

Diffusion of hydrogen in $\text{Nb}_{1-y}\text{V}_y$ alloys

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A model is proposed for interstitial diffusion in a disordered alloy. Diffusion is described in terms of single-jump processes with an activation energy and a prefactor depending on the chemical and physical structure of the initial and final sites. Site-dependent activation energies, prefactors, selective blocking factors, and attractive interstitial-interstitial interactions are taken into account. Using the site energies and the density-of-sites function as measured by Feenstra *et al.*, we calculate for the first time the temperature and concentration dependence of the diffusion coefficient for hydrogen in the complete $\text{Nb}_{1-y}\text{V}_y$ alloy system without any further fit parameter. The agreement between calculated and experimental activation energies is excellent by taking the same saddle-point energy as for pure Nb and V over the complete $\text{Nb}_{1-y}\text{V}_y$ alloy system. By combining data extracted from pressure-composition isotherms with diffusion data, it is possible to obtain information on the density of sites, the site energies, and the saddle-point energies of a complete binary alloy system.

I. INTRODUCTION

Diffusion of interstitials (H,D,T,O,N,C) in metals has been a subject of intensive theoretical and experimental research for many years.¹⁻⁴

Most of the theories proposed so far have dealt with the motion of a *single* light interstitial in a *pure* metal. For example, Flynn and Stoneham⁵ gave a *quantum-mechanical* treatment of interstitial diffusion in metals in the nonadiabatic, Condon, and Born-Oppenheimer approximations. Because of the light mass of hydrogen and its isotopes, quantum effects are expected, especially in the bcc metals with a small jump distance of approximately 1.1 Å between the interstitial sites (Fig. 1). Hydrogen tunneling^{6,7} has indeed been observed in Nb

doped with N or O. Furthermore, the existence of local modes (~ 110 and ~ 170 meV in the bcc metals V, Nb, and Ta) and the low activation energy for diffusion (~ 100 meV) indicate that even around room temperature quantum effects are important.⁸ At high temperatures the diffusion process becomes classical and hydrogen will diffuse by over the barrier jumps. Emin *et al.*⁹ showed the importance of hydrogen atoms following metal atoms adiabatically. Teichler and Klamt¹⁰ went beyond the Condon approximation in showing that the transition matrix element could be dependent on the host-lattice configuration. Sugimoto and Fukai calculated the transition matrix element for hydrogen atoms in bcc metals.^{1,11,12} Recently, Kondo calculated the jump rate of interstitials in the regime where the electron-screening cloud cannot follow the motion of the interstitial adiabatically.¹³

A relatively small number of theoretical works have focussed on diffusion in pure metals at high interstitial concentration. Kehr, Kutner, and Binder treated the problem of diffusion in concentrated lattice gases with an attractive as well as a repulsive interaction between particles.¹⁴⁻¹⁶ These theoretical results are important for the concrete interpretation of diffusion experiments which are commonly carried out on samples with a finite concentration of interstitials (such as nuclear-magnetic resonance or quasielastic neutron scattering) or with a concentration gradient (such as in resistance-relaxation or Gorsky-relaxation experiments).

To our knowledge, only little attention has been given to diffusion of interstitials at finite concentrations in random alloys. Diffusion of interstitial atoms at low concentrations in dilute alloys without any interstitial-interstitial interactions was described by Oriani and Koiba.^{17,18} McLellan and Yoshihara treated the diffusion of interstitials in terms of a cell model in concentrated alloys, not taking into account blocking and interstitial-interstitial interactions.¹⁹⁻²¹ Kirchheim demonstrated the effects of site filling, blocking, correlation, and varying saddle-

