstructed by me. With help from the workshop at the Physics Department (In particular, Pierre Fredriks- son.), I designed and constructed the *in-situ* X-ray diffraction chamber. Computer software for data acquisition-, and analysis, was also developed by me. As is reflected in the position of the authors in the included papers, I have been main responsible for all measurements, analysis, and manuscript preparation in all papers, except paper [VII], where I participated as a co-author. I also prepared the samples used in paper [III] and [VI].
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Introduction

The topic of hydrogen (H) in metals has attracted attention from the scientific community due to very different reasons. The questions addressed over the time have concerned both fundamental physics as well as pure technological matters. Despite its smallness, hydrogen has the potential to both destroy and to save the world. The invention of the H-bomb demonstrated that the power of the sun also can be unleashed on the earth. Hopefully, in the future, the power of hydrogen can be utilized in a more controlled fashion, and for a more friendlier purpose, in fusion power reactors. The small size compared to the other elements, also gives the hydrogen atom a number of unique properties. One well-known property is that hydrogen, which is dissolved on interstitial sites in metals, moves very freely in the metal lattice, the mobility is comparable to the mobility of water molecules in liquid water. The nature of hydrogen embrittlement of metals and compounds has been a challenging subject for both metallurgists and scientists. The energy crisis in the beginning of 1970’s triggered a new wave of scientific work in the field. The cause was that metals and metallic compounds were considered to be promising candidate materials for hydrogen storage in a future hydrogen society [1]. Great efforts have been spent to tailor a suitable compound for hydrogen storage and to understand the mechanisms of hydride formation. Studies of interstitial hydrogen in metals have also helped to understand similar systems, e.g. interstitial carbon or nitrogen in metals or interstitial impurities in semiconductors.

Apart from its technological importance, the hydrogen and metal system has a number of properties that are interesting from a fundamental point of view. The hydrogen sub-lattice in a metal is a real example of an interacting lattice-gas and parts of the hydrogen phase diagram exhibit great similarities with fluids and Ising ferromagnets. Whereas the interactions in fluids or ferromagnets give rise to a different behavior close to a second order phase transition than predicted by the classical description (i.e. mean field theory), the similar phase transition of hydrogen, in i.e. Nb and Pd, appears to be exactly represented by the mean field approach [2, 3]. Because the mean field picture is exact only for infinite ranged interactions, the success of the mean field approach has been proposed as an unambiguous evidence that these types of phase transitions of hydrogen in metals is driven by elastic interaction via the hydrogen-induced and infinite-ranged displacement field of the metal.
atoms, which was originally proposed by Alefeld [4]. The work of Wagner and Horner on elastic H-H-interaction and phase transitions of hydrogen in coherent metal-hydrogen-systems provided a theoretical foundation in the field. The infinite-ranged nature of the elastic H-H interaction and particularly the role of the elastic boundary condition were treated explicitly in two papers published in 1974 [5, 6]. As predicted by the theory, shape-dependent macroscopical hydrogen density modes, were experimentally observed 1979 in single crystal Nb samples [7].

After the pioneer work on the fundamental properties of hydrogen in metals, the scientific activities in the field decreased until 5-10 years ago when the metal-hydrogen-system once again was in focus. The main reason for the renewed interest was the discovery that, by alloying thin metallic films and multilayers with hydrogen, it is possible to switch their physical properties. Two spectacular examples are the transformation of a thin film from a shiny metal to a transparent isolator [8], and the change of sign of the magnetic coupling between magnetic layers in multi-layered thin films [9, 10]. The possibilities that, in such a controlled way, fine-tune the properties of the metal opens up new routs to investigate phenomena as metal-isolator transitions and quasi-2D magnetism.

The subject of hydrogen in superlattices was first brought up by Miceli et al. [11]. They discussed the influence of the (artificial) chemical modulation on the critical behavior of the hydrogen lattice-gas. The first studies on hydrogen in quasi-2D structures are due to Hjörvarsson et al. [12]. This thesis is an attempt to illustrate the usefulness of studying hydrogen in thin films and superlattices when it comes to address dimensionality aspects of phase transitions and phase formation of H in metals. The purpose for studying these kinds of phenomena is two-fold. Firstly, there is of fundamental interest to understand the link between the dimensionality and phase transitions. Secondly, the role of the spatial extension of the metal on the properties of its hydride state is basic knowledge that is not understood, and can provide a key when constructing new efficient materials for hydrogen storage.
The absorption of hydrogen in metals

The reaction between hydrogen in gas phase ($H_2$) and hydrogen in solid solution in a metal ($H$), can usually be separated in three different steps, as shown in Figure 2.1. Each step shown in Figure 2.1, is associated with a potential barrier that the hydrogen atoms have to pass. The over-barrier jumps are usually thermally activated, but particularly for the diffusion process, quantum tunneling has to be considered to explain the high mobility at low temperatures of light interstitial, as muons or hydrogen, in some metal [see Ref. [13] and references therein]. The potential energy as seen by an hydrogen atom as it dissolving in the metal is shown in Figure 2.2. For metals that reacts exothermically with hydrogen ($\Delta H_H < 0$) the rate limiting step for the overall absorption process is usually the activation energy needed for dissociation ($\Delta E_{\text{diss}}$) of the hydrogen molecule. One important exception from this is Pd where hydrogen atoms can be chemisorbed without any hindering energy barrier (non-activated adsorption). A number of metals with positive $\Delta H_H$ also shows non-activated dissociation, i.e. Ni and Pt.

Figure 2.1: The different steps included in the process of hydrogen absorption in metals. Gaseous hydrogen adsorbs at the metal surface dissociates and adsorbs at the chemisorption sites, and finally diffuses into the bulk of the metal.
2.1 Effective medium theory

Energy-band calculations of the enthalpy of formation for metal-hydrides have been performed for several kinds of systems. The calculations are however very time-consuming and often fail to reproduce the general trend of $\Delta H_H$ among metallic elements and inter-metallic compounds. In addition, the essential physics controlling the absorption potential can be difficult to grasp. The task can be greatly simplified by adopting an effective medium approach (EMT), which replaces the role of the metal host with a homogeneous electron gas, and the deviations from the real metal are treated in form of correction terms [14]. The density of the electron gas is set to be equal to the average electron density at the interstitial site populated by hydrogen. The embedding energy, i.e. the difference between the energy of a free hydrogen atom (in vacuum) and the energy of a hydrogen atom in a transition metal at position $R$, can be expressed as [15]:

$$\Delta E(R) = \Delta E_{\text{hom}}(\tilde{n}(R)) + \Delta E^c(R) + \Delta E_{\text{hyb}}(R) + \xi(R), \quad (2.1)$$

where $\tilde{n}(R)$ is the electron density, $\Delta E^c$ is the strictly repulsive interaction of the hydrogen with the metal core electrons, and $\Delta E_{\text{hyb}}$ is the hybridization energy of the hydrogen state with electron states, which not are accounted
Figure 2.3: A qualitative picture of the potential energy of a hydrogen atom introduced in a metal. (a) The path of the H-atom. (b) To the left: Electron density as a function of position in the metal. To the right: $\Delta E_{\text{eff}}^{\text{hom}}$ as a function of electron density. (c) $\Delta E_{\text{eff}}^{\text{hom}} (\bar{\mathbf{n}})$ as a function of position. The interstitial sites have the lowest electron density, however the value is above the optimal, and a strong dependence of the enthalpy of solution on the interstitial electron density is expected.

for by the effective medium. The effective medium approach was originally applied on the transition metals, and also works best for those type of metals. The hybridization term is mainly determined by the number of filled d electron states and tends to be most attractive for the metals with half-filled d band. The interstitial electron density has showed to be a key parameter determining the enthalpy of solution of hydrogen in transition metals. Fig. 2.3 gives a qualitative description of the absorption potential of a hydrogen atom in a transition metal lattice. Note the parabolic behavior of $\Delta E_{\text{eff}}^{\text{hom}}$, thus there exists an optimal electron density with maximum energy gain. The electron density at interstitial sites in metals is however always above this value and a strong dependence of the H-solution energy on the electron density is expected. The effective medium term in Equation. 2.1 has also been expressed in a parametric form, see [16]:

$$\Delta E_{\text{eff}}^{\text{hom}} (\bar{\mathbf{n}}) = 398 (\bar{\mathbf{n}} - 0.0127)^2 + 31 \bar{\mathbf{n}} - 2.81 \ (eV) (eV)$$

(2.2)
In this form, Eq. 2.2 can be very useful, e.g. the change in embedding energy due to a small change in electron density can be obtained as:

$$\delta \Delta E = (796 \bar{n} + 20.9) \delta \bar{n}.$$  

(2.3)

The trend in the heat of solution for hydrogen absorption in transition metals can qualitatively be described by the above expression 2.1. The original version of the EMT, as stated in 2.1, is neglecting the lattice relaxation due to the displacements of the metal atoms in the neighborhood of a hydrogen atom. For the transition metals, where the interstitial electron density is higher then the optimum, the nearest metal atoms will be displaced away from the hydrogen. The balance between the energy gain due to the lowering of the interstitial electron density and the energy loss coming from the elastic deformation of the lattice has been evaluated by Nordlander [17]. The elastic energy tend be more important for bcc metals and is of the order of 0.1 eV.

2.2 Thermodynamics of hydrogen in metals

Hydrogen in metals is sometimes treated as a separate entity where the metal lattice only take a passive role as a host for the hydrogen. This picture is inadequate and fails to explain the behavior of the hydrogen-metal system and the two main reasons for this are: First, the presence of hydrogen induces distortions of the metal lattice, and second the hydrogen electron tends to react with the metal. The latter property is the key mechanism that actually stabilizes the hydride. However, in order to simplify the picture, the dissolved hydrogen and the metal is hereafter treated separately and the effect from hydrogen on the metal lattice is treated in form of effective H-H-, and H-M interactions.

The thermodynamic state of an open system is usually defined using three variables. Due to practical reasons the most natural set of variables are the pressure \( (p) \), temperature \( (T) \) and the amount \( (N_H) \). The thermodynamic potential associated with these variables is the Gibbs free energy \( (G) \). The samples used in this thesis were loaded, under controlled conditions, by exposing the sample to an hydrogen atmosphere. The reaction of the hydrogen gas with the metal can then be written as:

$$\frac{1}{2}H_2 \rightarrow H_o(\text{in the metal})$$  

(2.4)

The driving force for the reaction 2.4 is the difference in \( G \) between the reactants and the products. As, \( \Delta G = \Delta H - T \Delta S \), and because \( \Delta S \) does not vary much between different metals, the reactivity is determined by the heat of formation \( (\Delta H) \). The most direct way to determine \( \Delta H \) is through calorimetry, but this type of measurements are inconvenient when working with samples.
containing such small amount of hydrogen as the thin films described in this thesis. An alternative way to determine the thermodynamics is by measuring the solubility isotherms, from which a number of relevant properties, including $\Delta H$ and $\Delta S$, can be derived.

At equilibrium, $dG = 0$, which for the reaction described by Equation 2.4
gives:

$$\frac{1}{2} \mu_H = \mu_\alpha,$$

(2.5)

where the $\mu_H$ and $\mu_\alpha$ is the chemical potentials of the hydrogen gas and dissolved hydrogen, respectively. The variation of the chemical potential of (ideal) hydrogen gas with pressure is equal to [18]:

$$\mu_H = \mu_H^0 + kT \ln p,$$

(2.6)

where $\mu_H^0$ is a reference state (usually one atmosphere).

2.2.1 Single phase solubility

By combining Equations 2.5 and 2.6 the following is obtained.

$$\Delta \mu_H = k_B T \ln \sqrt{p} = \Delta \mu_H - T \Delta S_H,$$

(2.7)

where $\Delta \mu_H = \mu_\alpha - \frac{1}{2} \mu_H - \frac{1}{2} \mu_H^0$, $\Delta S_H = \bar{S}_\alpha - \frac{1}{2} \bar{S}_H$, and $\mu_\alpha = \mu_H - \frac{1}{2} \mu_H^0$. The bar notation indicates that it is the respective partial quantities. The applicability of Equation 2.7, can be demonstrated by considering the typical desired properties of a metal hydride for hydrogen storage, $p = 1$ atm at $T \approx 100$°C. $\Delta S_H$ does not vary much between different metals, a typically value is between 0.85-1.3 mK/H-atom [19], which means that one should look for metals with $-0.3 \lesssim \Delta \mu_H \lesssim -0.5$ eV/H-atom.

