PHYSICAL REVIEW B **95**, 064310 (2017)

Influence of site occupancy on diffusion of hydrogen in vanadium

Lennard Mooij, Wen Huang, Sotirios A. Droulias, Robert Johansson, Ola Hartmann, Xiao Xin, Heikki Palonen,
Ralph H. Scheicher, Max Wolff,[*] and Björgvin Hjörvarsson
Department of Physics and Astronomy, Uppsala University, P.O. Box 516, SE-75120, Uppsala, Sweden

(Received 4 February 2016; revised manuscript received 1 February 2017; published 28 February 2017)

We investigate the effect of site occupancy on the chemical diffusion of hydrogen in strained vanadium. The diffusion rate is found to decrease substantially, when hydrogen is occupying octahedral sites as compared to tetrahedral sites. Profound isotope effects are observed when comparing the diffusion rate of H and D. The changes in the diffusion rate are found to be strongly influenced by the changes in the potential energy landscape, as deduced from first-principles molecular dynamics calculations.

DOI: 10.1103/PhysRevB.95.064310

With technology moving towards nanoscaled materials it becomes more and more important to understand the influence of finite size as well as surface and proximity effects on physical properties such as ordering temperature and dynamics. Recently, it was shown that the magnetic ordering temperature and the formation of ordered hydride phases exhibit the same scaling with thickness [1]. Hence, the phase diagram and the critical temperature of layers are strongly affected by their thickness when these are in the monolayer range. Not only are the thermodynamic properties affected, finite size can also influence the diffusivity in, for example, liquids [2]. Hydrogen in metals offers unique possibilities in this context since the chemical as well as self diffusion of hydrogen in transition metals has been thoroughly investigated [3]. This in combination with the possibility to tailor the absorption of hydrogen in artificially layered structures such as metallic superlattices [4,5] has opened completely new routes towards investigations of confinement and strain on phase formation and dynamics.

The influence of site occupancy on diffusion is strongly related to the impact of the local strain field on interstitial motion of hydrogen [6,7]. Thus, the diffusion of hydrogen/deuterium involves the combination of the proton/deuteron and the associated local strain field. The hydrogen and the associated local strain field can be regarded as a quasiparticle, often referred to as the small polaron, or lattice polaron [6]. The site occupancy of hydrogen in vanadium [8] is highly sensitive to strain [9] as demonstrated by the strain driven tetrahedral to octahedral site change in bulk vanadium [10,11]. A superdiffusion driven by the change from tetrahedral to octahedral site occupancy in strained vanadium was proposed [12] but later falsified [13]. The impact of site occupancy on diffusion is currently not fully understood and investigations of the diffusion of hydrogen in strained vanadium could therefore offer valuable insight.

In this paper, we study the diffusion of hydrogen and deuterium in artificially strained vanadium, wherein H and D reside in octahedral-z (O_z) sites at low concentrations. Hydrogen is forced to reside in the O_z site using a biaxial compressive strain in the vanadium (001) layers. The strain state is engineered in the sample in the growth process [14], resulting in a O_z-site occupancy [15,16]. O_{xy} sites are not occupied due to the clamping of vanadium to both the substrate and the restoring force of the Fe layers. The diffusivities of H and D residing in O_z sites is compared to diffusion in T sites (low c bulk V and thin film V) and in O_z sites at high concentration ($c > 0.5$). Furthermore, *ab initio* molecular dynamics (MD) simulations of diffusion in unstrained and strained vanadium lattices were performed to support the experimental findings.

Single crystal Fe/V(001) superlattices were deposited on MgO (001) substrates ($10 \times 10 \times 1.0$ mm^3) by magnetron sputtering using the process developed by Isberg *et al.* [14]. The binding energy of hydrogen in Fe and V is 0.3 eV and −0.3 eV, respectively. As a result, the diffusivity measured in our experiments can be seen as hydrogen motion in the V layers exclusively. The superlattices consist of 12 repetitions of Fe/V bilayers (21 monolayers V and 3 monolayers Fe), with a final V layer of 21 monolayers deposited on top. A sketch of the sample design is represented in Fig. 1. A Pd layer (7 nm) is used to protect the superlattice from oxidation and to catalyze the dissociation of hydrogen gas to atomic hydrogen. The Pd layer is capped by a 20 nm layer of amorphous Al_2O_3, while leaving two approximately 0.5 mm wide strips of Pd at the two opposing sample edges uncovered (Fig. 1). These catalytically active regions allow hydrogen to enter the superlattice upon exposure to hydrogen gas. The use of two windows provides symmetric boundaries and ensures appropriate boundary conditions, as described below. The sample design enables observation of lateral diffusion of hydrogen in the Fe/V superlattice, as the diffusion rate of hydrogen is several orders of magnitude higher in V as compared to Pd. Thus lateral diffusion of hydrogen in Pd can be ignored, while the aspect ratio of the catalytically active region ensures well defined boundary conditions.