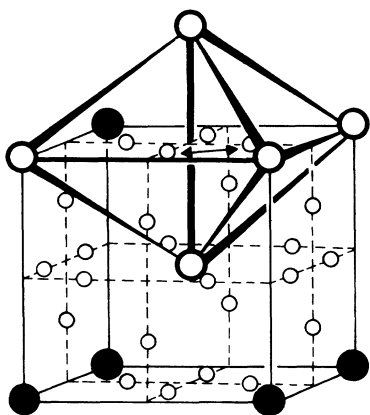


FIG. 1. Structure (bcc) of the $\text{Nb}_{1-y}\text{V}_y$ alloy system. The Nb and V atoms are randomly distributed among the lattice sites. Hydrogen atoms diffuse through the lattice by "jumping" from one tetrahedral site to another. Two neighboring tetrahedral sites have three nearest-neighbor metal atoms in common (●, metal atoms; ○, metal atoms of two neighboring tetrahedral sites; ○: tetrahedral sites).

point energies in various papers.²²⁻²⁵ None of models presented so far take into account interstitial-interstitial interactions in concentrated alloy systems. They are, strictly speaking, only applicable to real systems at low interstitial concentrations. Another problem in the application of these models is the many unknown parameters which cannot be determined from diffusion experiments alone.

In this paper we shall show that a relatively simple model which incorporates a distribution in site energies and site-blocking effects as well as effective interstitial-interstitial interactions is able to describe quantitatively the variation of the diffusion coefficient of interstitials in disordered alloys as a function of alloy composition and interstitial concentration. As a test case, we have chosen hydrogen in disordered $\text{Nb}_{1-y}\text{V}_y$ alloys. This choice is motivated by (i) the detailed knowledge available on hydrogen in the constituent metals V and Nb, (ii) the simple metallurgy of these alloys, and (iii) the remarkable concentration dependence of the hydrogen diffusion coefficient measured by Peterson and Herro²⁶ in $\text{Nb}_{1-y}\text{V}_y$, as shown in Fig. 2. With increasing vanadium concentration the hydrogen diffusion coefficient decreases sharply, reaches a minimum around $y \sim 0.4$, and increases towards the diffusion coefficient of V. Another very interesting feature is the hydrogen concentration dependence of the diffusion coefficient in the $\text{Nb}_{1-y}\text{V}_y$ alloy system. Whereas the diffusion coefficients of hydro-

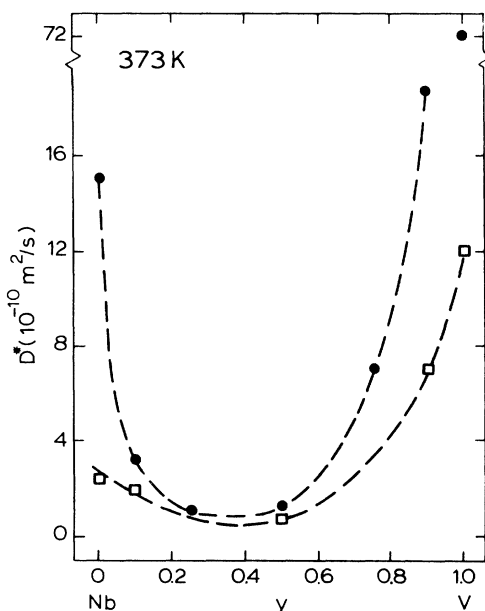


FIG. 2. Chemical diffusion coefficients D^* at 373 K for hydrogen in the $\text{Nb}_{1-y}\text{V}_y$ alloy system as a function of the vanadium concentration. Solid circles, diffusion coefficients extrapolated to zero hydrogen concentration ($c=0$); open squares, $c=0.02$ with c equal to the number of hydrogen atoms (N) divided by the number of tetrahedral sites (M). As there are six tetrahedral sites per metal atom in a bcc structure, the atomic fraction is equal to $6c$. The diffusion coefficients for the alloys are from Peterson and Herro in Ref. 26; the data for Nb and V are from Ref. 2.

gen in Nb and V decrease sharply with increasing hydrogen concentration (Fig. 2), the diffusion coefficients of the alloys with $y \sim 0.4$ show merely a very weak concentration dependence.