Sievert’s law

The partial entropy of the interstitial hydrogen can be divided in one configurational (c) and one non-configurational (nc) term:

$$\bar{S}_\alpha = \bar{S}_\alpha^{nc} + \bar{S}_\alpha^c$$

(2.8)

The partial configurational entropy for random distribution of interstitial hydrogen can be written as:

$$\bar{S}_\alpha^{nc} = -k_B \ln \frac{x}{\beta - x}$$

(2.9)

where $x$ is the hydrogen to metal atomic ratio and $\beta$ is the number of interstitial sites per metal atom. At very high temperature and low concentrations, the solubility is solely determined by the configurational entropy according
to Equation 2.9: By combining Equations 2.7, 2.8, and 2.9 the following is obtained:

$$\Delta \mu_H = k_B T \ln \sqrt{p} = \Delta \bar{H}_H^0 - T \Delta \bar{S}_H^0 + k_B T \ln \left[ \frac{x}{\beta - x} \right],$$  \hspace{1cm} (2.10)

where $\Delta \bar{H}_H^0 = \bar{H}_H^0 - \frac{1}{2} \bar{H}_H^0$, and $\Delta \bar{S}_H^0 = \bar{S}_H^0 - \frac{1}{2} \bar{S}_H^0$, are concentration independent and are called the relative partial enthalpy and entropy at infinite dilution, respectively. As $\beta - x \approx \beta$ for small $x$, Equation 2.10 can be rearranged to get Sievert’s law:

$$\sqrt{p} = K_S(T) x \hspace{1cm} (2.11)$$

The parameter $K_S(T)$ is the Sievert’s constant and is equal to:

$$K_S(T) = \exp \left( \frac{\Delta \bar{H}_H^0}{k_B T} - \frac{\Delta \bar{S}_H^0 + k_B \ln \beta}{k_B} \right), \hspace{1cm} (2.12)$$

The non-configurational contribution to the entropy can be further divided in three terms:

$$\bar{S}_{nc} = \bar{S}_a + \bar{S}_o + \bar{S}_e,$$

where the subscripts are referring to the entropy due to the changes in the acoustic vibration modes of the metal (a), the entropy of the optical modes of hydrogen vibrating within the interstitial site (o), and the entropy of the due to the changes in the electronic structure of the metal (e). The different contributions to the non-configurational entropy has extensively been investigated for different kinds of metal hydrogen systems. A comprehensive summary can be found in Ref. [20].

**Non-ideal solubility**

The deviations from the ideal solubility as described by Equation 2.10, is sometimes treated in terms of excess thermodynamic quantities. The excess chemical potential is defined as [21]:

$$\mu_{\alpha}^{xs} = \Delta \mu_H - \Delta \mu_H^0 - k_B T \ln \frac{x}{\beta - x},$$

where $\Delta \mu_H^0 = \Delta \bar{H}_H^0 - T \Delta \bar{S}_H^0$. For an ideal solution $\mu_{\alpha}^{xs} = 0$. The excess enthalpy and entropy are defined as:

$$H_{\alpha}^{xs} = \Delta \bar{H}_H - \Delta \bar{H}_H^0 \hspace{1cm} (2.13)$$

$$S_{\alpha}^{xs} = \Delta \bar{S}_H - \Delta \bar{S}_H^0 + k_B \ln \frac{x}{\beta - x} \hspace{1cm} (2.14)$$

The reason for deviation from ideal solubility is mainly due to interaction between the dissolved hydrogen. One has to distinguish between two different types of H-H interaction. Firstly, the long-ranged elastic H-H interaction,
which is treated in Sec. 3.2. Secondly, H-atoms appear to interact directly on very small distances (< 2Å). The direct interaction is usually treated as a hard-sphere type of interaction [see Refs. [22, 23] for more details]. The origin of the direct interaction between hydrogen is not fully understood, but is most frequently referred to be of electronic nature. However, the local strain field surrounding the hydrogen atom, which often is ignored, definitely plays a role in this context.

2.2.2 Two-phase solubility

If the dissolved hydrogen forms two phases (α and α’) in the metal, one have to consider the equilibrium between the two hydride phases and the hydrogen gas.

\[
\frac{1}{2}\mu_{H_2} = \mu_{\alpha} \tag{2.15}
\]

\[
\frac{1}{2}\mu_{H_2} = \mu_{\alpha'} \tag{2.16}
\]

\[
\mu_{\alpha} = \mu_{\alpha'} \tag{2.17}
\]

Within the α-α’ co-existence region, the degrees of freedom of the system are reduced from two (surface) to one (line), but for thin films the typical solubility experiment involves a virtually ”infinite” reservoir of hydrogen gas. The reaction corresponding to Equation 2.17 will then proceed to completion, and only one hydride phase will exists at equilibrium. However, by increasing the pressure in very small steps in the vicinity of the phase boundary, the plateau part of the isotherms inside the co-existence region can be mapped. Another way is to work with samples where the surface is poisoned, by e.g. an oxide, and thereby hindering the hydrogen from leaving the sample. In this case it is possible to perform equilibrium measurements inside the two-phase region by lowering the temperature below the phase boundary.
Phase transitions of hydrogen in metals

One way to classify different kinds of phase transitions of hydrogen in metals is to refer to the order parameter associated with the transition. Using this we can distinguish three different categories. (1) Condensation: The precipitation of hydrogen rich regions, where the condensed phase does not possess any long-ranged order. This type of phase transition is equivalent to a gas-liquid transition for a one-component system, and as order parameter one usually use the difference in density between the hydrogen rich and hydrogen poor regions. (2) Alignment of the axis of the local strain field: This type of phase transition is possible if hydrogen is occupying interstitial sites where the associated local strain field has lower symmetry than the metal. The order parameter can be taken as the ratio of the mean values of the local strain field projected onto two orthogonal axis relative the same ratio as $T \to \infty$. Transitions of this kind can be compared to a isotropic-nematic transition in liquid crystals. (3) Crystalline ordering: Hydrogen prefers sites that form a long-ranged ordered structure. As an order parameter, one usually uses an appropriate Fourier component of the hydrogen distribution. A particular phase transitions of hydrogen in a metal is generally a "mixture" of the above types.

3.1 Phase separation and critical behavior

The classic treatment of the stability of phases are due to Gibbs. The stability criterion is that the chemical potential of a component has to increase with increasing density:

$$\left( \frac{\partial^2 G}{\partial \rho^2} \right)_{\rho,T} \geq 0$$

(3.1)

The boundary to the region of unstable states (spinodal) is then:

$$\left( \frac{\partial^2 G}{\partial \rho^2} \right)_{\rho,T} = 0,$$

(3.2)

When crossing the spinodal, the system is unstable for fluctuations of the density. Gibbs originally distinguished between two kinds of fluctuations [see Ref. [24] and references therein]: those, which are large in extent but small in amplitude, and those, which are small in extent and large in amplitude. Two
theories of phase separation are based on the different kinds of fluctuations, the former has developed to the concept of spinodal decomposition, and the latter to the theory of nucleation and growth. In many cases, the energy of the interface between the two phases can neglected. Fluctuations of the density can in this case occur on all length scales, and the size is an irrelevant parameter. For metal hydrogen systems, on the other hand, the interface energy can play an important role. For a perfect metal without any lattice imperfections, an inhomogeneous distribution of hydrogen costs energy in form of coherence stresses. As the energy of a fluctuation scales with the volume and the interface with the area, long-ranged fluctuations can be expected to become unstable at higher temperatures than short-ranged fluctuations.

Hydrogen in metals is sometimes referred to as a real example of a lattice-gas [25]. The universality class of the criticality of lattice-gases is the same as for gases and Ising ferromagnets, which means that the critical exponents [26] for the transitions is equal. The exponent, \( \gamma \), describes the way that the response functions diverges when approaching the critical temperature:

\[
\kappa_T \propto |T - T_c|^{-\gamma}
\]

\( \kappa_T \) is the isothermal compressibility of the lattice-gas, and \( \chi \) is the magnetic susceptibility. The mean field approximation gives \( \gamma = 1 \) for both the lattice-gas and for the Ising ferromagnet. While real gases and Ising ferromagnets have proved to deviate from the mean field critical behavior [27, 28], it is evident from experiments that the critical indices describing the \( \alpha-\alpha' \)-transition of H in Pd [3, 29] and Nb [2] are well described by the mean field approximation. Deviations from the mean field close to the transition is expected as fluctuations has been neglected. The temperature range, where the mean field approximation fails, depends on the range of the interaction and on the dimensionality of the system. Fisher [30] has estimated this temperature range:

\[
t_{\text{nonclassic}} \approx A \left( \frac{a}{b} \right)^d
\]

where \( t \equiv \Delta T / T_c \) is the temperature relative the critical temperature for the transition, \( a \) is the "size" of the interacting particles, \( d \) is the dimensionality, \( A \) is a constant of order unity, and \( b \) is the maximum range that the particles can interact over. Two things can be noticed from Equation 3.4. (1) \( \gamma = 1 \) has experimentally been verified to \( t \sim 10^{-3} \) [3], which using \( a \sim 2\AA \) (typical smallest H-H distance in a metal) gives \( b \sim 20\AA \). Thus, the range of the interaction has to be at least of the order of \( \sim 200\AA \) to show a mean field behavior so close to \( T_c \). (2) The non-classical range depends on the dimensionality, which implies that deviations from a mean field behavior is more pronounced for low-dimensional systems.
3.2 Elastic interactions

The origin of the interaction of the dissolved hydrogen in a metal puzzled experimentalists for a long time. Alefeld was first to propose that the H-H interaction could be a result of elastic interaction mediated by the metal lattice [4]. A short description of the elastic interaction will follow below. First, some important concepts and properties of point defects in metals will be presented. The material is mainly based on the compilation by Leibfried [31].

3.2.1 Point defects in metals - The force dipole tensor

An absorbed hydrogen atom will induce a distortion of the metal lattice near the absorption site. The displacement field due to the distortion is usually derived by replacing the hydrogen atom with the imaginary force pattern, \( f_k(r) \), that is required to hold the neighboring metal atoms in the strained configuration if the hydrogen atom was removed. Using continuum elastic theory, the induced displacement field in a infinite metal, \( u(r) \), is given by:

\[
  u(r) = \int_V G(r - r') f(r') \, dr'
\]  

(3.5)

where \( G(r - r') \) is the static Green’s function. Analytical evaluation of the integral 3.5 is often impossible. However, the asymptotic displacement field far away from the hydrogen atom, i.e.: \(|r - r'| \gg \) the extension of \( f(r') \), is easier to treat. Placing the origin in the middle of the force distribution and expanding the Green’s function gives:

\[
  G_{ik}(r - r') = G_{ik}(r) - x_i' \partial_j G_{ik}(r) + \frac{1}{2} x_i' x_j' \partial_j \partial_j G_{ik}(r) + \ldots ,
\]

(3.6)

which corresponds to an expansion in powers of \( 1/r \), as \( G_{ik}(r) \approx 1/r \). The first term on the right hand side of Eq. 3.6 will vanish for force patterns with total force equal to zero. Inserting Eq. 3.6 in Eq. 3.5 gives:

\[
  u_i(\mathbf{r}) = -P_{sk} \partial_j G_{ik}(\mathbf{r}) + \text{higher order terms},
\]

(3.7)

where

\[
  P_{sk} = \int d\mathbf{r}' \mathbf{x}_s f_k(\mathbf{r}').
\]

The quantity, \( P_{sk} \), is called the dipole tensor of the force distribution, \( f_k(\mathbf{r}') \). An important property of the dipole tensor is that its value does not depend on the location of the force pattern. Furthermore, it can be shown that for force patterns with zero torque, the corresponding dipole tensor is symmetric, i.e. \( P_{sk} = P_{ks} \). Higher order terms are not important far away from the force distribution. The asymptotic displacement field produced by any force pattern,
of zero total force and torque, can thus solely be described by a symmetric
dipole tensor and it propagates as $1/r^3$. For a more comprehensive analysis and
discussion on the properties of point defects and the associated strain field in
metals, see Ref. [31].