The experiments were performed by placing the sample in a vacuum chamber, with base pressure below 10^{-9} mbar, in which the hydrogen/deuterium pressure can be changed to about 1 bar. The sample is heated in vacuum to a set-point temperature ($117\,^\circ\mathrm{C} < T < 250\,^\circ\mathrm{C}$) prior to the hydrogen exposure. After the temperature has stabilized, the sample is exposed to a well-defined hydrogen pressure, corresponding to an equilibrium condition of the intended hydrogen concentration ($c < 0.05$ H/M). The part of the sample below the open Pd window equilibrates with the hydrogen gas and obtains

---

[*] max.wolff@physics.uu.se

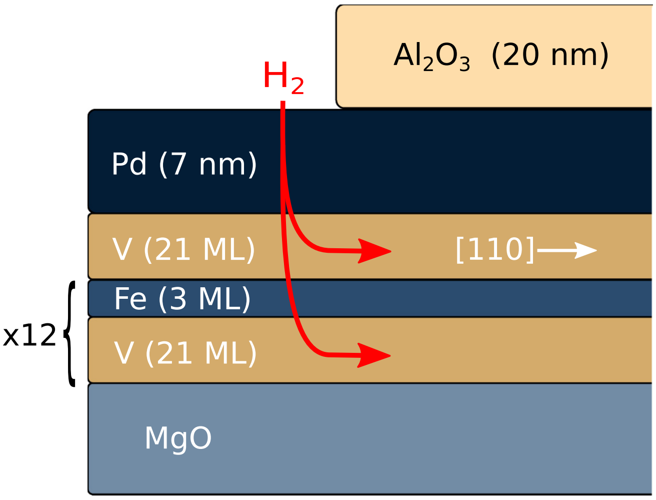


FIG. 1. Scheme of the sample geometry. The first layer deposited on the MgO substrate is a 21 ML V layer, which is followed by 12 repetitions of Fe/V bilayers. A Pd capping layer prevents the sample from oxidation and catalysis of the hydrogen dissociation into atomic hydrogen. Finally, 8 out of the 10 mm of the sample are covered with Al_2O_3, leaving open two 1 mm windows for hydrogen to enter the sample at opposing sides. Lateral diffusion of hydrogen is then observed in the Fe/V superlattice along the [110] direction.

a constant hydrogen concentration, typically within 10–50 s, which is short compared to the times (50–1000 s) for which the diffusion constants were extracted. This measuring procedure ensured that boundary conditions defined below were fulfilled.

The lateral diffusion is detected through the change in optical transmission caused by the hydrogen-induced changes in the optical constants. Lambert-Beer's law has been shown to be valid for determining the hydrogen concentration in Fe/V superlattices [1], whereby:

$$c_{\mathrm{H}}(x) = \alpha \ln \frac{I_{\mathrm{T}}(x)}{I_{\mathrm{T0}}(x)}. \tag{1}$$

Here, $c_{\mathrm{H}}(x)$ is the hydrogen concentration at position x in the sample, $I_{\mathrm{T}}(x)$ the recorded transmission at position x, I_{T0} the transmission of the sample without hydrogen, for $t < 0$ and at position x, and α the optical absorption coefficient, which is assumed to be independent of hydrogen concentration. An optical wavelength of $\lambda = 590$ nm was used in the experiments. A CCD grayscale camera (up to 15 frames per second, model: Imaging source, DMK41BU02.H) provides a lateral resolution of 10 μm per pixel and allows us to resolve the hydrogen concentration as a function of position and time. A more detailed description of the setup is given in Pálsson *et al.* [17].

