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Influence of vanadium spin-polarization on the dissolution of hydrogen in vanadium

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Transition-metal (TM)/V superlattices (TM=Cr,Fe,Mo) show certain peculiarities under hydrogen uptake. Here we investigate the influence of an induced magnetization of the V layers on the hydrogen dissolution by means of first-principles calculations. We find that below a certain value for the magnetic moment of the V host the hydrogen solubility is slightly reduced, whereas for larger moments the hydrogen dissolution becomes favored. The actual position of this transition depends on the tetragonal distortion of the V layers.

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I. INTRODUCTION

For quite some time now hydrogen storage in metals has been in scientific focus[1–5] due to a large spectrum of possible industrial applications. For example, H occupies only the V layers in transition-metal (TM)/V superlattices, where TM equals Mo, Cr, and Fe.[6] Additionally, it is known that not all layers of V are loaded with H. The interface V layers (approximately two to three layers adjacent to the metal spacer) are usually H depleted, known as "dead" layers.[7–9] In the case of Fe/V particularly sharp interfaces have been grown,[10,11] and it was found that the number of dead layers does not decrease to less than two to three layers with increased interface sharpness. The driving force behind formation of dead layers has earlier been argued to be found in the charge transfer between Fe and V (Ref. 12) but recently elastic effects have been identified to be crucial.[9]

In Fe/V supercells, a remarkable magnetic polarization is induced in the V layers adjacent to the Fe. The magnetic profile within these supercells has been the subject of many theoretical studies.[13–18] The magnetic moment within the V layers has both experimentally and theoretically been shown to be independent of the hydrogen concentration.[19] Experimentally a maximum induced interface V moment of $1.1\mu_B$ has been reported for superlattices with few V layers.[13,20] It has been shown that interface roughness and lattice distortions influence the magnetic moments at the interface of both Fe and V.[13] In this Brief Report we investigate by means of *ab initio* calculations the influence of the induced magnetic moment of V on the H dissolution in V, a topic that so far has been neglected in the literature.

In a TM/V superlattice one can distinguish between three different regions: the TM layers, the TM/V interface, and the V layers. In the TM/V interface region no hydrogen is present due to the above-mentioned "dead" layers. Earlier, we have calculated the energy barrier for hydrogen for entering the dead layers in Fe/V to be on the order of 0.5 eV and to be solely caused by elastic effects.[9] The modified hybridization at the TM/V interface due to an eventual magnetization will therefore not influence the hydrogen dissolution.

TM itself, where TM=Mo,Cr,Fe, is completely hydrogen depleted again due to elastic effects, i.e., it costs more energy to expand TM than V. The modified electronic structure of TM itself due to an eventually modified magnetization does therefore not influence the hydrogen dissolution. In this Brief Report we focus on V itself and calculate the variation in the hydrogen dissolution in V caused by an externally enforced magnetization to which, for example, the proximity to Fe in a Fe/V superlattice gives rise.

II. COMPUTATIONAL DETAILS

All calculations were performed using VASP, a self-consistent density-functional theory code with a plane-wave basis.[21,22] Projector-augmented wave (PAW) potentials within the generalized gradient approximation (GGA) were deployed.[23,24] Ionic, volume, and shape relaxations were allowed, but for reasons discussed below geometrical constraints are applied in many cases. Site-projected density of states [DOS(R_{WS})] and magnetic moments were obtained by projecting the wave functions onto spherical harmonics within spheres centered at the atoms.[25] To capture the structure of V in the multilayer supercell calculations were performed for a layered structure consisting of 6 ML of Fe and 6 ML of V. The maximum H loading is assumed to correspond to 67% filling of the octahedral sites within the V layers in parallel to the experimental findings in Ref. 26. The structure is chosen corresponding to Fig. 2 of Ref. 27. Only 67% of the octahedral sites are occupied because of the absence of hydrogen in the dead layers.[7,8] $12\times12\times4$ special k points[28] were used to perform the reciprocal space integration. We used an energy cutoff for the plane-wave expansion of 335 eV.

In order to study the effect of a magnetization of V on the dissolution of hydrogen, we calculated bulk V and bulk VH

TABLE I. Lattice parameters of the investigated V and VH body-centered-tetragonal systems.