### 3.2.2 Lattice expansion due to hydrogen

The displacement field in an (imaginary) infinite metal, as described in Sec. 3.2.1,
does not change the volume of any volume element not containing the defect.
The situation is however different when considering a finite metal, where sur-
face effects are important. The different elastic boundary condition of a finite
sample allows parts of the coherency strains, which are present in an infinite
metal, to "relax" on the (free) surface. An additional displacement field is
thereby produced, and the total displacement field of a finite metal can usually
be separated in two terms:

$$u = u^\infty + u^s,$$

where $u^\infty$ is the displacement field produced in an infinite metal, and $u^s$ is the
displacement field from the surface. Thus, the total volume change of the metal
due to hydrogen can also be separated in two terms:

$$\Delta V = \int_S (u^\infty + u^s) \, dS = \Delta V^\infty + \Delta V^s = (1 + \gamma_E) \Delta V^\infty$$

The coefficient $\gamma_E$ is called the Eshelby factor [32] and represents the con-
tribution from the surface to the total expansion. Eq. 3.8 can be solved by
considering the conditions of mechanical equilibrium,

$$\partial_i \sigma_{ik} + f_i = 0,$$

and a stress free surface:

$$\sigma_{ik} \, dS_k = 0,$$

The result for a homogeneous distribution of hydrogen [31] is:

$$\Delta V = S_{ii,nn} P_{nn},$$

where $S$ is the elastic compliance of the metal, and $P$ is the dipole tensor of
the defect. Eq. 3.9 shows that the total expansion depends only on the dipole
tensor and the elastic data of the metal, and not on the position of the defect.
The volume change due to a homogenous distribution of $N_H$ hydrogen in a
cubic metal is:

$$\Delta V = N_H \text{tr}[P]/3K,$$

where $N_H$ is the number of hydrogen atoms, and $K$ is the compressibility.
3.2.3 Elastic interaction - Dipole approximation

The elastic interaction between two interstitial hydrogen atoms is, within the dipole approximation, determined by the dipole tensor associated with the occupied sites. The dipole tensor for tetrahedral and octahedral sites in bcc-

![Diagram of tetrahedral and octahedral sites in bcc metals.](image)

**Figure 3.1:** The tetrahedral and octahedral interstitial sites in bcc metals. The metal atoms are removed for clarity reasons, and the shaded plates are inserted to emphasize the different orientations of the interstitial sites.

metals (see Figure 3.1) [4],

\[ P_{ij} = \begin{pmatrix} B & 0 & 0 \\ 0 & B & 0 \\ 0 & 0 & A \end{pmatrix}, \]

where \( A < B \) for tetrahedral sites and \( A > B \) for octahedral sites. The dipole tensor for the different orientations are obtained by permutation of the diagonal elements. The dipole tensor can be divided in two terms:

\[ P_{ij} = P^{(1)}_{ij} + P^{(2)}_{ij} = \frac{A + 2B}{3} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} + \frac{A - B}{3} \begin{pmatrix} 2 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}. \]

\( P^{(1)}_{ij} \) has the same symmetry as the host lattice (cubic) and \( P^{(2)}_{ij} \) represents the deviations from cubic symmetry. The former produces a homogeneous expan-
sion of the host-lattice and the latter introduces shear stresses. They will contribute to the elastic interaction in different ways. As an example: The homogeneous expansion part is directly responsible for the $\alpha - \alpha'$-transition in Nb, while the shear part is expected to play a role in phase transitions which is accompanied by a change of symmetry of the host metal, e.g. the $\alpha$-$\beta$-transition in V. However the role of the shear part is probably limited as short-ranged forces is dominating in these type of transitions.

In a metal with homogenous distribution of dilation centers ($P_{ij} = P_{\delta_{ij}}$), the average strain can with Eq. 3.10 be written as:

$$\frac{\Delta V}{V} = \frac{cPK}{\bar{V}_M},$$

where $c = \frac{N_H}{N_M}$, $K$ is the compressibility of the metal, and $\bar{V}_M$ is the atomic volume of the metal. Considering that the volume expansion does not depend on the positions of the hydrogen atoms, justifies a mean field approach, i.e. a hydrogen atom interacts with the mean displacement field produced by the others. An elastic dipole (hydrogen atom + strain field) couples with the local strain field, $\epsilon_{ij}^{\text{loc}}$, and the interaction energy of the dipole is equal to:

$$U = -P_{ij} \epsilon_{ij}^{\text{loc}},$$

The local strain field and the average strain are related:

$$\epsilon_{ii}^{\text{loc}} = \frac{\Delta V}{V} - \frac{\Delta V^{\infty}}{V},$$  \hspace{1cm} (3.11)

where $\Delta V^{\infty}$ is the average strain which would be produced in an imaginary infinite metal with same elastic constants (see Sec. 3.2.2). Eq. 3.11 can be rewritten using Eq. 3.8:

$$\epsilon_{ii}^{\text{loc}} = \frac{\Delta V}{V} \left( 1 - \frac{1}{\gamma_E} \right)$$  \hspace{1cm} (3.12)

The total interaction energy per hydrogen atom is then given by:

$$u = -\frac{P^2K}{\bar{V}_M} \left( 1 - \frac{1}{\gamma_E} \right),$$

From Eq. 3.2.3 it is clear that the Eshelby factor determines the sign of the interaction.

$$\gamma_E > 1 \implies \text{attractive interaction}$$  \hspace{1cm} (3.13)

$$\gamma_E < 1 \implies \text{repulsive interaction}$$  \hspace{1cm} (3.14)
Conditions 3.13 and 3.14 can give a qualitative understanding of how the H-H-interaction will be affected when changing the elastic boundary conditions. One can imagine a piece of metal containing hydrogen to be surrounded by a different metal, which does not contain hydrogen. The expansion of the inner metal, and therefore the elastic interaction, will depend on the ratio of the elastic modulus of the two metals.

**1D expansion**

For a perfectly clamped film the hydrogen induced expansion occurs in the out-of-plane direction only (e.g. the \( z \)-direction). In this case it is more instructive to single out the part of the dipole tensor that has the same symmetry as the induced displacement field. For a \( T_x \)-site in a bcc structure we have the following:

\[
P_{ij}^{T_x} = B \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} + \frac{A+B}{2} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} + \frac{A-B}{2} \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix}.
\]

The first term in 3.2.3 will contribute to the 1D-expansion and gives rise to attractive interaction energy. The second term cannot propagate to the surface and will give rise to repulsive interaction energy, and the third term will introduce shear strains, which are assumed to play a minor role, see above. For a \( T_z \)-site in a bcc structure we have the following:

\[
P_{ij}^{T_z} = A \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} + B \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix}.
\]

At low concentrations and high temperature, where the isotherms are obeying Sievert’s law, the hydrogen will be equally distributed on the tetrahedral sites. At higher concentrations and lower temperatures, when the H-H interaction plays a role, the difference in interaction energy between different sites will tend to redistribute from (for expansion in the \( z \)-direction) \( T_x \),\( T_y \),\( T_z \) to \( T_x \),\( T_y \) sites.

**3.2.4 Macroscopical spinodal decomposition**

Wagner and Horner have theoretically studied phase transitions of hydrogen in metals based on the assumption that the interaction is dominated by elastic interaction \[5, 6\]. The specially pointed out the peculiar sensitivity of the phase diagram on the boundary conditions. For short-ranged interactions, the boundary conditions are of minor importance, while for elastic interaction, which
is of infinite range, the boundary conditions play a key role determining the behavior of the spinodal decomposition [see Sec. 3.1]. For a perfect metal without lattice defects, fluctuations of hydrogen can only occur with wavelengths, which are compatible with the elastic boundary conditions. Long wavelength fluctuations are unstable at higher temperature than short wavelength fluctuations. When the temperature of a metal containing hydrogen is lowered just below the critical temperature, the theory therefore predicts excitation of macroscopical density fluctuations. This has also been experimentally been demonstrated in single crystal Nb [7].
4.1 X-ray diffraction from superlattices

X-rays have a typical wavelength of 1 Å, which makes it a suitable probe for interatomic distances. X-rays are scattered from electrons by two fundamental processes. Elastic scattering (Thomson scattering) that only involves momentum transfer between the x-ray photon and the electron, and Compton scattering that also transfer energy. Only elastic scattering will be considered here. The scattering amplitude from an atom (atomic form factor) is given by the

\[ Q = k - k' \]

where \( Q = 4\pi \sin \theta / \lambda \) is the scattering vector defined in 4.1, and \( r_0 \) is the electron Thomson scattering length. Thus, for an assembly of atoms at lattice points given by: \( \mathbf{R}_n = k\mathbf{a} + l\mathbf{b} + m\mathbf{c} \), the total scattering amplitude, in units of \( r_0 \), can be written as:

\[ F (Q) = \sum_{\mathbf{R}_n} f_0 (Q) e^{-iQ\mathbf{R}_n}, \]  

(4.2)
where $f_n^0$ are the atomic form factor of the atom at site $n$. When the scattering vector satisfies the relation,

$$Q \cdot R_n = 2\pi \times \text{integer}, \quad (4.3)$$

a strong peak in the diffractogram will appear (Bragg reflection). The set of scattering vectors fulfilling Equation 4.3 defines the reciprocal lattice of $R_n$ with basis vectors $a^*, b^*, c^*$:

$$G = ua^* + vb^* + wc^*. \quad (4.4)$$

The Bragg condition can be written as:

$$Q = G \quad (4.5)$$

### 4.1.1 One dimensional composition modulation

Considering a layered structure constituted from two types of atoms, A and B, as illustrated in Figure 4.2, the atomic form factor is modulated by a square wave with period $\Lambda$. Writing the modulation as a Fourier series gives (dropping $\Lambda$)

$$f_A + f_B \quad (4.6)$$

$$z_{n+1} - z_n = \alpha \Lambda \quad (4.7)$$

$\alpha$ is the ratio of the total $\Lambda$ that consists of atoms of type A.

*Figure 4.2: A one-dimensional composition modulated superlattice. $f_A$ and $f_B$ is the atomic form factors for the different atoms. The plane distances $z_i - z_{i+1}$, and the chemical modulation wavelength, $\Lambda$ are constant. $\alpha$ is the ratio of the total $\Lambda$ that consists of atoms of type A.*
the $Q$ dependence of the form factors):

$$f_n = \alpha f_A + (1 - \alpha) f_B + \sum_{s \neq 0} a_s e^{i k_s z_n},$$

where $(f_A - f_B) a_s$ are the Fourier coefficients of the square wave, and $k_s = 2\pi s/\Lambda$. The above atomic form factor gives the following scattering amplitude when inserted in Equation 4.2:

$$F = \left[ \alpha f_A + (1 - \alpha) f_B \right] \sum_n e^{-iQz_n} + \left( f_A - f_B \right) \sum_{s \neq 0} a_s \left[ \sum_n e^{-i(Q-k_s)z_n} \right]$$

(4.6)

The first term in the bracket in Equation 4.6, which is singular for $Q = G$, is the Bragg reflection (fundamental peak). The second term diverges whenever:

$$Q = G + k_s,$$

(4.7)

which gives rise to satellite reflection surrounding the fundamental peak. The ratio of the intensities of the satellites to the fundamental peak intensity can be obtained as:

$$\frac{I_s}{I_0} = \left( \frac{f_A - f_B}{\alpha f_A + (1 - \alpha) f_B} \right)^2 |a_s|^2 = \eta_s^2,$$

(4.8)

Since $|a_s| = |a_{-s}|$, satellites of the same order has equal intensity. Thus, for a superlattice with only a composition modulation, the intensities of the satellites symmetric with respect to the fundamental peak.