The hydrogen diffusion coefficient is obtained through fitting the concentration profiles with a solution of Fick's second law, in which the diffusion constant D is assumed to be concentration independent:

$$\frac{\partial c(x,t)}{\partial t} = D \frac{\partial^2 c(x,t)}{\partial x^2}. \tag{2}$$

The initial and boundary conditions are:

$$c(x,0) = 0 \quad \forall \quad x \geqslant 0, \tag{3a}$$

$$c(0,t) = c_0 \quad \forall \quad t > 0, \tag{3b}$$

$$\left.\frac{\partial c(x,t)}{\partial x}\right|_{x=L} = 0 \quad \forall \quad t \geqslant 0. \tag{3c}$$

Here L is a line across the center of the sample with a distance of 4 mm from the inner edges of both Pd stripes. The first condition implies that there is no hydrogen in the sample at $t = 0$. The second condition states that after exposing the sample to hydrogen, the concentration below the Pd window is constant and equal to c_0. The final condition implies that the line along the center of the sample acts as a mirror for hydrogen diffusion. Only profiles recorded for $t < 1000$ s over a limited sample width of $x \leqslant 4$ mm were fitted to minimize the influence of possible leaks of hydrogen through the sample edges. The solution to Fick's second law [Eq. (2)] given the above initial and boundary conditions (including the definition of $x = 0$) is [18]:

$$\begin{aligned} c(x,t) = c_0 \sum_{k=1}^{\infty} \Bigg[&\operatorname{erfc}\left(\frac{2(k-1)L + x}{2\sqrt{Dt}}\right) \\ &+ \operatorname{erfc}\left(\frac{2kL - x}{2\sqrt{Dt}}\right)\Bigg](-1)^{k-1}, \end{aligned} \tag{4}$$

where erfc is the complementary error function. Fitting with $k \leqslant 3$ is found to describe the data sufficiently well.

Figure 2 shows the resulting diffusion coefficients plotted versus $1/T$. Using the Arrhenius equation, $D = D_0 \exp -E_a/kT$, we performed a fit with weighted uncertainties. This results in an activation energy of 0.217(17) eV/atom and a D_0 of $4.4(19) \times 10^{-3}$ cm^2/s for hydrogen diffusion (closed circles), with 95% confidence bounds given between

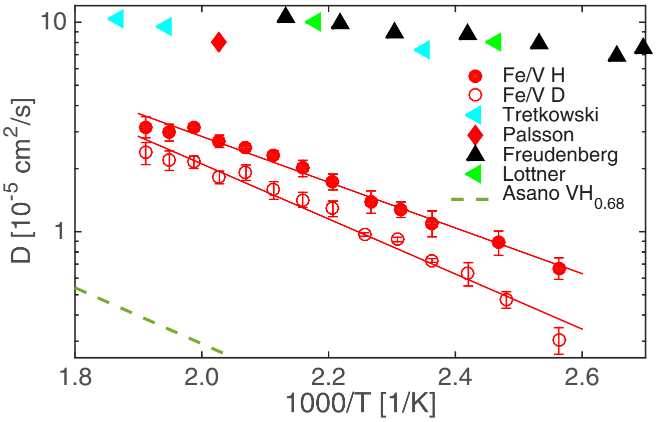


FIG. 2. Arrhenius plot with the data from this paper (filled circles, red online) and a linear fit (solid lines). For comparison, we added data from the literature on low concentration H in V as triangles from Lottner *et al.* [19] (neutron scattering), Freudenberg *et al.* [20] (Gorsky effect), Tretkowski [21] (Gorsky effect), and Pálsson *et al.* [17] (optical technique). High concentration bulk data for $VH_{0.68}$ is calculated from mean residence times from Asano *et al.* [22] (NMR, broken line).

brackets. The same procedure for deuterium diffusion (open circles) gives $E_a = 0.261(27)\mathrm{eV/atom}$ and $D_0 = 9.0(66) \times 10^{-3}\mathrm{cm}^2/\mathrm{s}$. The uncertainties represent the statistical uncertainty from the data evaluation and statistics in the detected light intensity and should be taken as a lower limit. Including systematic errors, such as a finite rise time, would result in increased uncertainties. In particular, for lower temperatures the rise of c_0 is close to exponential at early times which can be argued to be dominated by the reduction of the dissociation rate at the Pd surface. Using a modified diffusion equation to compensate for this rise time results in slightly increased diffusion constants and thereby in an about 25% lower activation energy and three times lower D_0. Over all the D_0 values are extracted from a very limited temperature resulting in relatively large uncertainties.