		V ($0\mu_B$)	V ($1.5\mu_B$)	VH ($0\mu_B$)	VH ($1.5\mu_B$)
Bulk	a (Å)	2.98	3.05	2.85	2.81
	c/a	bcc	bcc	1.31	1.41
SL	a (Å)	2.91	2.91	2.87	2.87
	c/a	1.04	1.04	1.26	1.26

for magnetic moments of up to $1.5\mu_B$ per V atom. We use body-centered-tetragonal cells with two V atoms per cell. For VH we used a similar cell; in addition, two H atoms were placed to fill the octahedral sites. $12\times12\times12$ special k points[28] were used for the reciprocal space integration and an energy cutoff of 350 eV. The V magnetization was obtained by forcing the electron distribution within the supercell to a spin-polarization of twice the desired magnetic moment per atom. To discuss the influence of the volume change and the magnetic polarization separately, calculations for a fixed volume with varying magnetization and fixed magnetization with varying volume were performed.

III. RESULTS AND DISCUSSION

Primarily, we are interested in the hydrogen dissolution energy in TM/V multilayers at the central V sites as a function of the induced magnetization. In the following, we use Fe/V as our reference supercell because Fe enforces a large magnetization within the V layers. In our earlier calculations of the site-projected magnetic moments of Fe/V superlattices, we calculate the V interface moment to be $-0.4\mu_B$ and the V moment in the third layer from the interface to be about $0.1\mu_B$.[27] Since hydrogen only dissolves within the central V layers, we model these layers by two different V bulk systems: one with the lattice dimensions fixed to that of the central V layer in a Fe/V (Fe/VH) superlattice, in the following, called the superlattice systems. For the second setup we start from bcc V bulk and bulk VH, respectively, and allow for volume and shape relaxations, in the following, called the bulk systems.

For the superlattice system, we take the lattice parameter of tetragonal V (VH) from an Fe_6/V_6 (Fe_6/V_6H_4) supercell calculation by extracting the in-plane lattice constant and the V atomic layer spacing at the central V sites (see Table I). Since the lattice dimensions are fixed to the central V layers of an Fe/V supercell, we do not allow for any lattice relaxations. To obtain the dissolution energy of hydrogen of an Fe/V superlattice, $E_{\mathrm{diss}}^{\mathrm{SL}}$, we subtract the total energy of tetragonal V, $E_{\mathrm{V}}^{\mathrm{SL}}$, from the total energy of VH, $E_{\mathrm{VH}}^{\mathrm{SL}}$, calculated in the structures derived from the Fe/V(VH) supercell calculation,

$$E_{\mathrm{diss}}^{\mathrm{SL}} = E_{\mathrm{VH}}^{\mathrm{SL}} - E_{\mathrm{V}}^{\mathrm{SL}}. \tag{1}$$

In principle, we should add the chemical potential of H, μ_{H_2}, to obtain the dissolution energy. The hydrogen dissolution energy for the full spin-polarized Fe/V superlattice we calculate in this sense is -7.38 eV for two hydrogen atoms.

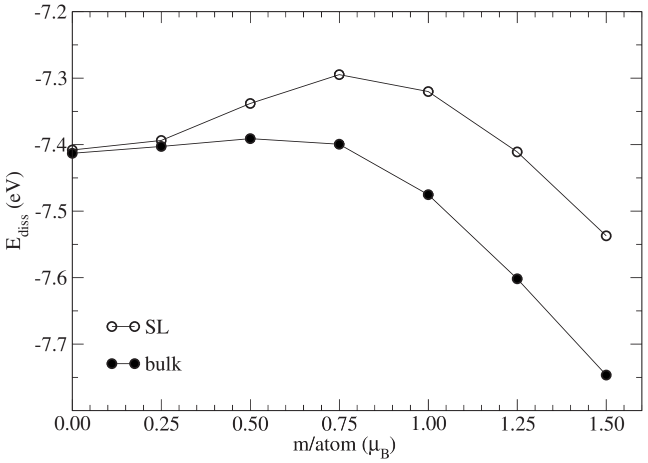

FIG. 1. $E_{\mathrm{diss}}^{\mathrm{SL}}$ and $E_{\mathrm{diss}}^{\mathrm{bulk}}$ as a function of the V magnetic moment m according to Eqs. (1) and (2).

