PHYSICAL REVIEW B **93**, 134107 (2016)

Hydrogen in vanadium: Site occupancy and isotope effects

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(Received 6 January 2016; revised manuscript received 10 March 2016; published 15 April 2016)

We discuss the influence of site occupancy on the absorption of the hydrogen isotopes H and D in thin V(001) layers. By growing V(001) under biaxial compressive strain in Fe/V(001) superlattices, the hydrogen (H as well as D) is forced to reside exclusively in octahedral (O_z) sites, even at the lowest concentrations. A weakening of the isotope effects is observed when hydrogen resides in octahedral as compared to tetrahedral sites.

DOI: 10.1103/PhysRevB.93.134107

I. INTRODUCTION

The relative mass differences of the hydrogen isotopes (H, D, and T) are the largest of any elements and therefore are often regarded as the model system for investigations of isotope effects. Substantial work has been devoted towards investigations of these effects in metal hydrides [1], for example, with respect to isotherms, phase boundaries, vibrational energies, and diffusion. Although isotope effects can be viewed as reasonably well understood, there are still questions that remain unresolved. For example, the solubility of the hydrogen isotopes exhibits completely different behavior in V as compared to Pd: In the α phase, H exhibits higher solubility in Pd than D, while the opposite is observed in V [2]. The ordered phases (for example, the β phases) exhibit similar anomalies. The ordering temperature of the V_2H β phase is higher than that of V_2D, while the opposite effect is found in Nb [1].

Isotope effects are not always observed in transition metal hydrides, for example, the incoherent spinodal temperature appears to be the same for H and D in Nb and Ta, while pronounced differences are observed in V [3]. Similar trends are observed in the concentration dependence of the activation energies of H and D: Clear isotope effects are observed in the diffusion of H and D in Nb and Ta at low concentrations. The difference diminishes with increasing concentrations of H(D) in Nb, while the difference is retained at all concentrations in Ta [4].

The presence of pronounced isotope effects has caused considerable interest for V hydrides. The early work on H and D in V includes, for example, the determination of the phase diagram of V-H(D) using x-ray diffraction measurements [5,6]. In these experiments, the ordering temperature (T_c) of V_2H was determined to be about 75 K higher than that obtained for V_2D. Later, Pesch and Schober presented more accurate V-H(D) phase diagrams, including the hydrogen site occupancy in which the T_c of V_2H is determined to be about 70 K higher than the one for V_2D [7]. V-T was reported to have the same general tendencies as V-D while exhibiting an even lower ordering temperature ($\simeq$375 K) [8]. Replacing H with D can result in large changes in the phase diagram. For example, the ϵ phase (O_z sites are filled with probability 1/2) exists in V_2H between 448 and 470 K. This phase is not observed when H is replaced with D [7] and the local vibrational modes of the hydrogen isotopes are identified as the major cause of the changes [9].

Here, we address, experimentally as well as theoretically, the implications of site occupancy on the isotope effects of H and D in V. The choice of V is based on the possibility to alter the site occupancy as well as the thermodynamic properties of hydrogen, by strain and confinement of hydrogen in the V layers. In bulk V, H and D reside in tetrahedral sites (T sites) at low concentrations (α phase) [10] while one specific O-site is occupied in the ordered β phase (typically defined as O_z). Corresponding changes are not observed in Nb and Ta hydrides [1]. In V, a shift from tetrahedral- to octahedral-site occupancy is possible [11], even at the lowest concentrations [12], by applying biaxial compressive strain on V. This biaxial compressive strain state can, e.g., be obtained by growing Fe/V(001) superlattices on MgO(001) substrates [13]. The hydrogen uptake in Fe is strongly endothermic and the hydrogen concentration in the Fe layers can therefore safely be neglected. A structural coherency in a strained superlattice can only be obtained up to a critical thickness of the constituents. When the layer thickness exceeds this upper limit, the samples exhibit a profound increase of structural defects [13,14]. The investigations were therefore performed on V layers in the few monolayer limit. The extreme confinement results in profound finite size effects in the hydrogen uptake [15] which need to be accounted for. The influence of confinement on the results is elucidated by investigating two samples with different thicknesses of the V(001) layers (7 and 21 monolayers).