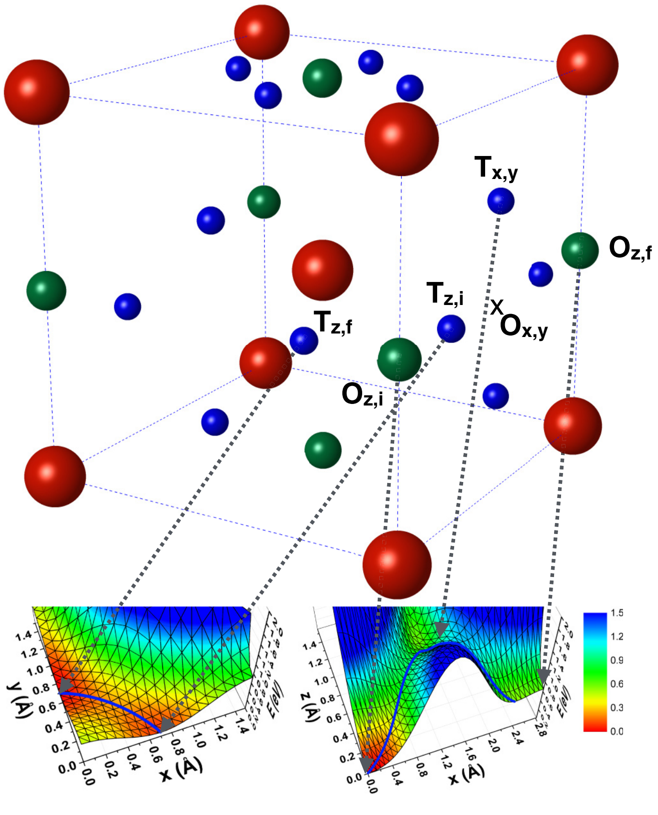
For comparison in Fig. 2, data for H diffusion in bulk vanadium at low concentration (T sites) measured with various techniques [19–22] are plotted. The graph also includes results for a 50 nm thin film of vanadium [17] obtained using the same optical technique as used here (see caption of Fig. 2 for details). The diffusivities in the superlattice are significantly smaller than that observed in bulk V. In addition, the slope and therefore the (apparent) activation energy is much smaller for bulk than for the Fe/V superlattices. Activation energies (H) between 0.043 eV and 0.08 eV are observed in bulk, while we obtain an activation energy of 0.217(17) eV. Thus, the activation energy of H diffusion in O_z sites appears to be about three to five times larger than that of diffusion between T sites.

We now compare the measured activation energies with literature data. Asano *et al.* [22] determined the activation energy of hydrogen diffusion in β_2-phase $VH_{0.68}$ to be 0.27 eV using NMR. The authors report mean residence times from which we have calculated diffusivities illustrated in Fig. 2 (green dash-dotted line). These results are well in line with the findings of Richter *et al.* [23] using neutron scattering on single crystal V_2H: $D = 6 \times 10^{-7}\mathrm{cm}^2/\mathrm{s}$ at $T = 440\,\mathrm{K}$ ($1/T = 2.3 \times 10^{-3}$). Given the agreement between data from Asano *et al.* and Richter *et al.* we take these as a reference value for diffusion of hydrogen occupying O_z sites. While the NMR data provide lower diffusivities than obtained in the Fe/V superlattice (see Fig. 2), there is a good agreement between the activation energies. We conjecture that the activation energy is governed by the energy landscape set by the tetragonally distorted V lattice, while the diffusivities themselves are lowered by the increased probability of blocking due to the increased concentration in the β_2 phase. The agreement of the activation energy is good even though here we only observe (chemical) diffusion in the [110] direction, while an NMR experiment involves (self) diffusion in all directions. However, the thermodynamic factor at low concentration is almost one and the difference between chemical and self-diffusion should therefore be very small. The directional dependence of the self-diffusion can be determined using quasielastic neutron scattering as demonstrated by Richter *et al.* [23] using an ordered β_1-V_2H single crystal. They measure a diffusion constant of $D = 6 \times 10^{-7}\mathrm{cm}^2/\mathrm{s}$ at $T = 440\,\mathrm{K}$ both parallel and perpendicular to the [110] direction. Using the diffusion coefficients from Richter and Mahling-Ennaoui [23], we obtain activation energies of, respectively, 0.6 eV and 0.8 eV for diffusion perpendicular and parallel to the occupied (110) planes. We may thus conclude that the activation energy indeed increases with a site change from T to O_z sites.