This agrees rather well with the here calculated dissolution energy for the so-called superlattice system (see Fig. 1).

For the bulk systems, the calculated lattice parameters are listed in Table I. To obtain the hydrogen dissolution energy in V bulk, $E_{\mathrm{diss}}^{\mathrm{bulk}}$, we subtract the total energy of bcc bulk V, E_{V}, from the total energy of bulk VH, E_{VH},

$$E_{\mathrm{diss}}^{\mathrm{bulk}} = E_{\mathrm{VH}} - E_{\mathrm{V}}. \tag{2}$$

Since μ_{H_2} is independent of the V magnetic moment, in the following, we neglect the constant shift of μ_{H_2}.

In Fig. 1 we show the calculated dissolution energy according to Eqs. (1) and (2) as a function of the V-induced magnetic moment. For $E_{\mathrm{diss}}^{\mathrm{bulk}}$ the volume and shape of the computational cell were allowed to relax fully, whereas for $E_{\mathrm{diss}}^{\mathrm{SL}}$ no magnetovolume effect was allowed (see Table I). From the figure it is seen that the hydrogen dissolution is unfavored by a small magnetization of the V host, but for larger magnetizations the solubility is considerably enhanced. This effect is more pronounced for the lattice structure defined by the Fe/V superlattice. The dissolution energy increases by about 110 meV in maximum in the superlattice system. At a moment of $1.1\mu_B$ which was found experimentally in Fe/V superlattices,[20] the dissolution energy is still increased by about 50 meV. For magnetic moments larger than about $1.25\mu_B$ the hydrogen dissolution becomes favored.

In the bulk system the increase of the dissolution energy is less pronounced than in the superlattice system. The hydrogen dissolution energy increases in maximum by 22 meV and the dissolution is favored by a V magnetization larger than about $0.75\mu_B$.

In summary, we find that small induced magnetic moments in vanadium increase the hydrogen solubility energy, whereas larger magnetic moments give rise to a decreased hydrogen solubility energy. The exact range of magnetic moments for which this is valid depends on the vanadium lattice distortion. In the superlattice system the maximum energy gain due to a magnetization in the range investigated here is about 0.1 eV which is much smaller than the calculated energy barrier (0.5 eV) for hydrogen to enter the “dead” layers.

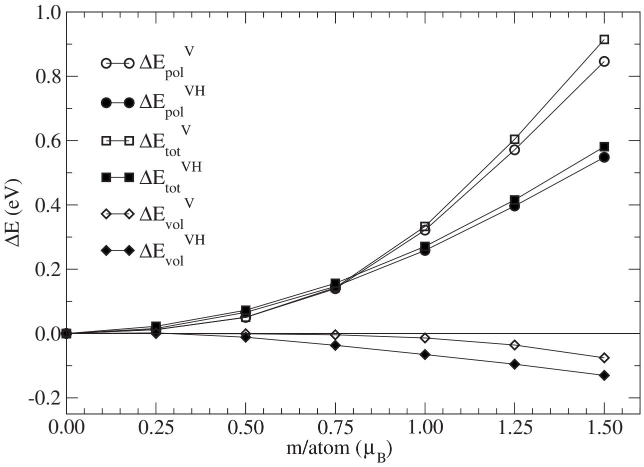

FIG. 2. Energy change with increasing magnetic moment for bcc V (open symbols) and VH (closed symbols) according to Eqs. (4)–(6).

Even for an induced moment at the V interface layer of $1.5\mu_B$, the interface V layer would remain hydrogen depleted.