II. EXPERIMENTAL DETAILS

The Fe_1/V_7 (001) and $(FeV)_6/V_{21}$ (001) samples used in this study were epitaxially grown on $10 \times 10 \times 0.5$ mm^3 MgO(001) substrates using the recipe developed by Isberg *et al.* [13]. The subscript represents the number of monolayers (ML) of each layer. The total number of bilayers was chosen to be 25 and the samples were capped with 5 nm palladium layers, facilitating hydrogen dissociation and recombination. The Pd layers also provide protection from oxidation upon exposure to air.

The use of a superlattice instead of a single V layer implies substantial benefits: By using a superlattice with 25 repeats, we simultaneously investigate the hydrogen uptake of 25 V layers. Furthermore, the strain state of the layers, the crystal quality, and the thickness variations of the layers are easily determined by x-ray analysis [13]. The choice of materials determines the sign of the biaxial strain field in the constituents, while their thickness ratio determines the amount. For example, the epitaxial growth of Mo/V(001) superlattices results in a biaxial tensile strain in the V layers [14] while the growth of Fe/V(001) yields a biaxial compressive strain state in V [13].

Finally, the use of multiple layers increases the accuracy of the measurements, as the penetration depth of the light is substantially larger than one repeat distance of the Fe/V bilayers.

The experimental setup used for the absorption measurements consists of an ultrahigh vacuum chamber with two pressure gauges (1 and 1000 Torr full scale). The samples were mounted on a ceramic holder inside an externally heated silica tube in which the temperature of the sample and the surrounding gas can be controlled (300–650 K). The Fe_1/V_7 sample was investigated in the temperature range 323–443 K, while the temperature range for the experiments on the $(FeV)_6/V_{21}$ sample was 441–553 K. These temperatures were chosen with respect to the ordering temperatures of the hydrogen in the V layers. Simultaneous determinations of the transmission of light and changes in resistivity were used to extract pressure-composition-temperature (p-c-T) isotherms and ordering in the hydrogen, respectively, as described by Prinz *et al.* [16]. A light-emitting diode (LED) with a wavelength of 639 nm was used to determine the changes in the optical transmission and the change in resistivity was determined by a combined sourcemeter and nanovoltmeter. The calibration of the optical response was obtained by using isotherms determined by neutron reflectivity [17] for one of the samples.

III. THEORETICAL METHODS

The calculations were performed using the Vienna *ab initio* simulation package (VASP) [18–21]. We used a modified version of VASP, in which it is possible to perform constrained cell relaxations with one or more lattice vectors fixed (National Supercomputer Centre at Linköping University). The interactions between the electrons and the nuclei were obtained using the projector-augmented-wave method [22,23]. The generalized gradient approximation (GGA) in the parametrization of Perdew-Burke-Ernzerhof (PBE) [24,25] approach was used to approximate the exchange and correlation terms [26,27]. A conjugate gradient algorithm was used to relax the position of the atomic nuclei, minimizing the total energy. A $21 \times 21 \times 21$ Γ-centered Monkhorst-Pack [28] k-point grid was used to sample the Brillouin zone. The energies of the H_2 and D_2 molecules were calculated in a ($8 \times 8 \times 8$ Å) cell using only the Γ point to sample the Brillouin zone. The zero-point energies (ZPEs) were calculated using the harmonic approximation.

For T-site occupancy (bulk), the hydrogen concentration corresponding to $[H(D)/V] = 0.25$, a $(1 \times 1 \times 4)$ supercell was used. For the concentrations corresponding to $[H(D)/V] = 0.50$ and 1.00, we used a $(1 \times 1 \times 2)$ supercell. For $[H(D)/V] = 1.00$, two maximally separated T sites were chosen for H occupancy in order to minimize the repulsive H-H interaction. For O_z-site occupancy, a $(1 \times 1 \times 4)$ supercell was used for $[H(D)/V] = 0.25$ and a $(1 \times 1 \times 2)$ supercell for $[H(D)/V] = 0.50$, while the two atoms' bcc unit cell was used for $[H(D)/V] = 1.00$. For T-site occupancy of the H(D) atoms, the unit cells are allowed to expand (or contract) freely in all directions during volume relaxation, while for O_z-site occupancy, the volume changes were constrained to the z direction. This constraint was used to mimic the experimental conditions in clamped layers such as in epitaxial superlattices. The lattice constants in the x and y directions were set to 2.98 Å for the calculations of O_z-site occupancy.