To obtain more detailed information on the energy landscape created by the vanadium atoms *ab initio* MD simulations for unstrained (c/a = 1.00, H in T sites) and strained ($c/a = 1.05$ and $c/a = 1.10$, H in O_z sites) V were performed using the VASP code [24–27], utilizing the generalized gradient approximation [28] (GGA) and the projector-augmented-wave method [29,30] (PAW). The Γ point was used to sample the Brillouin zone. The simulations were performed using a 128 vanadium atoms supercell with periodic boundary conditions. The strain states corresponding to $c/a = 1.05$ and 1.10 were obtained by fixing the a and b lattice constants at 2.89 Å and 2.82 Å, respectively and performing constrained cell relaxations in the c direction. The temperature was fixed at 600 or 1000 K throughout the simulations together with the volume and the number of particles which were also kept fixed. The total simulation time is 400 ps for each simulation. The velocities were rescaled after each time step of 1 fs. Three simulations were performed: with $c/a = 1.00$, $c/a = 1.05$, and $c/a = 1.10$ to capture the influence of site occupancy on the diffusion. When $c/a = 1.00$, hydrogen occupies T sites, while for $c/a = 1.05$ and 1.10 O_z sites are occupied. For $c/a = 1.10$ the residence time of the hydrogen at the O_z sites is too long to obtain sufficient statistics for 600 K.

We have mapped the potential energy surfaces (PES) of one hydrogen atom for being self-trapped for the extreme cases in a T site for $c/a = 1.00$ and in an O_z site for $c/a = 1.10$ in a 128 vanadium atoms supercell (Fig. 3). For $c/a = 1.00$, one quadrant of the (001) bcc unit cell has been mapped while for $c/a = 1.10$, half of the (010) bcc unit cell has been mapped. The vanadium atoms are kept fixed while the hydrogen atom is moved away from its initial self-trapped position to extract the surrounding PES. The minimum value of the surfaces has been set to 0 eV. The zero-point energy (ZPE) has been computed at the initial, transition, and final states. The ZPE energies extracted from the calculations are on the order of 0.25 meV in the trapped as well as in the transition state. Since the lattice has not been relaxed in the calculations at the transition state, the energies calculated and displayed in Fig. 3 are upper limits. Still, a qualitative understanding of the increase in activation energy of H/D diffusion residing in O_z sites versus T sites can be inferred from the tetrahedral distortion of the vanadium lattice and the associated change in site occupancy. The V layers are contracted in-plane, resulting in an out of plane expansion of about 3%. This causes the hydrogen to reside in O_z sites, already at low concentrations. The expansion causes nearest neighbor vanadium atoms of the O_z sites to move away, thus lowering the energy for hydrogen at these sites. Figure 3 depicts the vanadium unit cell with the respective sites the hydrogen might occupy together with the energy landscape (lower panels) plotted for the unstrained and strained lattice. The lines in the PES show the path of the hydrogen between self-trapped sites.