This paper is organized as follows. In Sec. II we present a macroscopic model of diffusion in concentrated alloys, taking into account interstitial-interstitial interactions, to relate the results of diffusion experiments to site-dependent activation energies E_{ij} and prefactors D_{ij}^0 . In Sec. III we calculate the temperature and hydrogen concentration dependence of the diffusion coefficient for various alloys in the $\text{Nb}_{1-y}\text{V}_y$ system. In Sec. IV we compare our calculations with experimental diffusion data. We show that the interstitial diffusion process is sensitive to the microscopic chemical and physical structure of an alloy and that, in principle, one can use hydrogen as a probe for the local structure of an alloy (Sec. V).

II. THE MODEL

The starting point in the analysis of macroscopic diffusion experiments is Fick's first law:

$$\mathbf{J} = -D^* n \nabla c, \quad (1)$$

with \mathbf{J} the current density (in $\text{m}^{-2}\text{s}^{-1}$), c the interstitial concentration (the number of interstitial atoms, N , divided by the number of interstitial sites, M), n (in m^{-3}) the site density (the number of interstitial sites, M , per unit volume), and D^* the macroscopic or chemical diffusion coefficient determined experimentally. The individual jump process is described by the mobility $M(c)$ defined as the velocity per unit force. The mobility is a function of concentration due to blocking and to the concentration dependence of the potentials surrounding the interstitial. The relation between the mobility $M(c)$ and the current density is

$$\mathbf{J} = -M(c)nc\nabla\mu, \quad (2)$$

where μ is the chemical potential. The macroscopic diffusion coefficient D^* is related to the mobility $M(c)$ by Eqs. (1) and (2). If μ is a function of position only through the concentration, Eqs. (1) and (2) yield

$$D^* = M(c)c \frac{\partial\mu}{\partial c}. \quad (3)$$

To find the tracer diffusion coefficient D , interstitial-interstitial interactions are eliminated by dividing D^* by the so-called thermodynamic factor $f = (c/RT)(\partial\mu/\partial c)$ and, neglecting correlation effects, we find

$$D = M(c)RT. \quad (4)$$

The tracer diffusion coefficient D is experimentally found to follow an Arrhenius relation, with a prefactor $D^0(c)$ and an activation energy $E(c)$. Combining this experimental information with Eq. (4), we obtain

$$M(c) = \frac{D^0(c)}{RT} \exp\left\{-\frac{E(c)}{RT}\right\}. \quad (5)$$

The concentration dependence of the mobility contains a factor $(1-sc)$, which is the probability of finding a free-

interstitial site. The blocking factor s is the number of interstitial sites blocked by one interstitial atom. Boureau²⁷ derived an analytical expression for the blocking factor s in a *pure* metal and showed that s is concentration dependent. However, for hydrogen atoms in a bcc metal a good agreement with experimental entropies²⁸ is obtained by taking a constant value $s=4$ for the blocking factor, which is, in fact, the same value as calculated by Boureau for high hydrogen concentrations. Writing $D^0(1-sc)$ for $D^0(c)$ and combining Eq. (5) with Eq. (3), we obtain

$$D^* = \frac{D^0}{RT} c(1-sc) \exp\left[\frac{-E(c)}{RT}\right] \frac{\partial \mu}{\partial c}. \quad (6)$$

The physical meaning of the various terms in Eq. (6) is as follows. The probability of finding an interstitial atom on a certain site is c and the probability of finding a free site (next to an interstitial) is $1-sc$. The Boltzmann factor $\exp[-E(c)/RT]$ is the probability that an interstitial jumps to another site. The gradient in the chemical potential μ is the driving force for diffusion.