Next, we investigate the influence of magnetostriction on the dissolution energy. We note that a change in magnetic moment is accompanied by a change in volume. The dissolution energy therefore depends, in principle, on both the chosen volume (vol) and the chosen magnetic moment m. For the definition given in Eq. (2) the volume vol(m) was fully relaxed at a given magnetic moment m, so the equation can be expressed like

$$E_{\mathrm{diss}}^{\mathrm{bulk}}(m) = E_{\mathrm{VH}}[\mathrm{vol}(m),m] - E_{\mathrm{V}}[\mathrm{vol}(m),m]. \tag{3}$$

In order to separate this dependence, we have calculated the total-energy difference $\Delta E_{\mathrm{tot}}(m)$ of fully relaxed spin-polarized bulk V (VH) relative to fully relaxed bulk V (VH) with zero-magnetic moment,

$$\Delta E_{\mathrm{tot}}^{X}(m) = E_X[\mathrm{vol}(m),m] - E_X[\mathrm{vol}(0),0], \tag{4}$$

where X is either V or VH. ΔE_{tot} is simply the total-energy cost of magnetization of V (empty squares) and VH (filled squares) shown in Fig. 2.

In addition, we have calculated the polarization energy $\Delta E_{\mathrm{pol}}(m)$ of polarized structural relaxed V (VH) relative to V (VH) for a zero-magnetic moment but with the volume fixed to the fully relaxed volume for that magnetic moment,

$$\Delta E_{\mathrm{pol}}^{X}(m) = E_X[\mathrm{vol}(m),m] - E_X[\mathrm{vol}(m),0], \tag{5}$$

where again X is either V or VH. $\Delta E_{\mathrm{pol}}^{X}$ is a measure of the polarization energy because the only difference in total energy is due to the spin-polarization. The energy difference due to the volume increase caused by the magnetic polarization does not enter ΔE_{pol} as shown in Fig. 2 by circles.

Moreover, we have calculated the magnetovolume energy $\Delta E_{\mathrm{vol}}^{X}$ of structural relaxed V (VH) relative to V (VH) with the volume fixed to the volume of the nonmagnetic system,

$$\Delta E_{\mathrm{vol}}^{X} = E_X[\mathrm{vol}(m),m] - E_X[\mathrm{vol}(0),m], \tag{6}$$

where again X is either V or VH. E_{vol} is a measure of the magnetostriction energy because the only difference in total energy is due to the volume expansion.

ΔE_{tot}, ΔE_{pol}, and ΔE_{vol} are presented in Fig. 2. The figure shows that the change in the polarization energy $\Delta E_{\mathrm{pol}}^{V}$ for V follows almost the behavior of ΔE_{tot}. This implies that the volume change accompanied by the magnetization (magnetostriction) is of minor importance. Accordingly, it is seen that ΔE_{vol} is negligible compared to ΔE_{tot}. Compared to the dissolution energy of hydrogen E_{diss} (Fig. 1), the energy connected to the magnetostriction ΔE_{vol} is smaller by a factor of about 5.

Comparing E_{diss} of the SL and bulk system (see Fig. 1), one realizes that both show similar qualitative behaviors but that they differ quantitatively. The difference between $E_{\mathrm{diss}}^{\mathrm{SL}}$ and $E_{\mathrm{diss}}^{\mathrm{bulk}}$ is about 0.2 eV for a magnetization of $1.5\mu_B$. The magnetostriction energy, on the other hand, is on the order of 0.1 eV (Fig. 2). Since the volume of V^{SL} is 3% smaller than of V^{bulk} and the magnetostriction going from $0.0\mu_B$ to $1.5\mu_B$ gives rise to a 7% volume increase in V^{bulk}, the difference between $E_{\mathrm{diss}}^{\mathrm{SL}}$ and $E_{\mathrm{diss}}^{\mathrm{bulk}}$ is understandable as a consequence of magnetostriction.

Assuming that the magnetostriction in V^{SL} is similar as in V^{bulk}, we approximate the maximum energy gain in hydrogen solubility to be about 0.2 eV. Thus the earlier statement about the stability of the dead layers remains valid even after including magnetostriction to the consideration.

In the following we explain the qualitative behavior of the hydrogen dissolution energy (Fig. 1). As stated earlier, from Fig. 1 it is clearly seen that the hydrogen solubility is unfavored up to a magnetic moment of about $0.75\mu_B$ but favored for larger magnetizations. The electron density, i.e., the number of valence electrons per unit-cell volume, within VH is about 30% larger than in V. Since it costs less energy to spin polarize localized electrons and recalling the definition of the dissolution energy [Eqs. (1) and (2)] it becomes obvious that the hydrogen dissolution becomes unfavorable with increasing magnetization.