When H/D occupies O_z sites in V, the diffusion mechanism changes. As can be seen in Fig. 3, a hop between O_z sites (e.g., $O_{z,i}$ to $O_{z,f}$) requires a passing through an intermediate T_{xy} site. Occupation of O_x and O_y sites is energetically



c/a = 1 c/a = 1.1

FIG. 3. Illustration of the V lattice (V in red) and positions of tetrahedral (blue) and octahedral-z sites (green). Only the tetrahedral sites on the faces on the front are drawn. Furthermore, only one O_{xy} site (black cross) is drawn for sake of clarity. The lower panels show the energy landscape for a proton residing in the center $T_{z,i}$ and $O_{z,i}$ site, left and right panel, extracted from the DFT calculations, where the effect of self-trapping due to the strain field can be seen by the increased energy of the next $O_{z,f}$ site.

unfavorable, due to the strain state of the lattice. From DFT calculations we found that the enthalpy of formation relative to the dissociation and absorption of the hydrogen gas molecule is 0.22 eV/atom for O_{xy} occupancy and −0.42 eV/atom for O_z occupancy at $c/a = 1.10$. The residence in the T_z site is intricate, because the O_z site can be viewed as including the region normally considered as a T_z site [31]. Here we refer to the 4T site as a O_z site as the time integrated expectation value of the occupancy is the same for these types of sites. The energy landscape illustrated in Fig. 3 shows this very clearly. The T sites are not at the same geometrical tetrahedral positions as in an unstrained lattice but so close to the O_z that effectively one large site is created. The flattening of the energy landscape within the 4T ring has been shown by Fukai using quantum mechanical calculations [31].

Given the in-plane contraction, the T_{xy} sites will have higher energy, as suggested by recent DFT calculations [16]. Once the energy landscape has been calculated the diffusion constants can be obtained by the transition state theory as shown for the diffusivity of hydrogen in nickel [32,33]. Doing this implies relaxation of the lattice after moving the hydrogen atom around and finding the lowest energy path between self-trapped states. This is computationally very demanding and here we have chosen to calculate diffusion coefficients (see Table I) [34] from the inverse of the residence times as proposed by Rowe *et al.* [35] and recently used for the calculation of the diffusivity of self-trapped hydrogen in niobium [7]. The ratio of the diffusion coefficient in the unstrained system, where the hydrogen atom occupies T sites, and the diffusion coefficient is in the strained system with O_z site occupancy, is found to be $D_{1.00}/D_{1.10} = 4.95$. This is in good agreement with the ratio between 3 and 5, depending on temperature, found experimentally for bulk and superlattices. However, the absolute value of the diffusion constants is underestimated by the MD simulations. From the diffusion constants given in Table I and extracted from the reciprocal residence time in the MD simulations the activation energy can be calculated from the Arrhenius behavior:

TABLE I. Diffusion constants extracted from the residence times at the self-trapped state in the MD simulations.

c/a	T [K]	D [10^{-5} cm^2/s]	Mean H-V dist [nm]
1.00	600	9.00	0.167
1.05	600	1.85	0.166
1.00	1000	20.5	0.165
1.05	1000	13.0	0.163
1.10	1000	4.14	0.166

$$E_a = k_b \frac{T_1 T_2}{T_2 - T_1} \ln \frac{D(T_1)}{D(T_2)} \tag{5}$$

with k_b the Boltzmann constant and T the temperature, 600 or 1000 K. As a result, we obtain 0.11 eV and 0.25 eV for a c/a ratio of one and 1.05, which is in excellent agreement with the experimental results.

We conclude that site occupancy has a strong effect on the diffusion of H and D in V, in which the diffusion rates are significantly smaller when hydrogen resides in O_z sites as compared to T sites. The diffusion rates between O_z sites are higher at low concentration as compared to the ordered β_2 phase, which is consistent with blocking at higher concentrations. A decrease in the zero-point energy is obtained when hydrogen changes from T- to O_z-site occupancy, as seen in the DFT calculations which provides partial cause for the changes in the diffusion rates. These results are consistent with the increase in activation energy inferred from the experimental results for both the isotopes. Thus, a qualitative and general description of the influence of site occupancy on classical diffusion emerges, a description which needs to be tested using other material combinations.

The Swedish National Infrastructure for Computing (SNIC) and the Uppsala Multidisciplinary Center for Advanced Computational Science (UPPMAX) provided computing time for this project.

[1] X. Xin, G. K. Pálsson, M. Wolff, and B. Hjörvarsson, Phys. Rev. Lett. **113**, 046103 (2014).

[2] T. L. Spehr, B. Frick, M. Zamponi, and B. Stuhn, Soft matter **7**, 5745 (2011).

[3] Y. Fukai, *The Metal-Hydrogen System, Basic Bulk Properties*, 2nd ed. (Springer-Verlag, Berlin, Heidelberg, 2005).