IV. RESULTS AND ANALYSIS

A. Enthalpy and site occupancy

The enthalpy and entropy of the hydrogen isotopes were obtained from a Van't Hoff analysis as described in Ref. [29]. The results are shown in Fig. 1 along with literature data on bulk V taken from Ref. [30]. All concentrations are in the atomic ratio of the elements and the isotherms are shown as an inset in the figure. These were obtained from the disordered phase of hydrogen in V, well above the critical temperature of the hydride formation. The absence of ordering was verified by resistivity measurements, as described in Ref. [16]. As seen in Fig. 1, there are clear differences in the results obtained from the superlattices and those obtained from bulk. In bulk V, pronounced isotope effects are observed in Δh. This is in stark contrast to the results obtained from the superlattices, in which isotope effects are smaller than the uncertainty in the measurements. Similar trends are observed in Δs and Δh.

The differences between bulk and superlattices can be argued to be dictated by three contributions: (i) Hydrogen resides in octahedral sites in the superlattices [12,31] while

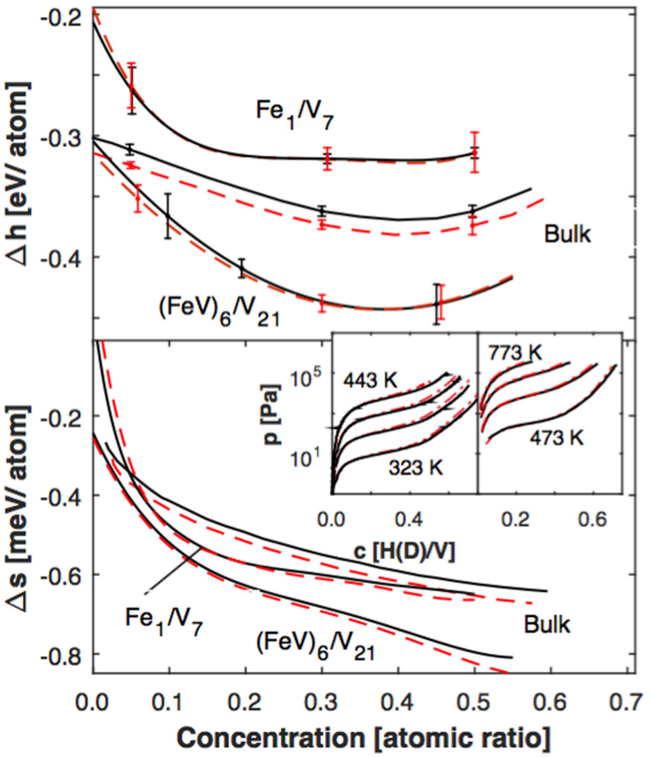

FIG. 1. Enthalpy (Δh) and entropy (Δs) of superlattices and bulk V as a function of H (solid lines) and D (dashed lines) concentration. All concentrations are defined as the atomic ratio of the elements. The inset shows isotherms for H (solid black) and D (dashed red) in the Fe_1/V_7 superlattice (left inset). Results obtained for bulk V [30] are displayed for comparison (right inset). The accuracy is specified by the error bars. The precision is significantly better than the obtained accuracy.

in bulk it occupies tetrahedral sites [1]; (ii) the superlattices are free to expand in one direction only, due to clamping to the substrate as well as the restoring effect of Fe on the V layers; and (iii) finite size effects, which provide the largest contribution to the observed differences in the absorption [32]. While all these contribute to differences between the bulk and superlattices, the finite size effect can be taken as the sole source of changes in the two superlattices, in which large changes are observed upon confinement (in both Δh and Δs). However, although the effect of confinement is large, it appears to have a small or negligible effect on the obtained isotope effects. Thus, although there are large differences in the hydrogen uptake in the 7 and 21 monolayers, the isotope effects remain negligible.

