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Metallic superlattices: quasi two-dimensional playground for hydrogen

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Abstract

Hydrogen in superlattices, whose constituents have different hydrogen affinities, comprises a new class of hydrogen absorbing materials. The period of the absorption potential can be made as small as two monolayers, which implies highly anisotropic host mediated hydrogen–hydrogen (H–H) interactions. As the correlation between the hydrogen atoms can be influenced in an almost arbitrary way, it is possible to create an ensemble whose nature is neither three- nor two-dimensional, but something in between.

By changing the strain state of the constituents, the interaction between the hydrogen atoms in vanadium can be changed from being attractive (for biaxial tensile strain) to repulsive (for biaxial compressive strain). This has been observed experimentally for, e.g., 2 nm vanadium layers in Mo–V and Fe–V superlattices. The biaxial strain state is shown to have a gigantic effect on the hydrogen induced lattice expansion. By changing the strain state from tensile to compressive, in ≈2 nm V layers, the hydrogen induced lattice expansion is altered by a factor of ten. This feature is expected to affect the diffusion properties of hydrogen in these structures dramatically.

The principal orientation of the crystal axis of the host material, with respect to the boundary planes, is found to have large impact on the host mediated H–H interactions. The theoretical understanding of hydrogen in quasi-two-dimensional potentials is still rudimentary, and more theoretical and experimental work is required for a detailed understanding of these problems.

In the present work, we will treat the implications of the extension and amplitude of the hydrogen absorption potential, and we will demonstrate the existence and impact of weak and strong modulation of the host potential on the hydrogen uptake. The influence of the strain state on the hydrogen absorption and the host mediated H–H interactions will also be treated, and we will show that the phase diagram can, in some cases, be altered in a controllable way.

Keywords: Hydrogen; Superlattices; Lattice expansion; Phase formation; Dead layers; Strain; 68.65.+g; 01.30.Rr; 65.50.+m; 64.75.+g; 62.20.Dc; 61.10.−i

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1. Introduction

During the last century, solid state physics has undergone a dramatic development. In the beginning of the century, pure materials were the topic of interest. The next step was to investigate alloys and composite materials. After using up these degrees of freedom, the spatial distribution of the chemical elements became the next variable to explore, which is the current topic of interest. The most refined materials of this kind are the superlattices and quantum dots.

The interest in metallic superlattices and multilayers has increased dramatically during the last years. One of the main reasons for the intensified activity is the discovery of the giant magneto resistance (GMR). During the same period the quality of the chemically modulated samples has improved dramatically, and growth of epitaxial superlattices with atomically sharp interfaces has been demonstrated for a number of metal combinations. These materials exhibit a number of interesting properties, such as increased hardness and wear resistance [1], quantised vortex growth [2], large neutron reflectivity (used in supermirrors) [3], as well as GMR [4].

The pioneering investigations of interaction of hydrogen with artificial superlattices were performed by Miceli, Zabel and co-workers [5–7]. Their investigations of the Nb–Ta superlattices revealed many novel phenomena related to the finite size of the host material, including hydrogen induced strain modulation [5] and hydrogen phase related critical fluctuations [6,7]. The absorption potentials in Nb and Ta are similar and give rise to only a weak modulation in the hydrogen concentration, at all but low temperatures. This material combination can therefore be classified as having a weak modulation potential, with respect to hydrogen absorption.

Material combinations where the constituents have a large difference in hydrogen affinity can be classified as having strong modulation potentials. Examples of such combinations are Mo–V [8], Fe–V [9,10], and Nb–Fe [11] multilayers. The hydrogen uptake and the associated lattice

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changes for Mo–V (001) and (011) samples were investigated by Hjörvarsson and co-workers [8,12–14]. For Mo–V and Fe–V, the difference in the absorption potential is large (≈0.6 eV), which implies that the hydrogen is exclusively located in the vanadium layers in a broad temperature range. When Mo–V superlattices are grown epitaxially, the coherence strain causes the lattice parameter perpendicular to the growth direction to increase in V and decrease in Mo, compared to their bulk values. In Fe–V superlattices the coherence strain causes the lattice parameter perpendicular to the growth direction to decrease for V. Thus both electron transfer and non-isotropic lattice parameter changes can be expected in epitaxially grown Mo–V and Fe–V superlattices. Both effects are expected to influence the hydrogen uptake of these materials.