### 4.1.2 Strain and composition modulation

The lattice parameter mismatch of the superlattice constituents induces a displacement field $u(R_n)$ in the sample. Additionally displacements are produced upon hydrogen absorption. The scattering amplitude is in this case equal to:

$$F(Q) = \sum_{R_n} f_n(Q) e^{-iQ(R_n + u(R_n))},$$

(4.9)

The effect of the displacement field on the scattered intensity can be analyzed using Fourier series. For small displacements the exponential argument in Equation 4.9 can be Taylor expanded and by inserting the Fourier series version of the displacement field (see Reference [33]):

$$u(R_n) = \sum_k u_k e^{i k R_n},$$

(4.10)

in Equation 4.9, the intensity ratios of the satellites and the fundamental peak can be obtained as (calculated to second order in the expansion):

$$\frac{I_s}{I_0} \approx \left[ \eta_s - \varepsilon_s \left( 1 \pm \frac{\Lambda}{3d} \right) \right],$$

(4.11)
where $\varepsilon_s$ is the amplitude of the strain modulation and $d$ is the average lattice plane distance. From 4.11 it is clear that in a superlattice with both a strain-, and composition modulation, which are in-phase, the intensities of satellite reflections belonging to the same order will be different. For large or arbitrary displacements, the scattering amplitude has to be calculated directly from Equation 4.9.

### 4.1.3 Specular x-ray reflectivity from multilayers

Information concerning the layer thicknesses and overall thickness of a multilayered thin film, and to some extend, the interface quality can be obtained by X-ray reflectivity. In this type of experiment, the angle of incidence of the X-rays beam is so small that the reflected beam is determined by the scattering from interfaces between materials with different electron density, and the atomic arrangements has no relevance. The reflectivity ($R$) of the beam at the interface is governed by the Fresnel equation:

$$R = \left( \frac{Q - Q'}{Q + Q'} \right)^2,$$

where $Q = 2k \sin \alpha$ and $Q' = 2nk \sin \alpha'$ with $k = 2\pi/\lambda$. The angles $\alpha$, $\alpha'$ are defined in Figure 4.3. The index of refraction of x-rays, $n$, is slightly smaller than one, and give rise to a peculiar behavior at very low incident angles. Below a critical angle ($\alpha_c$), almost all incident radiation is reflected (total external reflection). Well above the critical angle, the reflected beam has low intensity and varies as $Q^{-4}$. For a thin film, of thickness $D$, the reflected beams at the two interfaces (top and bottom) interfere and gives rise to oscillations of the reflected intensity with a period of $2\pi/D$ in $Q$. For a multilayered film constituted from two materials (A and B), as the one depicted in Figure 4.4, the exact solution for the $Q$ dependence of the reflectivity is complicated but can

![Figure 4.3: The reflection and transmission of X-rays at an interface. $k$ is the wavevector of the incident wave, and $nk$ is the wavevector of the transmitted wave, where $n$ is the index of refraction. The angle $\alpha'$ is smaller than $\alpha$ for X-rays.](image-url)
be solved, i.e. the Paratt formalism [34, 35]. The problem is however much simpler if one consider the kinematical approximation, i.e. single scattering events and no refraction effects. The kinematical approximation works well at higher angles were the scattering is weak. The amplitude reflectivity from a thin sheet (thickness \(d \ll 1/Q\)) of a material can within this approximation be written as (see Reference [36] for details):

\[
r_{\text{kin}}(Q, d, \rho) \approx -\frac{4\pi i \rho r_0 d}{Q},
\]

where \(r_0\) is the Thomson scattering length, \(\rho\) is the electron density and \(\lambda\) is the x-ray wavelength. Using Equation 4.12, the total reflectivity of a multilayer with bilayer thickness equal to \(\Lambda\) can be obtained by summing the contributions from every layer and taking into account the phase factors and the absorption with the result [36]:

\[
r(Q) = r_1(Q, \Gamma, \Delta, \rho_{AB}) \frac{1 - e^{iQ\Delta N} e^{-\beta N}}{1 - e^{iQN} e^{-\beta}}.
\]

where

\[
r_1(Q, \Gamma, \Delta, \rho_{AB}) = r_{\text{kin}}(Q, \Gamma, \Delta, \rho_{AB}) \frac{\sin \frac{Q\Gamma \Delta}{2}}{\rho_{AB}},
\]

In Equations 4.13 and 4.14, \(\Gamma\) is the fraction of the bilayer thickness constituted of material A, \(N\) is the number of bilayers, \(\rho_{AB}\) is the difference in electron density between material A and B, and \(\beta\) is the average coefficient of absorption. The reflectivity pattern arising from Equation 4.13 will show
superlattice peaks with a period of $2\pi/\Lambda$ in $Q$. The position of the superlattice peaks is determined by the following expression:

$$Q_{\text{max}}^2 = Q_c^2 + \left(\frac{2\pi}{\Lambda}\right)^2 s^2,$$

where $Q_c = 2k_0 \sin \alpha_c$ and $s$ is an integer defining the order of the superlattice peaks.

4.1.4 X-ray scattering of materials containing defects

**Off specular reflectivity**

From specular reflectivity it is possible to collect some information concerning the surface quality or interface quality of a multilayer. Simulations of specular reflectivity scans only gives an rms value of the height variations. It is however not possible to distinguish, i.e., if the interface is roughened or suffer from interdiffusion. Furthermore, the specular scan can not give a value for the correlation lengths of the structure. The height variations of a real interface reduces the measured specular intensity. It is important to distinguish whether the height variations are correlated or not. Un-correlated roughness only reduce the reflected intensity, analogously as the reduce in intensity of the Bragg peak due the thermal vibrations the atoms, while correlated roughness give rise to diffuse (or off-specular) scattering. Thus, by working with both off-specular and specular geometry it is possible to gain more detailed information concerning the structure of the interfaces. In the case of multilayers, one also has to take in account the correlation in the thickness variations in the out-of plane direction.

**Rocking curves**

Despite the superlattices considered in this thesis are single crystals it does not imply an infinite correlations length in the positions of the atoms. The usual way to deal with this is to picture that the sample possess a mosaic structure. The angle between the mosaic “blocks” are typically below $1^\circ$, and the spread of the blocks can be measured by performing scans at fixed $2\theta$-values and rotating the sample around an axis perpendicular to the plane of the incoming beam (rocking curve or $\omega$-scan). The width at half of the maximum intensity is then a measure on the mosaic spread. The crystal coherence length, both in lateral projection and out-of plane direction, can be determined by a complete mapping of the reciprocal space in the vicinity of two Bragg reflections with different orientation in $\omega$.

**Diffuse x-ray scattering due to hydrogen**

As x-rays mainly are scattered due to variations in the electrostatic potential, the small charge of a hydrogen atom makes it in-visible for x-rays. However
the hydrogen-induced displacement field affects the scattering potential and can be evaluated. The presence of the hydrogen atoms will increase the average distances between the metals atoms, which causes the position of the Bragg peak to shift to lower angles. The actual displacements of the metal atoms surrounding the hydrogen atom will decrease the scattered intensity. The attenuation of the intensity can, in analogy with the thermal Debye-Waller Factor (DWF), be described by a static Debye-Waller factor (DWF), \( e^{-2L} \). For uncorrelated defects the DWF can be determined by summing the contributions from all defects on the displacement of a atom at site \( m \), i.e.:

\[
2L = 2x(1-x) \sum_n (1 - \cos Qu_{mn}) ,
\]

where \( x \) is the probability of a defect site to be occupied \( (x = Nc, \text{ where } N \text{ is the number of interstitial sites per metal atom and is the hydrogen and metal atomic ratio}) \) and \( u_{mn} \) is the displacement of the atom. The sum over all defects can be converted to a sum over the average surrounding of a defect:

\[
2L = 2x(1-x) \sum_m \langle(1 - \cos Qu_{mn})\rangle.
\]

When \( Qu_{mn} \) and \( x \) is small this reduces to:

\[
2L \approx x \left\langle \sum_m (Qu_{mn})^2 \right\rangle.
\]

Thus, by measure the DWF the actual displacement of the metal atoms close to hydrogen can be measured, see Ref. [37]. In addition to the reduce in intensity of the Bragg peak a diffuse component, with a Lorenzian peak shape centered at the Bragg peaks, will develop (Huang Diffuse Scattering, HDS). For small concentrations of randomly distributed hydrogen the intensity of the HDS can be shown to be proportional to the concentration:

\[
I_{HDS} = cF^2(Q)|\mathbf{Q} \cdot \tilde{u}(Q)|^2 ,
\]

where \( \tilde{u}(Q) \) is the Fourier transform of the average displacement field. Measurements of the diffuse intensity is by far the most direct methods to determine the long-ranged displacement field and thus the dipole tensor described in Section 3.2.1.
Thermodynamical analysis

This thesis is partly based on the results derived from pressure-composition isotherms (p-x-isotherms). A number of quantities, such as the enthalpy, entropy and compressibility, can be directly determined from the isotherms. This chapter gives a very short description how this was done.

5.1 Enthalpy and entropy

Infinite dilution limit

In the low concentration limit, the relative partial enthalpy and entropy can, if they are temperature independent, be determined from the slope and intercept of a plot of $\ln K_S(T)$ versus $1/T$:

$$\ln K_S(T) = \frac{\Delta\tilde{H}_H^0}{k_B T} - \frac{\Delta\tilde{S}_H^0 + k_B \ln \beta}{k_B}$$  \hspace{1cm} (5.1)

The partial enthalpy of the hydrogen is simply obtained as:

$$\Delta\tilde{H}_H^0 = k_B \times \text{slope}$$  \hspace{1cm} (5.2)

If $\beta$ is known, the non-configurational partial entropy of the dissolved hydrogen is obtained as:

$$\Delta\tilde{S}_H^0 = -k_B \times (\text{intercept} + \ln \beta)$$  \hspace{1cm} (5.3)

Concentration dependence in the solid solution range

In any region of continuous solubility of hydrogen in a metal, the relative partial enthalpy-, and entropy, are obtained from the solubility isotherms as:

$$\Delta\tilde{H}_H = \Delta \mu_H - T \frac{\partial \Delta \mu_H}{\partial T} = k_B \frac{\partial \ln \sqrt{p}}{\partial \frac{1}{T}}$$

$$\Delta\tilde{S}_H = -\frac{\partial \Delta \mu_H}{\partial T} = -k_B T \frac{\partial \ln \sqrt{p}}{\partial T}$$  \hspace{1cm} (5.4)

Thus, by determining the temperature dependence of $\Delta \mu_H$ at different concentrations, one can derive the concentration dependence of $\Delta\tilde{H}_H$ and $\Delta\tilde{S}_H$. In particular, if $\Delta\tilde{H}_H$ and $\Delta\tilde{S}_H$ is temperature independent, which often is the case
for hydrogen in metals, one can simply determine $\Delta \tilde{H}_H$ and $\Delta \tilde{S}_H$ using the van ’t Hoff isochore equation [18]:

$$\ln \sqrt{p} = \frac{\Delta \tilde{H}_H}{k_B T} - \frac{\Delta \tilde{S}_H}{k_B}.$$  (5.5)

The relative partial enthalpy-, and entropy, are obtained, in a similar way as $\Delta \tilde{H}_H^0$ and $\Delta \tilde{S}_H^0$, from the slope and intercept of a plot of $\ln \sqrt{p}$ versus $1/T$:

$$\Delta \tilde{H}_H = k_B \times \text{slope}$$  (5.6)
$$\Delta \tilde{S}_H = -k_B \times \text{intercept}$$  (5.7)

A non straight line relation between $\ln \sqrt{p}$ and $1/T$, implies that $\Delta \tilde{H}_H$ and/or $\Delta \tilde{S}_H$ is temperature dependent. In that case it is impossible to distinguish between the enthalpy and entropy terms: However, if the temperature dependence is small, and the isotherms (i.e. $\Delta \mu_H$) are measured with a small step in temperature, the enthalpy and entropy can be determined directly from Equation 5.4.