In random alloys the many different local surroundings of an interstitial atom result in a distribution of prefactors D_{ij}^0 and of activation energies $E_{ij}(c)$, with i denoting the type of the initial site and j the type of the final site (see Fig. 3). The probability that interstitial atoms occupy sites of type i with energy ϵ_i is given by a Fermi-Dirac distribution function as we assume that multiple occupation of a given state is forbidden,^{22,29-31}

$$c_i = \frac{p_i}{s_i + \exp\{[\epsilon_i + f(c) - \mu]/RT\}}, \quad (7)$$

where c_i is the number of interstitial atoms, n_i , on sites of type i divided by the total number of interstitial sites, M , and p_i is the number m_i of interstitial sites of type i divided by the total number of interstitial sites, M (so $c_i = n_i/M$ and $p_i = m_i/M$; thus c_i/p_i is the fractional occupation of sites of type i). c_i depends on the total concentration c through the effective interstitial-interstitial interaction term $f(c)$ for reasons discussed in Refs. 29 and 30. The selective (site-dependent) blocking factor s_i is the number of sites of type i blocked by one interstitial atom on a site of type i . As mentioned above, in the *pure* metals V and Nb the exact value of the blocking factor s is not very important at low interstitial concentrations and a good agreement with experiment²⁸ is obtained by taking for s the limiting value for high interstitial concentrations ($s=4$ for hydrogen in a bcc metal).

In analyzing interstitial diffusion experiments in concentrated *alloy* systems, it is of importance to use site-dependent (selective) blocking factors s_i . If, for example, in an $A_{0.90}B_{0.10}$ alloy a given interstitial atom blocks on the average four interstitial sites, the blocking factor for an interstitial on an A_4 site is ~ 4 , but the blocking fac-

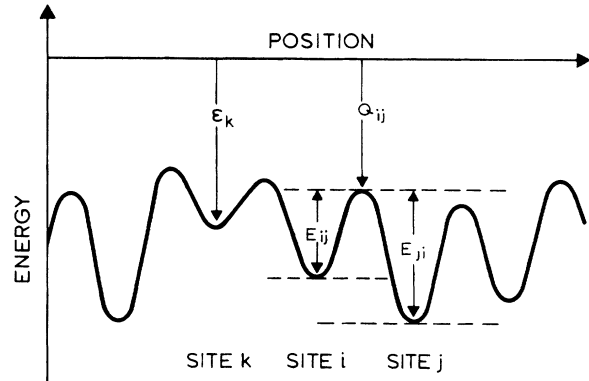


FIG. 3. Schematic representation of site energies ϵ_i and saddle-point energies Q_{ij} . The activation energy E_{ij} for diffusion from a site of type i to a site of type j is the difference between the site energy ϵ_i and the saddle-point energy Q_{ij} . Note that $Q_{ij} = Q_{ji}$, but, in general, $E_{ij} \neq E_{ji}$. The saddle-point energy is correlated with the site energy: if the site energy decreases, the saddle-point energy is also lowered. Due to this correlation the lowest barrier E_{ij} for diffusion is always found near a trapping site.

tor for an interstitial on a B_4 site is ~ 1 (the probability of finding another B_4 site next to the interstitial is small).

Assuming local equilibrium between the interstitial sites and averaging over all possible jumps from sites of type i to sites of type j , Eq. (6) for an alloy becomes

$$D^* = \sum_i \sum_j \frac{D_{ij}^0}{RT} c_i q_{ij} \left[1 - \frac{c_j}{p_j} s_j\right] \exp[-E_{ij}(c)/RT] \frac{\partial \mu}{\partial c}, \quad (8)$$

with c_i the probability of finding an interstitial atom on sites of type i , $1 - (c_j/p_j)s_j$ the probability that sites of type j are empty, and q_{ij} the probability of finding sites of type j next to sites of type i .