In this article, we will give a brief summary of the work on hydrogen in superlattices, emphasising the work on strongly modulated potentials. The phase formation and the interaction potentials will be discussed. These materials are interesting on their own, and at the same time provide valuable ways of testing models for the interaction of hydrogen in materials, including phase transitions of the hydrides and the corresponding (critical) fluctuations. The acquired knowledge can be used to tailor materials with desired properties. As an example, phase separation can be hindered by choosing the appropriate boundary conditions.

2. Weakly modulated potentials

A summary of the current understanding of hydrogen in Nb–Ta superlattices is found in a recent article [15]. No other superlattices having a weak modulation of the hydrogen concentration have been studied to our knowledge.

Nb and Ta are both bcc metals and have close to identical lattice parameters, which ensures almost strain free samples. The samples investigated so far were all Nb–Ta (011). Only low hydrogen concentrations were considered, as the samples were found to lose crystal coherence at concentrations exceeding the α-phase limit. The hydrogen induced lattice expansion was found to be gigantic, almost three times larger than the bulk values of the constituents. No plausible interpretation of the origin of the anomalous lattice expansion is presently available to our knowledge.

When the samples are cooled with constant average hydrogen concentration, there is a change in the intensity of the ±1 satellites in the X-ray diffractogram. The implication of the change in intensity is a preferential population of the Nb layers, which is consistent with the enthalpy changes of the constituents. The host-mediated hydrogen interaction in the Nb layers is repulsive, which prohibits the completion of the one-dimensional hydrogen modulation in the growth direction. Ab initio electron structure calculations of hydrogen in Nb–Ta are found in [16].

3. Strongly modulated potentials

By far the most extensively investigated hydrogen absorbing material embedded in a non-absorbing matrix is vanadium. Consequently, the main emphasis here will be on Fe–V and Mo–V superlattices. Other works of interest are the hydrogen diffusion measurements in Ni–Ti multilayers [17], improved neutron reflectivity of hydrogen loaded Ni–Ti multilayers [18], the Mössbauer investigations of the magnetic properties of hydrogenated Fe–Ti multilayers [19], and hydrogen induced changes of the magnetic and structural properties of Fe–Ce [20].

3.1. *“Dead” layers*

During the initial investigations of the hydrogen uptake of Mo–V superlattices, it was discovered that only a part of the V layers absorbed hydrogen [8]. This observation was interpreted as an interface effect originating in a charge transfer from Mo to V. At low hydrogen concentrations, three monolayers closest to the interfaces were found to be almost depleted of hydrogen. Multilayered superlattices (i.e. superlattices with different wavelengths built on top of each other) were chosen for these experiments to exclude all uncertainties in the loading conditions. The hydrogen concentration was measured in the multilayered superlattices using the $^{1}H(^{15}N, \alpha\gamma)^{12}C$ nuclear resonance reaction. A typical sample sequence is illustrated in Fig. 1, where we also define the concepts interior and interface regions. We refer to the interior region when discussing concentrations throughout the article, if not otherwise stated. The extension of the depleted region in V is surprisingly large, as one would expect that only hydrogen atoms in the V plane nearest to the Mo interfaces should be affected, since the charge transfer (which was inferred to be the cause) is expected to be of short range. With increasing hydrogen content in the superlattices the interfaces were gradually filled, but still leaving the last V monolayer empty at an interior concentration $H/V=1.0$ [21]. The difference in the absorption potential between the third and the fourth atomic planes was later determined to be approximately 25 meV [22]. This interpretation was supported by ab initio calculations of the free electron density in Mo–V superlattices [23].

The influence of alloying in the spacer layer, which alters the strain state and the modulation of the interstitial electron density, on the hydrogen uptake was investigated in Mo_xV_{1-x}–V ($x=0.5$, 0.75, 1) superlattices [24]. The experimental results are displayed in Fig. 2. The extension of the charge transfer was measured using the relation between hydrogen solubility and interstitial electron density. In Mo–V superlattices the extension of the charge