**Power expansion of $\tilde{H}_H$ and $\tilde{S}_H$ in concentration**

By assuming that $\Delta \tilde{H}_H$ and $\Delta \tilde{S}_H$ are temperature dependent it is possible to fit the measured isotherms all together. The concentration dependence of $\Delta \tilde{H}_H$ and $\Delta \tilde{S}_H$ is expanded in power series.

$$\Delta \tilde{H}_H = \sum_{i=0}^{N} h_i x_i$$
$$\Delta \tilde{S}_H = \sum_{i=0}^{N} s_i x_i.$$  (5.8)

In order to improve the fit, it is often more convenient to subtract the ideal partial configurational chemical potential from the measured isotherm, i.e.:

$$\Delta \mu_H = k_B T \ln \left[ \sqrt{p} (6 - x) / x \right] = \sum_{i=0}^{N} h_i x_i - T \sum_{i=0}^{N} s_i x_i.$$  (5.9)

The coefficients, $s_i$ and $h_i$, that best reproduces the measured data can then be determined by solving the general least square equation.

### 5.2 Compressibility

The compressibility of hydrogen dissolved in a metal can easily be derived from the solubility isotherms, and is given by the concentration dependence of the hydrogen pressure surrounding a metal ($p_{H_2}$) [29]:

$$\kappa_T \propto x^2 T \left. \frac{\partial \ln p_{H_2}}{\partial x} \right|_T ,$$  (5.10)
5.3 Using Matlab to analyze solubility isotherms

In appendix A, a Matlab program ("iso") is listed, which was written to simplify the handling of the solubility isotherms. The measured data can be read in and presented graphically, and the solubility isotherms can then be fitted to a polynomial. Using the polynomial representation, the isotherms are then converted to isochores, which are used to derive $\Delta H_H$ and $\Delta S_H$ according to Equation 5.7. The alternative way to derive $\Delta H_H$ and $\Delta S_H$, described in Section 5.1 is also implemented in the program. The slope of the isotherms and the compressibility can also be derived using the program. In all calculations, the error from the fit of the isotherms is propagated, in order to give an estimation of the error in the derived properties. Below a screenshot from the graphical user interface is shown, and the different steps in the program is described.

![Figure 5.1](image-url)

*Figure 5.1:* The different steps in the Matlab program for analyzing solubility data, which is listed in Appendix A. (1) The data is loaded and plotted. (2) The isotherms can be fitted, and the residual data is plotted. (3)-(4) The slope and inflection points of the isotherms can be determined. (5) All measured data can be fitted simultaneously using the model described in 5.9. (6)-(7) The desired isochores is deduced from the fitted data and presented graphically. (8) The enthalpy and entropy is determined according to Equation 5.7.
Experiments

6.1 Growth and properties of the samples

The samples studied in papers [I-VI] were grown by the dual-target magnetron sputtering technique. The Fe/V superlattices were prepared at Materials Physics at Uppsala University, while the Nb/W-, and Mo/V superlattices were fabricated at the Thin Film Physics Division at Linköping University. Details of the experimental setups in Uppsala and Linköping can be found in Refs. [38], and [39] respectively. The Nb-films were grown at the Royal Institute of Technology using MBE (see Ref. [40]). Several groups have studied epitaxial growth of Fe, Mo, and V, and it is clear that, under appropriate conditions, Fe/V(001) and Mo/V(001) superlattices can be sputtered onto MgO(001) substrates, with very good crystal quality and interfaces sharpness. Crystal coherence lengths up to 500-600 Å, both in-plane and out-of-plane, and an estimated roughness of the Fe(Mo)-V interface of ±1 Å, have been reported [38]. Further improvements of the quality of the Mo/V superlattices has been accomplished by alloying the Mo with V [41]. Figure 6.1 shows a typical result for the scattered x-ray intensity in the specular direction ($\theta - 2\theta$, $\omega = 0$). The low angle (reflectivity) range ($0^\circ < 2\theta < 20^\circ$) shows a number of “multilayer” reflections from the chemical repetition length, and in the high-angle range a number of strong peaks appears. The high-angle peaks are centered around the average (002) lattice parameter, and are due to the superlattice structure (see Sec. 4.1).

Figure 6.1: Specular X-ray scattering from a MoV/V superlattice. The peaks at low angle is from the reflectivity from to the chemical modulation and the high angle peaks are due to superlattice structure.
Superlattices of Nb/W, on the other hand, had never been grown before, but the first results show that it is possible to grow Nb/W(110)-superlattices with good quality. See Paper [VI]. However, there is a correlation between the quality and the thickness of the W-layers, i.e. the quality of the superlattices degrades when the W-layers thickness is increased. This is presumably due to reconstruction of the W-surface, which hinders a perfect epitaxial growth.

6.2 Strain state, hydrogen site occupancy and expansion

6.2.1 The intrinsic strain of the layers

Epitaxial growth of different materials on top of each other will introduce strain in the individual layers. The strain-state is determined by the lattice parameter mismatch and the thickness ratio of the constituents. Tab. 6.1 summarizes the strain-states of some superlattices.

Table 6.1: The lattice parameter mismatch for some superlattices in percent. The negative and positive values means that the hydrogen dissolving layers are under tensile- and compressive strain respectively. The materials containing hydrogen are typed in bold. References to relevant works are also given.

<table>
<thead>
<tr>
<th></th>
<th>Mo</th>
<th>Fe</th>
<th>W</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>-4.3[42]</td>
<td>5.0[43, 44]</td>
<td>-4.6</td>
</tr>
<tr>
<td>Nb</td>
<td>4.5</td>
<td>13[45]</td>
<td>4.2[46]</td>
</tr>
</tbody>
</table>

Fe/V-, and Nb/W superlattices are equivalent in the sense that the hydrogen dissolving layers (i.e. V and Nb respectively) are biaxially compressed in the film plane. For Mo/V superlattices, on the other hand, the hydrogen dissolving layers are biaxially expanded in the film plane. Due to the Poisson response, the lattice parameter in the out-of-plane direction \( a \) will be larger than bulk for the V- and Nb-layers, in Fe/V and Nb/W superlattices, and smaller than bulk for the V-layers in Mo/V superlattices.

If the elastic constants of the superlattice constituents are close to equal, the in-plane lattice parameter \( a || \) can be estimated as the weighted average of the respective bulk lattice parameter, i.e. for a Fe/V superlattice:

\[
a || = \frac{L_{Fe}a_{Fe} + L_{V}a_{V}}{L_{Fe} + L_{V}},
\]

where \( L_{Fe(V)} \) is the layer thickness of Fe(V), and \( a_{Fe(V)} \) the bulk lattice parameter of Fe(V). The out-of-plane lattice parameter can then be calculated using
linear elasticity. For a biaxial strain state in the x-y-plane, the relation between the out-of-plane strain and in-plane strain can be written as:

\[ \frac{\varepsilon_{zz}}{\varepsilon_{xx}} = (1 + \frac{2C_{12}}{C_{11}}), \]  

(6.2)

where \( C \) is the elastic constants in Voigt notation.

For Nb/W(110) superlattices, the situation is different. Here there is a big difference in the elastic constants and Equation 6.1 is unable to give a reasonable estimation of the strain state of the layers. The in-plane lattice parameters, \( a_{110} \) and \( a_{001} \), can be calculated using linear elasticity, using the fact that the elastic energy per unit area of the individual layers should be equal and in a minimum (mechanical equilibrium). The elastic density of a deformed body is equal to [47]:

\[ w = \sum_{ijkl} C_{ijkl} e_{ij} e_{kl} \]  

(6.3)

For small compression/expansion (\( e_{xx} = e_{yy} = e_{110}/\sqrt{2} \) and \( e_{zz} = e_{001} \)), the energy density in the individual layers can, using Equation (6.3), be obtained as:

\[ w = \frac{1}{2} (C_{11} + C_{12}) e_{110}^2 + \sqrt{2} C_{12} e_{110} e_{001}. \]  

(6.4)

At mechanical equilibrium, the in-plane lattice parameters can, using elastic data from Ref. [48], be estimated by requiring:

\[ \frac{\partial}{\partial a_i} (L_{Nb} w_{Nb} + L_{W} w_{W}) = 0, \]  

(6.5)

where \( a_i = a_{110}, a_{001} \).

### 6.2.2 Site occupancy and H-induced expansion

Particularly for H in V, the site occupancy is proved to be very sensitive for applied strain [49]. The normal interstitial site occupancy in bcc metals is tetrahedral (T). See Figure 3.1 for the definition of the sites. Calculations indicate that by elongating the [001] axis, the hydrogen changes interstitial site occupancy, first from T to a 4T configuration, and then to O_z [50]. In the 4T configuration, H is delocalized over the T-sites surrounding the O-site. See Fig. 6.2a. For Fe/V superlattices it is therefore reasonable that due to the elongation of the z-axis (film plane in x-y direction), the O_z sites are favored and more likely to be occupied than in bulk V. For Mo/V superlattices, where the x-y axes are elongated compared to bulk, one can, for similar reasons, expect a stabilization of hydrogen on O_x and O_y sites. The strong adhesion of the superlattices on the substrate ("clamping"), as well as the spacer layer, restricts the hydrogen-induced expansion to occur in the film normal direction. As hydrogen interacts through the induced strain field, the anisotropic expansion can
affect the occupancy as previously described in Section 3.2.3. The redistribution of hydrogen from one type of sites to another will affect the overall layer expansion. In variance to bulk samples, where the volume expansion per hydrogen atom does not vary with concentration in the solid solution range, the volume of a hydrogen atom in a superlattice generally varies with concentration as hydrogen on different sites causes different layer expansion. This is nicely illustrated in Figure 6.2c, where the volume expansion for three different superlattices is shown as a function of the initial strain state of the V lattice. As an comparison, the expansion of a V sample with bulk lattice parameters and free surfaces is also plotted in Figure 6.2c. H occupies the T-sites in bulk V, and the structure remains cubic within the single phase solubility range (α-phase). For concentrations higher than \( c = c' \) (bulk), the β-phase(V₂H) nucleates, which is close to tetragonal with \( c/a \approx 1.1 \).
6.3 Concentration determination

While it is relatively easy to measure the temperature and the hydrogen pressure, it is more difficult to determine the hydrogen concentration on an absolute scale. Different techniques, which directly or indirectly can be used to determine the hydrogen content, are summarized in Tab. 6.2.

Table 6.2: A summery of techniques used to determine the hydrogen content of materials.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Determination</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volumetrical</td>
<td>Direct</td>
<td>[51]</td>
</tr>
<tr>
<td>Gravimetrical</td>
<td>Direct</td>
<td>[52]</td>
</tr>
<tr>
<td>$^{15}$N nuclear reaction</td>
<td>Direct</td>
<td>[53]</td>
</tr>
<tr>
<td>Neutron reflection</td>
<td>Direct</td>
<td>[10]</td>
</tr>
<tr>
<td>Sample dilation</td>
<td>Indirect</td>
<td>[52]</td>
</tr>
<tr>
<td>Resistivity</td>
<td>Indirect</td>
<td>Sec. 6.3.2 in this work</td>
</tr>
</tbody>
</table>

The indirect methods assume knowledge of the relation between concentration and sample dilation and resistivity respectively. No general expressions for these relations have been derived and the results have to be calibrated by measuring the composition directly with one of the other methods.