The change in site occupancy has large effects on both the H-H interaction as well as the absorption at the lowest concentrations, through the resulting local strain fields affecting the interstitial electron density of the layers. Although the hydrogen is disordered, it occupies the same site as in the ordered bulk β phase (O-sites). Furthermore, as the V layers are under biaxial compressive strain, only one of the possible O-sites is occupied (O_z sites) [12]. This results in a uniaxial strain field perpendicular to the V(001) layers (uniaxial strain in the [001] direction), which can be viewed as a polarization of the local strain field arising from the interstitial site occupancy of hydrogen [33]. These effects will remain the same in the superlattices, while they constitute one of the main differences between hydrogen in bulk and the superlattices.

The experimentally inferred changes in the enthalpy in the low concentration limit are illustrated in Fig. 2. The energy of H_2 is always higher than that of D_2, due to the mass dependence of the vibrational energy (ν). In the gas phase the energy of H_2 molecules (including binding, vibrational, and rotational energies) are 70.4 meV/H_2 (35.2 meV/atom) higher than for D_2 [34]. In the low concentration limit in bulk V, Δh_{H} and Δh_{D} are 302 meV/H and 316 meV/D (a difference of 14 meV/atom). This implies a difference in the enthalpies of H and D of 49.2 meV/atom in bulk. For both 7 and 21 monolayers of V, the isotope dependent shift in energy is close to identical at all the measured concentrations.

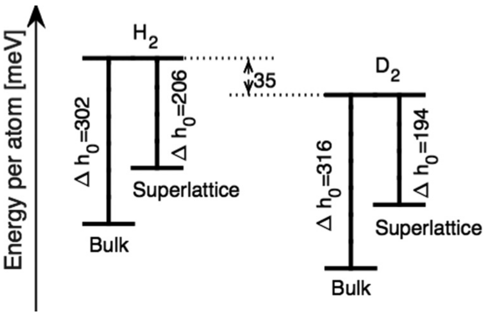

FIG. 2. Energy of H and D in gas and lattice for superlattice $\mathrm{Fe}_1/\mathrm{V}_7$ and bulk [30] in the low concentration limit. In the superlattice, $\Delta h_0 = -206 \pm 67$ meV for H, while for D, $\Delta h_0 = -194 \pm 61$ meV.

TABLE I. Formation enthalpies for H and D in T and O_z sites obtained from first-principles calculations. Lattice parameters were fixed at $a = b = 2.98$ Å in the calculations on the O_z-site occupancy. Volume expansion/contraction was only allowed in the z direction. For T occupancy the unit cells was allowed to expand/contract in all directions.

Occupancy	c[H(D)/V]	0.25	0.50	1.00
T	Δh_{H} (meV/H)	−251	−260	−292
	Δh_{D} (meV/D)	−286	−296	−326
	$\Delta h_{\mathrm{H}} - \Delta h_{\mathrm{D}}$ [meV/H(D)]	35	36	34
O_z	Δh_{H} (meV/H)	−171	−293	−296
	Δh_{D} (meV/D)	−201	−317	−305
	$\Delta h_{\mathrm{H}} - \Delta h_{\mathrm{D}}$ [meV/H(D)]	30	24	9

To elucidate the contribution of the site occupancy on the absorption of the two isotopes, we calculated the change in enthalpy from the difference between the total energy in the lattice and gas phase, using VASP:

$$\Delta h = \frac{E_{\mathrm{lat}}[\mathrm{V}+\mathrm{H(D)}] - \left(E[\mathrm{V}] + \frac{1}{2}E_{\mathrm{gas}}[H(\mathrm{D})_2]\right)}{N_{\mathrm{H(D)}}}, \tag{1}$$

where $N_{\mathrm{H(D)}}$ is the number of hydrogen atoms and the zero-point energy (ZPE) has been taken into account in both the lattice and in the gas phase of H(D). The energies of the $H_2(D_2)$ molecules are taken as a reference when calculating the formation enthalpy of the metal-H(D). The changes in enthalpy are therefore influenced by the ZPE in the lattice as well as in the gas phase. As seen in Table I, the calculated absorption energies are systematically shifted with respect to the experimental results, reflecting the challenge of capturing the contributions from local strain fields on the energy. Here we treat the uncertainty as a systematic shift, influencing the absorption of the isotopes to the same extent. Thus, we focus on the differences between the energies of the two isotopes when comparing the experimental and the theoretical findings. The calculations clearly overestimate the isotope effect, when taking the experimental results as a reference. However, the overall trends are reproduced as the isotope effects are on average smaller in O_z sites as compared to T sites, in line with the experimental findings. The small isotope effect on the volume expansion observed in the experiments is not reproduced by the calculations as no dynamical effect is taken into account. Hence, the volume expansions are identical for both isotopes in the calculations: 0.181(2) for O_z sites and 0.187(2) for the T sites.