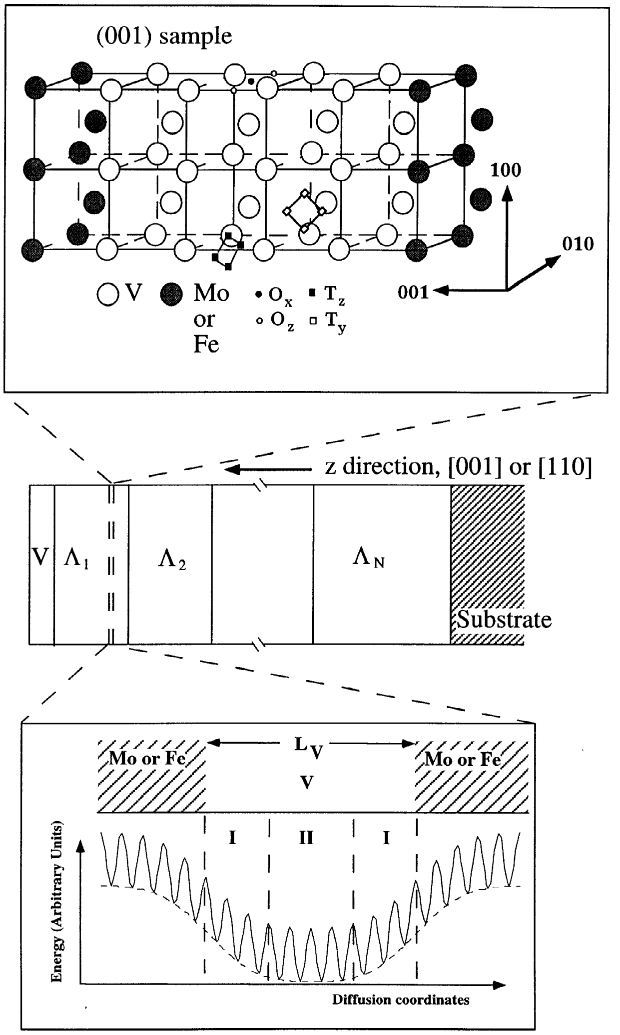

Fig. 1. Schematic illustration of a multilayered superlattice and the corresponding absorption potential for hydrogen. The regions marked I and II in the figure are referred to as interface and interior regions respectively.

transfer was found to be three monolayers as mentioned already. In $Mo_{0.75}V_{0.25}$–V the charge transfer region was found to be two monolayers, and in a $Mo_{0.5}V_{0.5}$–V no charge transfer was observed. Using a fairly crude theoretical estimation it was concluded that the strain and the effect of alloying (through the modulation of the interstitial electron density) influences the magnitude of the charge transfer equally. The resulting effect is a decrease of charge transfer with increasing degree of alloying of the Mo layer.

The existence of dead layers was also observed in Fe–V superlattices. The extension of the region with less energetically favourable sites was determined to be three monolayers, just as for the Mo–V superlattices. Surprisingly, the energy difference between the third and the fourth atomic plane was found to be larger than in Mo–V: roughly 90 meV as determined by van't Hoff analysis (87±6 meV) and the population of the different regions of a multilayered superlattice (97±5 meV).

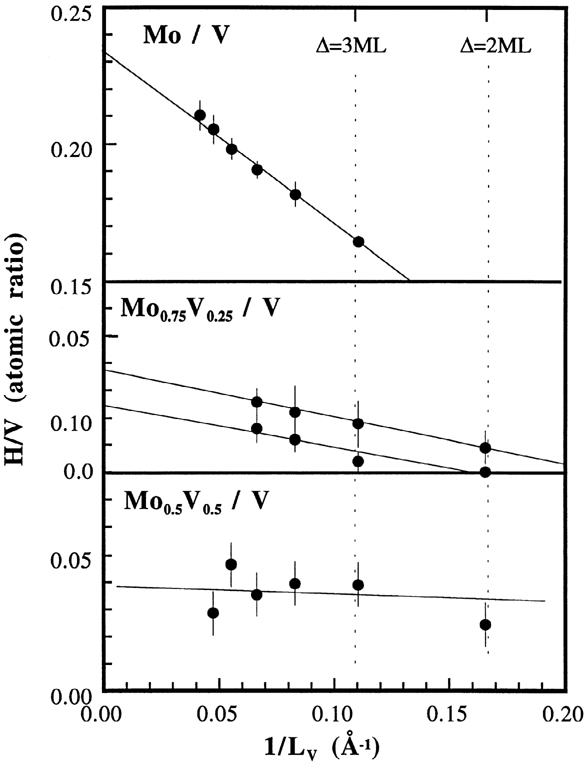

Fig. 2. The change of the distribution within a multilayered superlattice upon change in electron density modulation and strain state. For details, see Section 3.1. Adapted from [25].

3.2. Lattice expansion

The experimental results treated here are for (001) oriented samples. For the (110) orientations, see Section 3.4.