6.3.1 Concentration profiling using the $^{1}$H($^{15}$N, $\alpha\gamma$)$^{12}$C nuclear reaction

If a hydrogen containing material is bombarded with $^{15}$N ions there is a certain cross-section for a nuclear reaction producing excited $^{12}$C, which de-excite to the ground-state by sending out 4.43 MeV $\gamma$-particles. A sharp resonant peak of the cross-section exists at 6.4 MeV, which makes the method suitable to measure the total amount of hydrogen in a sample as well as for hydrogen concentration depth profiling. The yield is proportional to the hydrogen concentration, and the depth resolution is of the order of 100 Å (see Ref. [53]). Fig. 6.3 show the yield of the $^{1}$H($^{15}$N, $\alpha\gamma$)$^{12}$C reaction in a hydrogenated Nb/W superlattice. The hydrogen profiling of the samples used in paper [I] and [II] was performed in the Tandem Accelerator Laboratory in Uppsala. A description of the experimental setup can be found in Ref. [12].

6.3.2 Excess resistivity

At moderate temperatures, the resistivity of a metal or a M-H-alloy is determined by the degree of order of the constituents, the density of electronic states
Figure 6.3: The yield from the ${}^{1}H({}^{15}N, \alpha \gamma ){}^{12}C$ nuclear reaction in hydrogenated Nb/W(110)-superlattices. The closed circles and open squares show the results from a Nb(12ML)/W(8ML)-, and a Nb(12ML)/W(18ML)-superlattices respectively.

and the electron velocity at the Fermi level. The excess resistivity is defined as the difference between the pure metal and the hydrogen loaded metal, i.e.:

$$\Delta \rho_H = \rho_x - \rho_0,$$

where $\rho_0$ is the resistivity of the pure sample, and $\rho_x$ resistivity of the sample as it is loaded with hydrogen to a concentration $x$. The excess resistivity can essentially be decomposed in two different terms:

$$\Delta \rho_H = \rho_{\text{imp}} + \rho_{\text{elect}},$$

where $\rho_{\text{imp}}$ is the change of resistivity due to the scattering of the electrons by hydrogen acting as a point defect, and the other term includes all changes that hydrogen causes on the electronic structure of the metal. The latter contribution has proved to be significant for Fe/V superlattices, and will be discussed below. The first term in Equation 6.7 can basically be treated in the same way as Nordheim’s original analysis of the resistivity of a disordered substitutional alloy [54]. The resistivity change due to hydrogen can then be obtained as [55]:

$$\Delta \rho_{\text{imp}} (x) = 4x^2 \Delta \rho_{\text{imp}} \Delta \rho_{\text{max}} (x_{\text{max}} - x),$$

where $x_{\text{max}}$ is the maximum concentration, and $\Delta \rho_{\text{max}}$ is the maximum resistivity change, and is determined by the scattering strength of the defect. Watanabe et al. [56] have performed an extensive study of the resistivity change due to
hydrogen in V, Nb, Ta, and Pd, and the results are in reasonable agreement with Equation 6.8.

The resistance change when loading the superlattices with hydrogen showed different asymptotic behavior, see Fig. 6.4. While the resistivity change in

![Figure 6.4: Resistivity change during hydrogen loading of (a) a Mo/V superlattice, and (b) a Fe/V superlattice. The maximum in the resistivity change at \([H/M] = 0.5\) which usually can be noticed in the disordered phase in bulk metals, is apparent in the Mo/V sample, but not for the Fe/V sample.](image)

Mo/V- and Nb/W- superlattices can qualitatively be described using Equation 6.8, hydrogen in Fe/V-superlattices shows a completely different behavior. As seen in Figure 6.4, the resistivity increases monotonically as the sample is loaded to the maximum concentration. The discrepancy in the asymptotic behavior of \(\Delta \rho_H\) between Fe/V and Mo/V (Nb/W), can be ascribed to different effects from the added hydrogen on the electronic structure, i.e. the second term in Equation 6.7. In this context, one probably has to consider the effect from the anisotropic hydrogen-induced lattice expansion on the electronic band structure.

Deviations from the ideal impurity resistivity according to Equation 6.8 can also appear due to hydrogen ordering. If there is some short-ranged order in the position of the hydrogen, the Bloch condition (see e.g. Ref. [57] ) can be fulfilled locally and the resistivity will then be lower than for completely disordered hydrogen.
6.4 In-situ resistivity setup

Figure 6.5 describes schematically the experimental setup called "The Wall", which can be used for p-c-T measurements of hydrogen in superlattices and thin films. All parts of the system are UHV-compatible and the base pressure in the sample cell is typically $10^{-9}$ mbar. As determined by a Residual Gas Analyzer, the partial pressures of all gases, except hydrogen, are in the $10^{-11}$ mbar range. The hydrogen gas, originally of 99.99998% purity, is additionally purified in two steps: Firstly, using a West Associates ULTRAPURE gas purifier, and thereafter by absorption in a metal-hydride, which also serves as a storage for purified hydrogen gas. Capacitance pressure gauges are monitor-


...ing the pressure in the sample cell. The temperature at the sample surface is
measured by a CrAl thermocouple, with a precision of ±1 K. The resistivity of the sample is registered by a DC current-reversal technique as described in Figure 6.6, using a Keithley 2400 Sourcemeter and a Keithley 2182 Nanovoltmeter.

![Diagram of DC current-reversal technique](image)

Figure 6.6: The DC current-reversal technique for measuring the resistivity. The sourcemeter (2400) is producing a square modulated current and the voltage drop over the sample is measured by a nanovoltmeter (2182), which is phase-locked to the sourcemeter. The technique is very effective for reducing noise, i.e. thermal EMF in the current leads.

### 6.5 In-situ XRD setup

The *in-situ* x-ray scattering experiments were performed in a specially designed x-ray scattering chamber, see Figures 6.7 and 6.8. All parts of the chamber are UHV compatible. The windows for the x-ray beam are made of Beryllium and glued (UHV-type) on the chamber body, which is made of stainless steel. A four-point probe for measuring resistivity can be brought in contact with the sample from the outside. The temperature of the sample is measured by a chromel-alumel thermocouple in direct contact with the sample surface. The chamber can be evacuated to below $10^{-8}$ mbar using a turbo molecular pump attached to the front of the chamber via a flexible steel hose. The hydrogen used in the experiments was originally of 99.9996% purity, and additionally purified, first by a West Associates ULTRAPURE hydrogen gas purifier, and then through an absorption-desorption cycle in a metal-hydride powder. The pressure of the hydrogen gas was measured by two Inficon capacitance diaphragm gauges (accuracy 0.1% of full scale) with full scale: 10
and 1000 torr, respectively. The resistance of the samples was measured using a Keithley 2400 Sourcemeter in combination with a Keithley 2182 Nanovoltmeter using a DC current-reversal technique (see Figure 6.6). The samples were heated by a low resistance radiative heater mounted inside the chamber and the sample temperature is controlled within $\pm 0.1^\circ$ using a Eurotherm 2208 PID controller.

The X-ray reflectivity and x-ray diffraction patterns were measured by a Bruker-AXS D8 Discover equipped with a Cu source X-ray tube. $K_\alpha_1 (\lambda = 1.5406 \text{ Å})$ x-ray tube. The primary beam optics consists of a Göbbel mirror in combination with a V-groove beam compressor, which produces a parallel X-ray beam with a divergence smaller than 0.007$^\circ$ and a monochromatization ($\Delta \lambda/\lambda$) is better than 0.01%. The diffracted beam is defined using an ordinary slit system.

A typical experiment was performed as follows. The sample was first mounted and aligned with respect to the goniometer. Thereafter the chamber was evacuated and pumped for approximately 24 hours in order to reach the $10^{-9} \text{ mbar}$ range. Starting at the lowest pressure, the hydrogen pressure was then stepwise increased while the temperature was kept constant. After every change in pressure, the H-uptake of the sample could be monitored by the change in resistivity. When the sample and the hydrogen gas have reached equilibrium, the resistivity change were noticed and a XRD scan was performed.

Figure 6.7: Part of the setup used for in-situ x-ray scattering from thin films and superlattices. (1) UHV Scattering chamber with Be windows. (2) Flexible steel hose connected to a turbo molecular pump via a right angle valve. (3) Four-point probe for resistivity measurements. (4) Water cooled high current feedthrough to the heater. (5) Goniometer. (6) Bruker V-Groove beam compressor. (7) Göbbel mirror. (8) X-ray tube with line focussed Cu source. (9) Diffracted beam slit system.
Figure 6.8: Part of the setup used for in-situ x-ray scattering from thin films and superlattices. (1) Turbo molecular pump and a RGA. (2) Pressure and resistivity data acquisition units (similar to the p-c-T measurements setup). (3) Metal-hydride for hydrogen storage. (4) Pressure gauges: 10-1000 Torr. (5) Control units for turbo molecular pump and internal heater. (6) PC for data logging, pressure and resistivity. (7) PC for controlling the diffractometer.
Summary of papers I-VII

7.1 Paper I-III:

*Phase formation of hydrogen in quasi-2D V lattices with intrinsic biaxial compressive strain*

The H-H interaction and phase formation of hydrogen in \( \approx 20 \text{ Å} \) thick vanadium layers was explored. The hydrogen solubility isotherms were determined using a resistivity technique, and structural properties were explored by *in-situ* X-ray diffraction. In paper [I] special focus was on the role of the initial strain state of the V layers on the H-H interaction. Except in the low concentration range, the solubility isotherms appeared to be insensitive to variations in the intrinsic compressive strain. In accordance to previous measurements [58], a strong attractive mean H-H interaction is measured at low concentrations (H/V < 0.1), and at higher concentrations the mean H-H interaction is repulsive. In the concentration range that exhibits attractive interaction, the entropy of solution indicated that the "effective" number of absorption sites (\( \beta \)) is strongly reduced. Furthermore, \( \beta \) was found to scale linearly with the strain, where an increased compressive strain appear to result in a further reduction of \( \beta \). The thermodynamic properties and critical behavior was explored in details in paper [II]. The enthalpy and entropy of solution was found to be temperature dependent, which is in variance with hydrogen in bulk bcc transition metals. The origin of the temperature dependence was attributed to an initial distribution over both tetrahedral- (T), and octahedral z sites (O\(_z\)). The interaction energy between hydrogen on O\(_z\) sites and hydrogen on T sites are very different due to the one-dimensional hydrogen-induced expansion. Thus, temperature dependence in the enthalpy and entropy of solution in a result from that hydrogen occupies different sites with different interaction energy.

The divergence of the compressibility of the H lattice gas was found to show a Curie-Weiss behavior (i.e. mean-field) with a critical temperature of 251 ± 1 K (see Figure 7.1). As the thermodynamic-, and the structural properties (paper III) indicate a strongly interacting H lattice gas with a clear tendency of forming local configurations of hydrogen interacting on a microscopic length scale, the mean-field behavior is unexpected. The strong mean attractive H-H interaction in the low concentration range was not possible to be explained solely in terms of long-range elastic interaction. Furthermore, the H-induced expansion was found to be gigantic (roughly three times the bulk value) in the
Figure 7.1: The temperature dependence of the isothermal compressibility ($K_T$) of the hydrogen lattice gas evaluated at the points of inflection of the hydrogen solubility isotherms in a Fe/V superlattice. The inset show the results from fitting the compressibility according to: \( \ln K_T = \gamma \ln \left( \frac{T}{T_c} - 1 \right) \) for different values of \( \gamma \) and \( T_c \). The largest value for the linear correlation coefficient ($R^2$) correspond to: $T_c = 251 \pm 1$K and $\gamma = 1.01 \pm 0.01$.

concentration range ($0.07 \lesssim H/V \lesssim 0.15$), but in this concentration range, the H-H interaction is smaller than at lower concentrations.