The coefficients q_{ij} are equal to p_j in other models for diffusion in concentrated alloy systems.^{20,22} In a real metal the probability of finding sites of type j next to sites of type i is not equal to the probability p_j of finding sites of type j in the alloy, but depends on the configuration of both sites of type i and sites of type j (q_{ij}). For example, in a bcc metal with tetrahedral sites (Fig. 1) two neighboring interstitial sites have three nearest-neighbor metal atoms in common, and it is impossible ($q_{ij}=0$) to jump from an A_4 site to a B_4 site. By means of Eq. (7) we can express $\partial \mu / \partial c$ in terms of c_k , p_k , s_k , and the effective interstitial-interstitial interaction $f(c)$ in the following way:

$$D^* = \sum_i \sum_j D_{ij}^0 c_i q_{ij} \left[1 - \frac{c_j}{p_j} s_j\right] \exp[-E_{ij}(c)/RT] \left\{ \left[\sum_k c_k \left[1 - \frac{c_k}{p_k} s_k\right] \right]^{-1} + \frac{1}{RT} \frac{\partial f(c)}{\partial c} \right\}. \quad (9)$$

In Eq. (9) the diffusion coefficient for interstitial atoms in an alloy is expressed in terms of single jumps from sites of type i to sites of type j with site-dependent activation energies $E_{ij}(c)$ and prefactors D_{ij}^0 . Interstitial-interstitial interaction [$f(c)$] is taken into account, as well as selective blocking factors s_j and correlation between two neighboring sites (q_{ij}). Equation (9) reduces almost³² to Eq. (29) derived by Kirchheim in Ref. 22 by setting $q_{ij} \equiv p_j$, $s_j = 1$, and $f(c) = 0$.

In Eqs. (8) and (9) correlation effects between successive jumps are neglected. Lattice-gas effects and a disorder in the transition rates in some cases cause strong correlations.^{24,25,31} Correlation effects due to lattice-gas effects can be incorporated into the model by a concentration-dependent correlation factor. For $c < 0.03$ this factor is approximately 1.³¹ In the next section we calculate diffusion coefficients for hydrogen diffusion in $\text{Nb}_{1-y}\text{V}_y$ alloys using data from pressure-composition isotherms for the parameters in Eq. (9).

III. CALCULATION OF D^* IN THE $\text{Nb}_{1-y}\text{V}_y$ ALLOY SYSTEM

Until recently it was necessary to make rather drastic simplifications in using equations such as Eq. (7) or (9) because of the many unknown parameters which enter these expressions. Fortunately, Feenstra *et al.*^{28,33,34} recently determined the site energies ϵ_i and the density of sites p_i for hydrogen in the $\text{Nb}_{1-y}\text{V}_y$ system (for $y = 0, 0.1, 0.25, 0.5, 0.75, 0.90, 1.0$) from pressure-composition isotherms. In the approximation that only first-nearest-neighbor metal atoms determine the energy of a hydrogen atom on a tetrahedral site, a good fit to the isotherms was obtained by using five energy (ϵ_i) delta functions and a binomial site distribution p_i . The site energies ϵ_i are tabulated in Table I. Some of these energies are extrapolated values, as it is, for example, not possible to determine the site energy ϵ_i of a V_4 site in a $\text{Nb}_{0.90}\text{V}_{0.10}$ alloy from pressure-composition measurements due to the small fraction of V_4 sites (0.0001) in the alloy.³³ Considering the monotonous variation with alloy composition of the lattice parameter,³⁵ bulk modulus,³⁶ and electronic specific-heat coefficient,³⁷ and the uniformity of the hydrogen-induced lattice expansion³⁸ in the group-VB metals, the interaction energy $f(c)$ is simply linearly interpolated between the energy for hydrogen-hydrogen (H-H) interactions in V and Nb using the values of Table II. A monotonous variation of the interaction energy between Nb and V is also indicated by the smooth variation of the partial molar enthalpy at high hydrogen concen-

trations in Ref. 28. The probability of finding a certain site as a neighboring site (q_{ij}) is calculated for a binomial distribution and tabulated in Table III.