[4] P. F. Miceli, H. Zabel, and J. E. Cunningham, Phys. Rev. Lett. **54**, 917 (1985).

[5] B. Hjörvarsson, J. Rydén, E. Karlsson, J. Birch, and J.-E. Sundgren, Phys. Rev. B **43**, 6440 (1991).

[6] A. M. Stoneham, J. Gavartin, A. L. Shluger, A. V. Kimmel, D. M. Ramo, H. M. Rønnow, G. Aeppli, and C. Renner, J. Phys. Condens. Matter **19**, 255208 (2007).

[7] A. Blomqvist, G. K. Pálsson, C. M. Araujo, R. Ahuja, and B. Hjörvarsson, Phys. Rev. Lett. **105**, 185901 (2010).

[8] S. Takano, A. Makita, and H. Kojima, Mater. Sci. Eng. A **142**, 245 (1991).

[9] S. Koike and H. Kojima, Zeitschrift für Physikalische Chemie **179**, 383 (1993).

[10] E. Yagi, T. Kobayashi, S. Nakamura, Y. Fukai, and K. Watanabe, Phys. Rev. B **31**, 1640 (1985).

[11] E. Yagi, T. Kobayashi, S. Nakamura, F. Kano, K. Watanabe, Y. Fukai, and S. Koike, Phys. Rev. B **33**, 5121 (1986).

[12] T. Suzuki, H. Namazue, S. Koike, and H. Hayakawa, Phys. Rev. Lett. **51**, 798 (1983).

[13] R. C. Brouwer, H. Douwes, R. Griessen, and E. Walker, Phys. Rev. Lett. **58**, 2551 (1987).

[14] P. Isberg, B. Hjörvarsson, R. Wäppling, E. B. Svedberg, and L. Hultman, Vacuum **48**, 483 (1997).

[15] G. K. Pálsson, M. Wälde, M. Amft, Y. Wu, M. Ahlberg, M. Wolff, A. Pundt, and B. Hjörvarsson, Phys. Rev. B **85**, 195407 (2012).

[16] R. Johansson, R. Ahuja, O. Eriksson, B. Hjörvarsson, and R. H. Scheicher, Sci. Rep. **5**, 10301 (2015).

[17] G. K. Pálsson, A. Bliersbach, M. Wolff, A. Zamani, and B. Hjörvarsson, Nat. Commun. **3**, 892 (2012).

[18] J. Crank, *The Mathematics of Diffusion* (Oxford University Press, London, 1970).

[19] V. Lottner, A. Heim, and T. Springer, Z. Phys. B **32**, 157 (1979).

[20] U. Freudenberg, J. Völkl, J. Bressers, and G. Alefeld, Scr. Metall. **12**, 165 (1978).

[21] J. Tretkowski, Jül-Bericht (Kernforschungsanlage, Jülich, Germany), Jul-1049-FF (1974).

[22] K. Asano, S. Hayashi, Y. Nakamura, and E. Akiba, J. Alloys Compd. **507**, 399 (2010).

[23] D. Richter and S. Mahling-Ennaoui, Z. Phys. Chem. Neue Folge **164**, 907 (1989).

[24] G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (1993).

[25] G. Kresse and J. Hafner, Phys. Rev. B **49**, 14251 (1994).

[26] G. Kresse and J. Furthmüller, Comput. Mat. Sci. **6**, 15 (1996).

[27] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).

[28] J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13244 (1992).

[29] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).

[30] P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994).

[31] Y. Fukai, Jpn. J. Appl. Phys. **22**, 207 (1983).

[32] E. Wimmer, W. Wolf, J. Sticht, P. Saxe, C. B. Geller, R. Najafabadi, and G. A. Young, Phys. Rev. B **77**, 134305 (2008).

[33] Y. Wang, D. Conntable, and D. Tanguy, Acta Materialia **103**, 334 (2016).

[34] R. Johansson, G. K. Pálsson, R. Ahuja, O. Eriksson, B. Hjörvarsson, and R. H. Scheicher (unpublished).

[35] J. M. Rowe, K. Sko'ld, H. E. Flotow, and J. J. Rush, J. Phys. Chem. Solids **32**, 41 (1971).