7.2 Paper IV-V

*Phase formation of hydrogen in quasi-2D V lattices with intrinsic biaxial tensile strain*

The change of the intrinsic strain state of the V lattice, from compressive to tensile, proved to have a huge effect on the solubility of hydrogen. Similarly to paper [I-III], the solubility isotherms and the structure properties of hydrogen were studied by resistivity-, and in-situ X-ray scattering techniques. In strong contrast to biaxially compressed V, moderately tensile strained V showed a strong attractive mean H-H interaction over a broad concentration range ($0.2 \lesssim H/V \lesssim 0.7$). In the very low concentration range, the mean H-H interaction was close to zero. The concentration at the onset of the attractive interaction was the same concentration where hydrogen changes site from T to O$_2$ [41]. The change of site of hydrogen is driven by the anisotropic expansion of the lattice, and can be seen as a self-induced change of site occupancy, which is different from the change of site that can be produced by applying ex-
Figure 7.2: (a) An illustration of the 4T configuration. The hydrogen atom is delocalized over the T-sites that surrounds an O-site. The 4T-site is gradually transformed to the O-site when the radius, \( r \), goes to zero. (b) The H-H interaction, as deduced from the slope of \( \Delta \bar{H}_H \) versus concentration, plotted in the same graph as the expected H-induced expansion. [41] The symmetry of the figures on the top of the graph are reflecting the symmetry of the local strain field produced by hydrogen at the different site.

The relation between the site occupancy and H-H interaction is explored based on the assumption that the H-H interaction can be described in terms of elastic dipole interaction, which originally was proposed by Akeley [4]. As seen in Fig. 7.2, the attractive H-H interaction can be directly linked to the lattice expansion when hydrogen is redistributed according to the sequence: T\( \rightarrow \)4T\( \rightarrow \)O \( \rightarrow \)Z (see Figure 7.2), which is predicted from theoretical calculations [50]. As described in paper [V], the strong attractive H-H interaction allows an excitation of hydrogen density fluctuations with extension of the order of 100 Å. The inhomogeneities is seen as a split in the fundamental Bragg peak, and the size and amplitude is reduced when the temperature is increased, and at \( T_c = 675 \pm 25 \), the hydrogen is expected to be homogeneously distributed. In addition to the density variations, the resistivity data shows that hydrogen tend to order below \( T \approx 573 \). Thus the ratio of the ordering temperatures (i.e. gas-liquid and liquid-solid transition) is the opposite than in bulk V [4].
7.3 Paper VI-VII

*H-H interactions and solubility in Nb/W superlattices and thin Nb films*

The effect from compressive biaxial strain on the H-uptake and H-H interaction in Nb was explored by utilizing a series of Nb/W(110) superlattices, constituting spatially well defined (thickness ≈ 30 Å) hydrogen absorption potentials, but with a varying degree of intrinsic compressive strain (see paper [VI]). The hydrogen solubility isotherms were measured, and the solubility was found to be much less than for bulk Nb, which is in-line with previous investigations of the effect of strain on the hydrogen uptake in metals (see [20] and references therein). The mean H-H interaction energy was also found to be sensitive for compressive strain. The mean H-H interaction was reduced as the compressive strain was increased, and was repulsive for the most strained samples. However for the least strained sample (ε ≈ 1%), the H-H interaction depended strongly on the concentration, as can be seen in Figure 7.3, and was found to be more attractive than in bulk Nb at H/Nb ≈ 0.35. The critical temperature, as determined from the extrapolation of the measured data to lower temperatures, was determined to 287 K for the least strained sample, while no transition of this type could be predicted the samples with higher intrinsic strain. The low concentration solubility in Nb (110) films were investigated in

![Figure 7.3: Correlation between the initial in-plane strain, ε, of the Nb(110)-layers in Nb/W(110)-superlattices and H-H-interaction energy (\(u_{H-H}\)). \(u_{H-H}\) is taken as the slope of \(\Delta H_H\) versus \(c\), at two different concentration. At (\(H_{Nb}\)) = 0.35, \(u_{H-H}\) is close to the bulk-Nb value [51] for the least strained sample, and is repulsive for the most compressed sample. The influence of the initial strain on the H-H-interaction is smaller at low concentrations. An extrapolation of \(u_{H-H}\), at (\(H_{Nb}\)) = 0.35, to zero strain (dashed line) gives \(u_{H-H} \approx -0.75\) eV/H-atom.](image)
paper [VII]. In this concentration range, previous measurements have revealed a unusual large hydrogen-induced lattice expansion. The results in paper [VII] reveals the complexity in the absorption potential of thin films. However, when combining resistivity measurements and the $^{15}$N nuclear reaction method, we are able to explain the solubility in terms of multiple hydrogen site occupancy. The H-H interaction was found to be attractive at low concentrations, which is, due to the intimate link between interaction and volume change, consistent with the large hydrogen-induced lattice expansion.
Acknowledgement

The first part of my PhD studies was carried out at the Royal Institute of Technology (KTH) in Stockholm. First of all I would like to thank all the people I worked with during that time. I would like to thank Ulf Karlsson for giving me the opportunity to start as a PhD student at the Materials Physics group at KTH. I also appreciate the help I got at Linköping University from Erik Svedberg, while growing samples at the Thin Film Division. Without the "inne-bandy" teammates at KTH, the time at KTH would have been a great deal less enjoyable. During the first time I learned a lot about vacuum, and other practical things, from Andrius Miniotas - Thank you for that!

To the group of Materials Physics group at Ångström I would like to say: Thank you all, for contributing to the relaxed and pleasant atmosphere both in Uppsala and during our small excursions. In particular I want to thank Matts Björk and Rimantas Brukas for helping me with the sample growth. A special - Thank You! - I address to Pierre Fredriksson at the workshop at Ångström Laboratory for all your help when constructing the in-situ scattering chamber.

My supervisor, Björgvin Hjörvarsson, deserves many thanks from me. Most of all I appreciate your patience, ability to inspire, and never ending will to support me. I also thank my supporter in the hydrogen energy business - roommate since the old days - Emil Johansson, for the company during the long hours on the train. I also appreciate the help I got from Bill Lanford, when preparing the manuscript to this thesis.

The final words I save for the most important person in my life. I love you Susanna!
References


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[56] K. Watanabe and Y. Fukai, 10, 1795 (1980).


Matlab program for thermodynamic analysis
function varargout = iso(varargin)
% ISO Application M-file for iso.fig
% FIG = ISO launch iso GUI.
% ISO('callback_name', ...) invoke the named callback.
% Last Modified by GUIDE v2.0 13-Oct-2002 13:00:32

if nargin == 0
% LAUNCH GUI
fig = openfig(mfilename, 'reuse');
% Use system color scheme for figure:
set(fig, 'Color', get(0, 'defaultUicontrolBackgroundColor'));
% Generate a structure of handles to pass to callbacks, and store it.
handles = guihandles(fig);
guidata(fig, handles);
if nargin > 0
varargout{1} = fig;
end
elseif ischar(varargin{1})
% INVOKE NAMED SUBFUNCTION OR CALLBACK
try
[varargout{1:nargout}] = feval(varargin{:});
% FEVAL switchyard
catch
disp(lasterr);
end
end

% --------------------------------------------------------------------
function varargout = loadbutton_Callback(h, eventdata, handles, varargin)
prompt = {{'File path', 'Type'}};
title = 'Load isotherms';
def = {'c:\data\fev12_2slope2\', 'normal'};
%Give the default folder for the data
answer = inputdlg(prompt, title, 1, def);
path = answer{1};
s = dir(path);
N = length(s)-2;
for i=3:length(s)
  temperatures{i-2} = str2num(strtok(s(i).name, '.'));
%Read the temperatures
end
ip = isoplot(N,answer{2});
%Create isplot object
for i=3:length(s)
  filename = strcat(path,s(i).name);
  str = load(filename);
  iso{i-2} = isotherm(str,temperatures{i-2},answer{2});
end
ip = add(ip,iso);
%Add the isotherm object
hold on;
for i=1:length(ip)
  iso = getIsotherm(ip,temperatures{i});
  data = getData(iso);
  axes(handles.isoaxes);
  plot(data(:,2),data(:,1), 'ro--');
end
hold off;
set(handles.isolistbox, 'String', temperatures);
set(gcbf, 'UserData', ip);
%Save isoplot object

% --------------------------------------------------------------------
function varargout = isolistbox_Callback(h, eventdata, handles, varargin)
ip = get(gcbf, 'UserData');
string = get(handles.isolistbox, 'String');
seliso = str2num(string{get(handles.isolistbox, 'Value')});
isotherm = getIsotherm(ip,seliso);
p = getFitPar(isotherm);
data = getData(isotherm);

if isempty(p.fitPar)
  plot(data(:,2),data(:,1), 'ro--');
else
  order = p.S.order;
  x_fit = x(1):0.001:x(length(x));
  X = ones(length(x),order+1);
  X_fit = ones(length(x_fit),order+1);
  for i=2:order+1
    X(:,i) = x.^(i-1);
    X_fit(:,i) = x_fit.^(i-1)';
  end
  y_fit = p.fitPar'*X_fit';
  for i=1:length(y_fit)
    err = 1.761.*p.S.s.*sqrt(X_fit(i,:)*p.S.C*X_fit(i,:)');
    y_fit_u(i) = y_fit(i) + err;
    y_fit_l(i) = y_fit(i) - err;
  end
  plot(x,y, 'ro', x_fit,y_fit, 'k-', x_fit,y_fit_u, 'b:', x_fit,y_fit_l, 'r:');
end

% --------------------------------------------------------------------
function varargout = plotallbutton_Callback(h, eventdata, handles, varargin)
ip = get(gcbf, 'UserData');
string = get(handles.isolistbox, 'String');
stat = getStat(ip);
hold on;
for i=1:length(ip)
  iso = getIsotherm(ip,str2num(string{i}));
  data = getData(iso);
  p = getFitPar(iso);
  t = getTemperature(iso);
  x = data(:,2);
  y = data(:,1);
  if isempty(p.fitPar)
    plot(data(:,2),data(:,1), 'ro--');
  else
    order = p.S.order;
    x_fit = x(1):0.001:x(length(x));
    X = ones(length(x),order+1);
    X_fit = ones(length(x_fit),order+1);
    for i=2:order+1
      X(:,i) = x.^(i-1);
      X_fit(:,i) = x_fit.^(i-1)';
    end
    y_fit = p.fitPar'*X_fit';
    for i=1:length(y_fit)
      err = 1.761.*p.S.s.*sqrt(X_fit(i,:)*p.S.C*X_fit(i,:)');
      y_fit_u(i) = y_fit(i) + err;
      y_fit_l(i) = y_fit(i) - err;
    end
    plot(x,y, 'ro', x_fit,y_fit, 'k-', x_fit,y_fit_u, 'b:', x_fit,y_fit_l, 'r:');
  end
end

% --------------------------------------------------------------------
function varargout = printbutton_Callback(h, eventdata, handles, varargin)
fig = gcf;
print('-dpng', 'iso.png');
err = p.S.f(p.S.df).*p.S.s.*sqrt(X_fit(i,:)*p.S.C*X_fit(i,:)');
y_fit_u(i) = y_fit(i) + err;
y_fit_l(i) = y_fit(i) - err;
end
function varargout = inflbutton_Callback(hObject, eventdata, handles, varargin)
% Calculates the inflection points of the isotherm
isoplot = get(hObject UserData);
string = get(handles.isolistbox String);
selIso = str2num(string{get(handles.isolistbox Value)});

isotherm = getIsotherm(isoplot, selIso);
data = getStat(isoplot);
sinl = getFinl(isotherm);
fit = getFitPar(isotherm);
p = getFit(p, fit);

[dp, err_dp, p, err_p] = getSlope(a, c, log.txt);
% Displays the slope and error

% --------------------------------------------------------------------

function varargout = modelbutton_Callback(hObject, eventdata, handles, varargin)
% Fit the data to the model: DMU(x) = DH(x) - TDS(x)

isoplot = get(hObject UserData);
sTemp = get(handles.isolistbox String);

for i = 1:length(sTemp);
temp(i) = str2num(sTemp{i});
end

op = optimset('MaxFunEvals', 50000, 'MaxIter', 50000, 'TolX', 1E-8, 'TolFun', 1E-8);