In calculating the selective blocking factors s_i (Table IV), a repulsive interaction is assumed up to second-nearest-neighbor hydrogen atoms. At high hydrogen concentration ($c_i/p_i \rightarrow 1$) one hydrogen atom blocks on the average four tetrahedral sites.^{27,39} As the calculation of the selective blocking factors may be found in the Appendix, we consider here only a special case. As an illustration, for example, at low concentrations ($c < 0.02$) a hydrogen atom in a $\text{Nb}_{0.90}\text{V}_{0.10}$ alloy on a trapping site (V_4 site) has a probability of 0.1 to block another V_4 site (0.1 is the probability of finding a V_4 site next to a V_4 site in a $\text{Nb}_{0.90}\text{V}_{0.10}$ alloy; see Table III). Each site has four nearest-neighbor sites, yielding a blocking factor of approximately $(1 + 4 \times 0.1 =) 1.4$ for a hydrogen atom on a V_4 site, but a hydrogen atom on a Nb_4 site in a $\text{Nb}_{0.90}\text{V}_{0.10}$ alloy has a blocking factor of approximately 4 because the probability of finding only Nb_4 sites as neighbors is large. The exact values of the blocking factor s_i determine when sites of type i are filled completely. This is important in diffusion experiments where the diffusion coefficient is very sensitive to the number of trap sites.

The activation energies $E_{ij}(c)$ depend on the site energy ϵ_i , the saddle-point energy Q_{ij} between sites of type i and of type j , and the total concentration c (see Fig. 3). The hydrogen concentration dependence of E_{ij} is due to the changing potentials around a hydrogen atom by the expansion of the lattice. For the calculation we interpolate between the concentration dependence of the activation energy for diffusion of H in Nb and V on the same arguments as for the interaction energy. The values⁴⁰ used in the calculations are $E_V(c) = 4.3 + 83.3c$ and $E_{\text{Nb}}(c) = 10.2 + 65.1c$ in kJ/mol H and with $c = N/M$. From values for the site energy in pure Nb and V (Table I) and the activation energy for diffusion (Table V), we find the same saddle-point energy of -25.2 kJ/mol H in both Nb and V. For $\text{Nb}_{1-y}\text{V}_y$ alloys we shall take the same value for the following reasons. Although the saddle-point energies are expected to vary with the site energies (e.g., the saddle-point energy decreases when the site energy is lowered), the variation in the saddle-point energy is only a fraction of the variation of the site energy. Furthermore, Kirchheim^{24,25} showed by Monte Carlo simulations that correlated saddle-point energies result only in a relatively small increase in the diffusion coefficient because all the easy diffusion paths are directed to trap sites (Fig. 3). A constant saddle-point energy was also found by McLellan and Yoshihara²¹ in fitting

TABLE I. Site energies (in kJ/mol H) for various sites in the $\text{Nb}_{1-y}\text{V}_y$ alloy system. (Data from Feenstra and Griessen, Ref. 33.)

Site	Nb	$\text{Nb}_{0.90}\text{V}_{0.10}$	$\text{Nb}_{0.75}\text{V}_{0.25}$	$\text{Nb}_{0.50}\text{V}_{0.50}$	$\text{Nb}_{0.25}\text{V}_{0.75}$	$\text{Nb}_{0.10}\text{V}_{0.90}$	V
Nb_4	-35.3	-32.0	-26.8	-17.7	-9.0	-3.6	
Nb_3V		-37.8	-32.5	-23.5	-14.8	-9.0	
Nb_2V_2		-46.0	-40.5	-31.5	-22.5	-17.4	
NbV_3		-54.0	-49.0	-39.8	-30.8	-25.0	
V_4		-61.8	-56.5	-47.3	-38.5	-33.0	-29.6

TABLE II. Parameters A_i (in units of J/molH) entering the expression $f(c) = A_1c + A_2c^2 + A_3c^3 + A_4c^4$ for the effective H-H interaction $f(c)$ as calculated from data of Feenstra *et al.* (Ref. 28). The concentration c is given by the number of hydrogen atoms per tetrahedral site. The agreement with values from Veleckis and Edwards (Ref. 41) is excellent.