In the first article on the hydrogen uptake in Mo–V (001) superlattices [8], it was found that the hydrogen induced lattice expansion for coherent superlattices was insignificant compared to the H-induced expansion in bulk vanadium. However, the experimental data were limited, which called for more extensive investigations. The details of the hydrogen induced expansion were later explored by Stillesjö et al. [13], at temperatures above 200°C. The relation between the volume expansion and the lattice parameters for bulk samples is commonly approximated by,

$$\frac{\Delta V}{V} = k_b c_H \approx 3\frac{\Delta a}{a} \tag{1}$$

where a is the lattice parameter in any specific direction. The authors estimated the expected ratio of the bulk and the superlattice lattice expansion coefficients by including the clamping effects on the elastic response and the influence of the population of different sites by the hydrogen atoms on the strain components. It was assumed that the hydrogen atoms were equally distributed among the tetragonal x, y and z sites, and the stress in the 100, 010, and 001 directions was assumed to be the same for the superlattice as for a bulk sample. No discussion on the type of site was offered, but H is found in tetrahedral sites in bulk V under the current conditions.

Since two of the crystal directions are clamped, only the 001 stress component results in a strain of the lattice. The relation between the expansion coefficients is thereby reduced to,

$$k_s \approx (1 + 2\frac{C_{12}}{C_{11}})\frac{k_b}{3} \qquad (2)$$

where C_{11} and C_{12} are the elastic constants of V. The expected result is $k_s \approx 0.06$ using the elastic constants of bulk V, in a reasonable agreement with the obtained value of 0.042(3). The value of k_b for bulk vanadium is 0.19(1).

The hydrogen induced lattice expansion of Fe–V superlattices was found to deviate dramatically from that of Mo–V [10]. The expansion at concentrations $H/V < 0.2$ (atomic ratio), was found to be 0.35, i.e., almost ten times larger than in Mo–V superlattices. It is interesting to note that the only difference is the strain state of the vanadium layer. At concentrations above 0.2, the lattice expansion deviated significantly from linear behaviour. A collection of the experimental results is shown in Fig. 3, where the expansion is plotted versus the average hydrogen content. The concentration of the interior region is obtained by multiplying by a factor of 2.2.

A reasonable conclusion from these observations is that at low concentrations the hydrogen atoms reside in tetrahedral positions in Mo–V superlattices above 200°C, and in octahedral z sites in Fe–V superlattices in the temperature range 30–250°C.

3.3. Thermodynamics and phase formation

The thermodynamic properties of hydrogen in Mo–V [12] and Fe–V [9] are fairly well established experimentally. The investigated thicknesses of vanadium range from six to fourteen monolayers. By changing the strain state of V from tensile to compressive, the interaction potential changes sign. The host mediated hydrogen–hydrogen (H–H) interaction is attractive for eight monolayers of V under biaxial tensile strain and repulsive when compressive biaxial strain is applied. When the extension of the V layers is six monolayers the hydrogen interaction seems to vanish when biaxial compressive strain is present. In Fig. 4 we display the deduced enthalpy for ≈2 nm vanadium layers (≈14 monolayers) under biaxial tensile strain (Mo–V) and biaxial compressive strain (Fe–V).

The entropy change, with the gas phase as a reference, appears to be almost constant over the concentration range 0.2 to 1 in H/V, when biaxial tensile strain is present

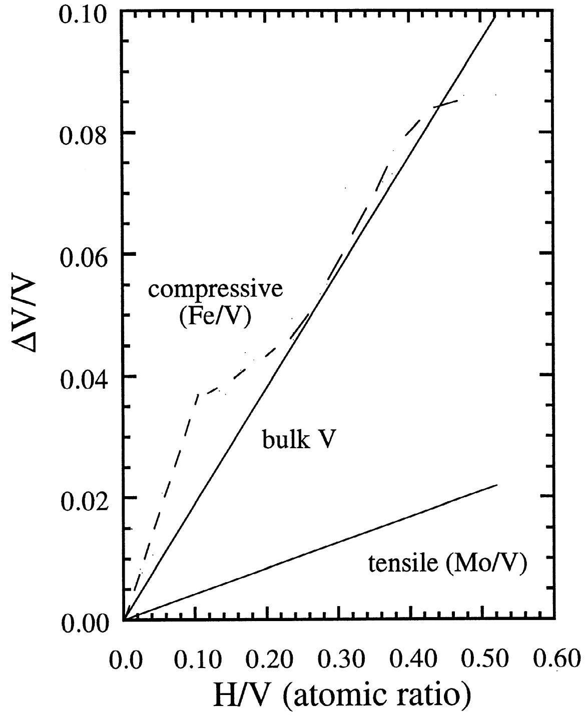

Fig. 3. Hydrogen induced lattice expansion of ultra thin vanadium layers under biaxial, compressive and tensile strain. The bulk vanadium values are also displayed. Observe that the hydrogen content and the expansion are average values. Adapted from [10,13].