The difference in energy between H and D ($\Delta h_{\mathrm{H}} - \Delta h_{\mathrm{D}}$) in the calculations originates solely from the differences in ZPE between the gas phase and the vanadium hydride/deuteride. A decrease of vibrational frequency by a factor of $\sqrt{2}$ is obtained in both O_z and T sites as well as in the gas phase, when changing from H to D. The difference in ZPE has been previously determined to be larger for T-site occupancy (narrow and steep in the x-y plane) than for O_z-site occupancy (broad and flat in the x-y plane) [2]. Its contribution for H(D) in T sites remains in principle unchanged with increasing concentration. For O_z-site occupancy, the ZPE contribution decreases with increasing concentration, as does the difference in enthalpy of the isotopes (which becomes smaller). We therefore conclude that the observed isotope effects are weak in the absorption of the two isotopes, when these are residing in

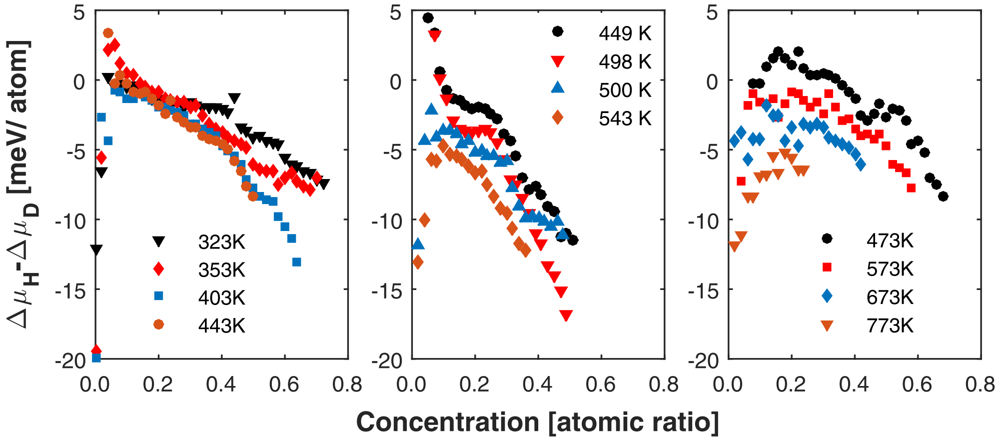

FIG. 3. The difference in the chemical potential for H and D in 7-monolayer-thick (left) and 21-monolayer-thick V layers (middle), and in bulk [30] (right panel).

the O_z sites of V. This weak isotope effect is argued to originate in the similarities of the vibrational states of hydrogen in the O_z sites and of the hydrogen molecules in the gas phase.

B. Concentration dependence in the thermodynamic potential

To further elucidate the concentration dependence of the isotope effects, we analyzed the difference in the chemical potential as a function of concentration using

$$\Delta\mu_{\mathrm{H}} - \Delta\mu_{\mathrm{D}} = (\Delta h_{\mathrm{H}} - \Delta h_{\mathrm{D}}) - T(\Delta s_{\mathrm{H}} - \Delta s_{\mathrm{D}}). \quad (2)$$

A selection from the obtained results is plotted in Fig. 3. Clear trends are observed: (i) When the hydrogen isotopes reside in octahedral sites (superlattices) the shift in the chemical potential scales approximately linearly with concentration. (ii) A pronounced temperature dependence is observed in the slope for the 7-monolayer-thick V layers, while the slope appears to be unaffected by temperature when the thickness of the V layer is 21 monolayers. (iii) When residing in T sites (bulk) a pronounced maximum is observed at around 0.2 in concentration, followed by a constant slope, smaller than obtained for the O_z sites. (iv) A change in temperature shifts the bulk data but no change in slope is observed.