N = 0; X = []; Y = [];
stat = getStat(isoplot);
order = str2num(get(handles.ordermodeledit string));
startmodel = str2num(get(handles.startmodeledit string));
endmodel = str2num(get(handles.endmodeledit string));

for i = 1:length(ip)
% Construct matrices for the least square fit

data = getData(getIsotherm(ip, temp(i)));
N = N + length(data(:, 1));
x = data(:, 2);
y = data(:, 1);
t = temp(i);
F = ones(length(x), 2 + 2 * order);
for i = 2:order + 1
f = x.^(i - 1);
F(:, i) = f;
end
F(:, i + 1) = F(:, i + 1) .* t;
for i = order + 3:2 + 2 * order
f = x.^(i - order - 2) .* t;
F(:, i) = f;
end
X = cat(1, X, F);
Y = cat(1, Y, y);
end

B = X \ Y;
% Calculate and display the least square coefficients

Y_est = B' * X';
% Estimated DMU values

axes(handles.resaxes);
plot(Y_est, Y - Y_est, 'ro');
% Plots the residual data
SSE = Y' * Y - B' * X' * Y;
df = N - order * 2;
s = sqrt(SSE / df);
C = (X' * X)^(-1);
sB = s .* sqrt(diag(C));
% Error

axes(handles.isoaxes);
hold on;
for i = 1:length(ip)
% Plot the fitted isotherms

data = getData(getIsotherm(ip, temp(i)));
L = length(data(:, 2));
x = data(1, 2):0.001:data(L, 2);
x = x';
t = temp(i);
X = ones(length(x), 2 + 2 * order);
for i = 2:order + 1
f = x.^(i - 1);
X(:, i) = f;
end
X(:, i + 1) = X(:, i + 1) .* t;
for i = order + 3:2 + 2 * order
f = x.^(i - order - 2);
X(:, i) = f;
end
Y = B' * X';
for i = 1:length(Y)
err = 1.67 * s .* sqrt(X(i, :) * C * X(i, :));
Yu(i) = Y(i) + err;
Yl(i) = Y(i) - err;
end
plot(data(:, 2), data(:, 1), 'ro', x, Y, 'k-', x, Yu, 'b:', x, Yl, 'r:');
Yu = [];
Yl = [];
end
hold off;
% Construct DM and DIF
text;
XMD = zeros(length(2 * order), order + 2);
XDR = [1 1 XMD];
for i = 1:order
x = x(i:i + order);
XDR(:, i + 1) = x;
end
X = zero(iso, length(order + 2));
XDR(1, 1) = XDR(1, 2) = XDR(1, order + 2) = 1;
for i = 1:order - 1
f = x(i:i + order - 1);
XDR(:, i) = f;
end
D = B' * XMD;
DIF = D - B' * XDR;
for i = 1:length(G Zero calculations)
D(i) = D(i) - y(i) * sqrt(XMD(i, order + 2));
DIF(i) = DIF(i) - y(i) * sqrt(XMD(i, order + 2));
end
end

axes(handles.dhaxes);
plot(x, DH, x, DHu, 'b:', x, DHl, 'r:');
% Plot the result
DH = [x DH' DHu' DHl'];
def = {'c:\tmp\DHDS\'}; %Default folder for the enthalpy and entropy
fname = strcat(def, 'DH.dat'); save(fname, 'DH', '-ascii');
axes(handles.dsaxes); plot(x,DS,x,DSu,'b:',x,DSl,'r:');

DS = [x DS' DSu' DSl'];
def = {'c:\tmp\DHDS\'}; %Default folder for the enthalpy and entropy
fname = strcat(def, 'DS.dat'); save(fname, 'DS', '-ascii');
function obj = isotherm(data,type)
%ISOTHERM Isotherm class constructor
if nargin == 0
    obj.x = [];
    obj.dmu = [];
    obj.temperature = 0;
    obj.x_max = 0;
    obj.x_min = 0;
    obj.fitType = '';
    obj.fitPar = [];
    obj = class(obj,'isotherm');
    return;
elseif isa(data,'isotherm')
    obj = data;
else
    [nr nc] = size(data);
    x = data(:,2);
    switch type
    case 'normal'
        obj.dmu = sqrt(0.987166E-3.*data(:,1));
%Load the data as sqrt of pressure in [atm.]
    case 'ex'
        obj.dmu = 8.617E-2.*t.*log(sqrt(0.987166E-3.*data(:,1)).*(6-x)./x);
%Load the data for fitting all temperatures
    end
    obj.x = x;
    obj.temperature = t;
    obj.x_min = x(1);
    obj.x_max = x(nr);
    obj.N = nr;
    obj.S = [];
    obj.fitType = '';
    obj.fitPar = [];
    obj = class(obj,'isotherm');
end
function t = getTemperature(obj)
    t = obj.temperature;
function ret = getN(obj)
    ret = obj.N;
function ret = getFitPar(obj)
    ret.fitPar = obj.fitPar;
    ret.fitType = obj.fitType;
    ret.S = obj.S;
function [dmu,serr,df,err95] = getDmu(obj,xdata,stat)
    dmu(1) = -1;
    serr = -1;
    df = -1;
    err95 = -1;
    p = getFitPar(obj);
    if (xdata < obj.x_max & xdata > obj.x_min)
        switch p.fitType
        case ''
            dmu = interp1(x,y,xdata,'cubic');
        case 'polynom'
            S=p.S;B=p.fitPar;
            X_data = ones(1,S.order+1);
            for i=2:S.order+1
                X_data(i) = xdata.^(i-1);
            end
            dmu = B'*X_data';
            serr = S.s.*sqrt(X_data*S.C*X_data');
            df = S.df;
            err95 = S.f(S.df).*serr;
        case 'spline'
            dmu = interp1(x,y,xdata,'cubic');
        case 'p_lattice'
            dmu = p_lattice(p{1},xdata,getTemperature(obj),'normal');
        end
    end
function data = getData(obj)
    data(:,2) = obj.x;
    data(:,1) = obj.dmu;
function obj = setN(obj,N)
    obj.N = N;
function obj = setFitPar(obj,p,type,S)
    obj.fitPar = p;
    obj.fitType = type;
    obj.S = S;
function obj = setData(obj,data)
    obj.x = data(:,1);
    obj.dmu = data(:,2);
function obj = isoplot(N,type)
%Isoplot class constructor
obj.isotherms = cell(N,1); %Storing isotherm objects
obj.nrIsotherms = 0;
obj.B = []; %Fitting parameters
obj.C = []; %Error
obj.xl = []; %Degrees of freedom
obj.stat.meanx = 0;
obj.stat.stdx = 0;
obj.type = type;
obj = class(obj,'isoplot');

function ret = getDmuAtConstX(obj,xs)
%Returns the fitted values for DMU at concentration X

for i=1:length(xs)
    k=1;
    for j=1:length(obj.isotherms)
        if ~isempty(obj.isotherms{j})
            [dmu,serr,df,error95] = getDmu(obj.isotherms{j},xs(i),stat);
            if (dmu ~= -1)
                dmus(k) = dmu;
                serror(k) = serr;
                dfs(k) = df;
                err95(k) = error95;
                temperatures(k) = getTemperature(obj.isotherms{j});
            end
        end
    end
    ret(i).data = [temperatures;dmus]';
    ret(i).x = xs(i);
    ret(i).serr = serror;
    ret(i).df = dfs;
    ret(i).err95 = err95;
    temperatures = [];
    dmus = [];
    serror = [];
    dfs = [];
    err95 = [];
end

function type = getType(obj)
    type = obj.type;

function stat = getStat(obj)
    stat = obj.stat;

function isotherm = getIsotherm(obj,t)
%Returns a isotherm of temperature t

isotherms = obj.isotherms;
for i=1:length(isotherms)
    if getTemperature(isotherms{i})==t
        isotherm = isotherms{i};
        break
    end
end

function obj = add(obj,isotherm)
%Add an isotherm object

obj.nrIsotherms = length(isotherm);
obj.isotherms = isotherm;
X = [];
for i=1:length(obj.isotherms)
    X = [X,obj.isotherms{i}];
end
obj.stat.meanx = mean(X);
obj.stat.stdx = std(X);

function obj = setIsotherm(obj,isotherm)
%Set a new isotherm object

t = getTemperature(isotherm);
for i=1:length(obj.isotherms)
    if getTemperature(obj.isotherms{i})==t
        obj.isotherms{i}=isotherm;
        break
    end
end

function n = length(obj)
    n = obj.nrIsotherms;
function obj = vanhoff(isoplot,X)
%Vanhoff class constructor
if nargin == 0
    obj.iso_x_lines = 0;
    obj = class(obj,'vanhoff');
else
    dmuc = vanhoff(isoplot);
    dmuc = isoplot;
elseif isclass(isoplot,'vanhoff')
    obj = isoplot;
else
    [nR nC] = size(isoplot);
    dmuAtConstX = getDmuAtConstX(isoplot,X);
    type = getType(isoplot);
    for i=1:length(dmuAtConstX)
        ydata = dmuAtConstX(i).data(:,2);
        xdata = dmuAtConstX(i).data(:,1);
        obj.iso_x_lines(i).x = dmuAtConstX(i).x;
        switch type
            case 'normal'
                obj.iso_x_lines(i).data = [xdata;8.617E-2.*(xdata).*log(ydata)];
            case 'ex'
                obj.iso_x_lines(i).data = [xdata;ydata];
        end
        obj.iso_x_lines(i).serr = dmuAtConstX(i).serr;
        obj.iso_x_lines(i).df = dmuAtConstX(i).df;
        obj.iso_x_lines(i).err95 = dmuAtConstX(i).err95;
    end
    obj = class(obj,'vanhoff');
end
function [a,b,siga,sigb,chi2,q] = wlinfit(obj,x,y,sig)
%Calculates weighted linear least square sig=stderror of input y data
ndata=length(y);
wt=1./(sig.^2);
ss=sum(wt);
sx=sum(x.*wt);
sy=sum(y.*wt);
sxoss=sx/ss;
t=(x-sxoss)./sig;
st2=sum(t.^2);
b=sum(t.*y./sig);
b=b/st2;
a=(sy-sx*b)/ss;
siga=sqrt((1+sx*sx/(ss*st2))/ss);
sigb=sqrt(1/st2);
chi2=sum(((y-a-b*x)./sig).^2);
q=gammainc(0.5*(ndata-2),0.5*chi2);
function [x,y,serr,df,err95] = getData(x,obj)
for i=1:length(obj.iso_x_lines)
    data = obj.iso_x_lines(i).x;
    test = obj.iso_x_lines(i).x-x;
    if (abs(test)<0.00001)
        x = obj.iso_x_lines(i).data(:,1);
        y = obj.iso_x_lines(i).data(:,2);
        serr = obj.iso_x_lines(i).serr;
        serr = serr';
        df = obj.iso_x_lines(i).df;
        df = df';
        err95 = obj.iso_x_lines(i).err95;
        err95 = err95';
    end
end
function [x,DH,serror,df] = hplot(obj)
%Construct DH from the linear least square
for i=1:length(obj.iso_x_lines)
    t = obj.iso_x_lines(i).data(:,1);
    dmu = obj.iso_x_lines(i).data(:,2);
    serr = obj.iso_x_lines(i).serr;
    serr = serr';
    err95 = obj.iso_x_lines(i).err95;
    err95 = err95';
    [a b siga sigb chi2 q] = wlinfit(obj,t,dmu,serr);
    DH(i) = a;
    x(i) = obj.iso_x_lines(i).x;
    serror(i) = siga;
    df(i) = length(dmu)-2;
end
DH = 1E-3.*DH';
x = x';
serror = serror';
df = df';
function [x,DS,serror,df] = splot(obj)
%Construct DS from the linear least square
for i=1:length(obj.iso_x_lines)
    t = obj.iso_x_lines(i).data(:,1);
    dmu = obj.iso_x_lines(i).data(:,2);
    serr = obj.iso_x_lines(i).serr;
    serr = serr';
    err95 = obj.iso_x_lines(i).err95;
    err95 = err95';
    [a b siga sigb chi2 q] = wlinfit(obj,t,dmu,serr);
    DS(i) = b;
    x(i) = obj.iso_x_lines(i).x;
    serror(i) = sigb;
    df(i) = length(dmu)-2;
end
DS = -DS';
x = x';
serror = serror';
df = df';
Acta Universitatis Upsaliensis

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