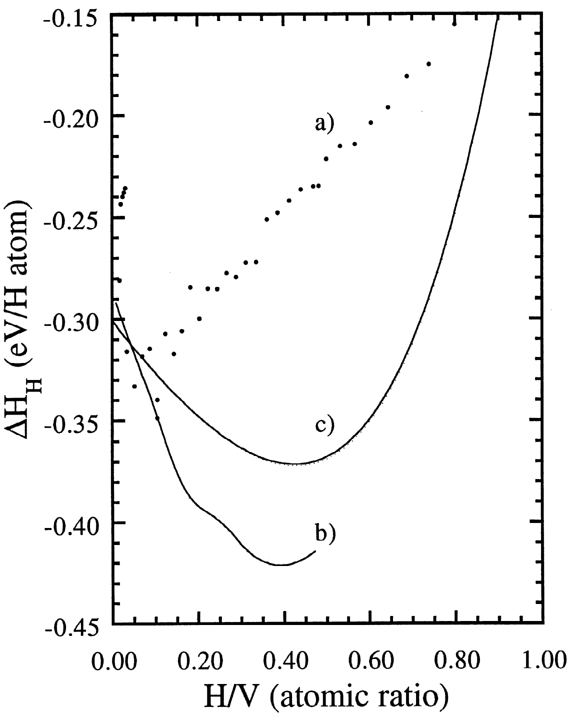

Fig. 4. The change in enthalpy in different strain states of vanadium. Results from Fe–V ($L_V = L_{Fe} = 2.0$ nm) is labelled by (a), Mo–V ($L_V = L_{Mo} = 2.1$ nm) is labelled by (b), and bulk vanadium by (c) in the figure. Adapted from [9,12].

(Fe–V). The implication is an absence of ordering, which is also supported by the enthalpy data and the invariance of $\delta^2\rho/\delta T^2$ (ρ is the in-plane resistance of the superlattice and T the temperature) at temperatures as low as 80 K [9]. For the samples with a H-containing interior region (i.e. those with $L_V > 6$ monolayers), a critical concentration was inferred. The critical concentration was found to be independent of temperature and corresponding to an interior concentration of 0.16 and 0.17, respectively, in the 1.6 and 2.0 nm vanadium layers. For the thinnest layers of V, a critical concentration of 0.2 was inferred. A similar feature is observed at low concentrations of hydrogen in bulk yttrium [25]. For temperatures up to 130°C and H/Y below approximately 0.20 a metastable, ordered solid solution denoted α^*-phase is observed instead of the regular, random α-phase. The critical concentration for the transition from the α^*- to the $(\alpha+\beta)$-region is independent of temperature, as observed for H in the thin V layers. If the interaction is purely repulsive in the concentration range considered, higher order poles in the elastic interaction are required to describe the H–H interaction [26], as direct interaction is not plausible at such low concentrations.

3.4. Orientation dependence

Almost no work has been performed on the influence of the orientation of the crystallographic axes, with respect to the boundary planes, on the hydrogen absorption. The only published data is from Hjörvarsson et al. [14], where it is shown that the dead layer is two monolayers at low concentrations for Mo–V (011) superlattices. The spatial extension of the interface region is therefore the same as for Mo–V (001). At higher concentrations the extension of the dead layer seems to increase, an effect which must be related to a preferential population of every second atomic plane like in the bulk β-phase. The hydrogen induced lattice expansion is found to be approximately 3% in the 001 direction at H/V=0.5. No detailed X-ray diffraction analysis at different hydrogen concentrations exists so far.

Thermodynamic properties have been investigated with the method used in the Mo–V (001) and Fe–V (001) experiments, and the results show that the host-mediated H–H interaction is repulsive [27]. A detailed study is in progress.

4. Current challenges

4.1. Phase formation

It is only in the last few years that experiments on phase formation in extremely thin metallic films have been realised. The fundamental theory of the effects of reduced dimensionality and strain states on the phase formation was established in the early 1970's by Alefeld, Wagner and their co-workers [26,28]. Although the fundaments are well established and the conceptual framework is functional, there remains a number of questions to be addressed. There is, first of all, the crossover from the long range elastic to the direct interaction between the hydrogen atoms, involving the electronic structure and higher order poles in the elastic field. The strain field theory is still unable to account for the anomalous lattice change in the bulk-like β-V_2H phase. Much work remains before obtaining the details for bulk materials and a quantitative description of hydrogen in multilayers and superlattices.