Finite size effects in thin films are typically found to scale as $1 - a/L$, where a is a constant and L the thickness of the layers. This holds, for example, when describing the changes in T_c of thin ferromagnetic layers and the ordering temperature of hydrogen in V [32], as well as the contribution from depleted interface regions to the hydrogen concentration [15]. Finite size effects must therefore be more prominent in 7-monolayer-thick V layers, as compared to 21 monolayers. We therefore ascribe the changes in slope to finite size effects in the 7-monolayer-thick V layers, while the shift can at least initially be ascribed to the intrinsic properties of the absorbing material. The intrinsic properties can be captured using a simple model: When residing in interstitial sites, hydrogen can be treated as a localized harmonic oscillator, without any contribution from rotational modes. The main effect arising from replacing H with D would therefore be a change in the vibrational frequency. In order to connect the isotope induced changes in the vibrational energy to the changes in the chemical potential, we use ($\mu = -kT \ln Z$) [9,35,36]

$$\Delta\mu_{\mathrm{H}} - \Delta\mu_{\mathrm{D}} = 3kT \ln\left(\frac{\sinh\left(\frac{h\nu_{\mathrm{H}}}{kT}\right)}{\sinh\left(\frac{h\nu_{\mathrm{D}}}{kT}\right)}\right) + aT + b. \quad (3)$$

Ebisuzaki identified the terms $aT + b$ as originating from the gas phase [9] and these are therefore independent of the absorbing material ($a = -0.024$ meV/K and $b = -285$ meV [9,30,34]). The concentration dependence of $\Delta\mu_{\mathrm{H}} - \Delta\mu_{\mathrm{D}}$ can thereby be assigned to changes in vibrational energy of the two isotopes. Furthermore, a linear shift with temperature is expected from the prefactor in Eq. (3), which is in line with results obtained from the bulk data and the 21-monolayer sample. The intrinsic concentration dependences of hydrogen in T and O-sites are therefore concluded to be dominated by the changes in the vibrational energies arising from changes in site occupancy and thereby the resulting local strain field.

When considering the changes in the thinnest V layer (7 monolayers), a different picture emerges. As seen in Fig. 3, a monotonic change in $\Delta\mu_{\mathrm{H}} - \Delta\mu_{\mathrm{D}}$ with concentration is observed, combined with a change in slope with temperature. We made an attempt to extract the temperature dependence of the slope, with the intention of separating the concentration and temperature dependence in $\Delta\mu_{\mathrm{H}} - \Delta\mu_{\mathrm{D}}$. An increase in slope with increasing temperature was obtained (as seen in the figure), while the scattering in the data prohibited a quantitative analysis of the results. Thus, the findings are consistent with effects arising from the occupation of sites with a difference in energies comparable to kT, hinting towards effects arising from changes in the concentration at the interfaces [15].

V. CONCLUSIONS

Large changes are observed in the hydrogen uptake of thin layers of V in Fe/V(001) superlattices, as compared to bulk V. These changes are governed by finite size effects and the strain state of the absorbing V lattice. The biaxial strain results in a polarization of the local strain fields, which gives rise to exclusive O_z-site occupancy [12,33]. The isotope effects are found to decrease when the hydrogen resides in O_z sites, as compared to T sites. This observation can be viewed as the result of similar zero-point energies of the isotopes in the gas phase and the O_z sites in the superlattices. The concentration dependence of $\Delta\mu_{\mathrm{H}} - \Delta\mu_{\mathrm{D}}$ in octahedral sites (superlattices) is monotonic, in stark contrast to the observed effect in tetrahedral sites which exhibits a well defined maximum at concentrations around 0.2. Thus, it is reasonable to conclude that the isotope effects observed in bulk V are at least partially caused by the differences in the zero-point energy of the isotopes in the T sites of V. The results highlight the importance of obtaining a better understanding of the effect of site occupancy and local strain fields on isotope effects, as these are currently only partially understood.

ACKNOWLEDGMENTS

The Swedish Research Council is acknowledged for financial support.

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