It is seen from Fig. 1 that for V^{bulk}, where we have allowed for magnetostriction, the hydrogen dissolution is almost unchanged for magnetizations below $0.75\mu_B$. This indicates that the magnetostriction energy and the effect due to the electron localization have the same order of magnitude.

A larger effect on the energy scale starts to dominate the qualitative behavior of the hydrogen dissolution energy at about $0.75\mu_B$. This effect becomes evident considering the site-projected density of states (local DOS) of the d bands. In Fig. 3 we show, respectively, the d DOS projected on V of fully relaxed bcc bulk V, fully relaxed tetragonal VH, and tetragonal V calculated at the VH lattice parameters.

In bcc bulk we note that the crystal-field splitting gives rise to the typical pseudogap. Also V with the structure extracted from the Fe/V supercell shows this pseudogap, as one would expect, considering the tiny distortion of V^{SL} compared to V^{bulk} (see Table I). In VH the situation is different. For VH the bcc pseudogap is absent due to the large tetragonal lattice distortion (see middle and lower rows in Fig. 3 and Table I. We want to emphasize that the disappearance of

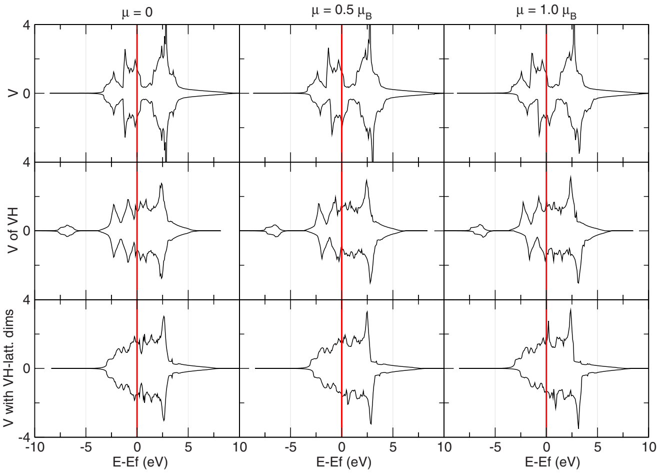

FIG. 3. (Color online) Site-projected spin-dependent local DOS of *d* states in bulk V, at the V site of VH, and bulk V with the VH lattice parameters for a magnetic moment per V atom of $0.0\mu_B$, $0.5\mu_B$, and $1.0\mu_B$. Note the shift of E_F from a bit below the pseudogap for zero-magnetic moment into the pseudogap for high magnetic moments in the case of bcc bulk V (upper panel).

the pseudogap is not a consequence of the hybridization between H and V.

As soon as the Fermi energy, as a function of the magnetization, approaches the pseudogap within the spin-up channel, the number of states at the Fermi energy available to occupy spin-down states becomes rather small. Assuming a rigid-band model the existence of a pseudogap at the Fermi energy makes necessary a larger band shift in order to obtain a certain magnetization. For a magnetization, for which the Fermi energy has approached the pseudogap in V, the energy cost of magnetization of V exceeds that of VH. This happens at about $0.75\mu_B$ (see Fig. 3, upper panel). Recalling the definition of the hydrogen solubility [Eqs. (1) and (2)], the larger cost of magnetization of V explains why the hydrogen solubility is favorable above $0.75\mu_B$.

IV. SUMMARY

We have performed *ab initio* calculations of the hydrogen dissolution in V. For small magnetic moments the solubility is decreased. The strength of the reduction depends on the lattice geometry. For bulk V the hydrogen dissolution is slightly reduced up to a magnetic moment of $0.75\mu_B$. For tetragonally distorted V layers, as the case in Fe/V superlattices, the dissolution energy is increased for moments up to $1.25\mu_B$. The reason is the higher electron density within VH compared to V. For higher magnetic moments of the V host, the hydrogen dissolution becomes favorable in all considered cases. The reason is the higher density of states at the Fermi energy of VH compared to V. In addition, we have shown that the magnetostriction effect is negligible compared to the hydrogen dissolution energy. We find the dead layers within Fe/V superlattices to be stable against a variation in the V magnetization.

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