4.2. Diffusion.

According to the Flynn–Stoneham theory of diffusion [29], the mobility of hydrogen in metals is closely linked to the atomic volume change. This phenomenon is often referred to as the self-trapping of interstitials. Self-trapping is especially important when the hydrogen resides in octahedral sites, and the transport is characterised by a direct transport. When residing in tetrahedral positions, the lattice activated diffusion is believed to be more prominent. The volume dependence of the diffusion rate for octahedral sites can be estimated, using [29]:

$$E_a \propto \left(\frac{\Delta V}{V}\right)^2 \tag{3}$$

As the change in strain state of vanadium may change the macroscopic expansion by an order of magnitude, we expect a very strong anisotropy in the diffusion barriers and a ‘‘quasi-two-dimensional’’ diffusion, which should exhibit large anomalies, in strained vanadium layers. These experiments are difficult to perform at present, as most methods require thicker samples than those available today. ‘‘Surface’’ muons and refined nuclear magnetic resonance techniques are expected to be accessible in the near future.

If a superlattice without steps at the interfaces could be realised, quantum effects would be expected to be large. The protons are localised in one dimension, which might cause a large two-dimensional delocalisation at low temperatures. The strain associated with atomic steps at the interfaces is however expected to cause inhomogeneities in the absorption potential, thereby hindering delocalisation and coherent tunnelling.

4.3. Fine tuning of magnetic properties

As noted in the introduction, the observation of the GMR caused an intensified activity in the field of multilayers and superlattices. The current mainstream is to combine metals and alloys in complex combinations to obtain the desired properties.

The simplest alloy of all is a metal hydride. The conductivity and magnetic properties of metal hydrides are well understood and the field has been self-sustaining for decades. The unique feature of metal hydrides is the reversibility of the chemical composition. It has been shown that the structural quality of superlattices can be maintained through hundreds of loading–unloading cycles. Even though this feature is interesting in itself, the possibility of gradually adjusting the chemical composition, and thereby the density of states at the Fermi level and the lattice parameter, is even more fascinating. In the early work on RKKY coupling, GdH_x $(0<x\leq3)$ was one of the most important systems for experimentally verifying the oscillatory nature of the magnetic coupling. Changing the chemical composition of a hydrogen absorbing spacer layer could prove to be an important way of obtaining the detailed nature of the interlayer coupling in magnetic superlattices.

There have been several attempts to change the magnetic coupling through the spacer layer by hydrogen loading. In Nb it has been demonstrated that the coupling can be switched in a reversible manner, from antiferromagnetic to ferromagnetic coupling of the Fe layers [11]. In V, the presence of hydrogen seems to reduce the coupling between the Fe layers [30], which is somewhat surprising. According to Coehoorn [31] the introduction of hydrogen was expected to make the vanadium layer more like chromium. Chromium is known to give rise to a strong coupling, in e.g. Fe–Cr superlattices.

4.4. Optical properties.

As the reflectivity is dependent of the total thickness of the film, optically active components may require material thicknesses which will not withstand repeated cycling, due to strain from phase separation. Although phase transitions can be suppressed by reducing the extension of the hydrogen absorbing material (e.g. by forming thin films), the formation of a superlattice could be more rewarding. As one of the driving forces for phase separation is the long range elastic interaction, a distortion of the strain field could facilitate a complete suppression of a disorder–order phase transition. The spacer does not by necessity have to be optically transparent in bulk form when transparency is required. The thickness of the ‘‘coherence killer’’ does not have to be larger than a few atomic planes. As the optical properties of thin YH_x $(0<x\leq3)$ films have gained much attention lately [32], this feature may be of significant interest.

5. Conclusions

Hydrogen in thin films, multilayers and superlattices is a new branch in the field of hydrogen in metals. The experimental activity has increased rapidly during the last years, but the influence of the finite size is only rudimentarily understood. The development of this field will result in a better understanding of the interplay between the host-mediated H–H long range elastic interaction and the direct interaction. This knowledge could be used for fine tuning of the properties of hydrogen absorbing materials to be used in a wide range of applications, such as optical and magnetic switches and sensors, and for energy storage.

Acknowledgments

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