	A_1	A_2	A_3	A_4
Nb	-1.93×10^5	2.10×10^6	-2.36×10^7	1.09×10^8
V	-2.22×10^5	4.35×10^6	-7.78×10^7	5.55×10^8

their cell model to activation energies for hydrogen diffusion in various $\text{Ti}_{1-y}\text{V}_y$ alloys. This alloy system is on the vanadium-rich side, in many respects comparable with the $\text{Nb}_{1-y}\text{V}_y$ alloy system.

The prefactors D_{ij}^0 contain a constant depending on the geometry of the system, the jump distance λ_{ij} between two sites, and the attempt frequency ν_i of hydrogen on a site of type i . The variation in the jump distance is relatively small and is interpolated between Nb and V. The attempt frequency ν_i depends on the exact configuration of the surrounding shell of nearest-neighbor metal atoms. There are no measurements available giving values of ν_i for different sites, so we take a constant value for D_{ij}^0 for all the different sites, and interpolate D_{ij}^0 between 3.1×10^{-8} m²/s for V and 5×10^{-8} m²/s for Nb, depending on the alloy concentration.

We have now assigned values to all the parameters entering Eqs. (7) and (9) and are in a position to calculate the chemical diffusion coefficients D^* as a function of temperature and hydrogen concentration for any $\text{Nb}_{1-y}\text{V}_y$ alloy without any fit parameter. The results are shown in Figs. 4, 5, and 8.

IV. COMPARISON WITH EXPERIMENT

The solid lines in Figs. 4 and 5 are calculated diffusion coefficients for $\text{Nb}_{1-y}\text{V}_y$ alloys, with $y = 0, 0.1, 0.25, 0.5, 0.75, 0.9, 1.0$, between 200 and 1000 K. The lines are calculated for a hydrogen concentration of 0.001 (N/M) (0.6 at. % H). The calculated diffusion coefficients for pure Nb and V are in agreement with data published by Völkl and Alefeld² and are plotted for the temperature range where experimental data exist. Dashed lines in Figs. 4 and 5 are diffusion coefficients as measured by Peterson and Herro²⁶ (PH) using the Matano interface

method. For the comparison of experimental and calculated data, the *slope* of the curves (the *mean* activation energy) in Figs. 4 and 5 was determined and plotted in Fig. 6 as a function of the alloy concentration. The open squares correspond to the experimental mean activation energies found by PH and the solid dots to the mean activation energies of the calculated curves. As the calculated curves in Figs. 4 and 5 are not straight lines, the averaged value of the mean activation energy was calculated between 225 and 500 K. In alloying V with Nb an almost linear increase in the mean activation energy up to $\text{Nb}_{0.7}\text{V}_{0.3}$ is observed, followed by a sharp decrease on the Nb side. Qualitatively, this behavior of the activation energy can be explained by assuming that hydrogen occupies only the most favorable sites (V_4 sites). In alloying V with Nb the energy of the V_4 sites decreases linearly with the Nb concentration (Table I) and the activation energy increases. On the Nb side of the alloy system the number of V_4 sites is so small that many hydrogen atoms occupy NbV_3 sites with higher site energy and correspondingly lower activation energy. The slope of the calculated and experimental curves agree within the experimental errors, except for the $\text{Nb}_{0.75}\text{V}_{0.25}$ and $\text{Nb}_{0.90}\text{V}_{0.10}$ alloys (Table V).

The reason for the deviation between calculated and measured activation energies for these two alloys is best discussed by considering the concentration dependence of the diffusion coefficients in detail. Consider Fig. 7, in which the diffusion coefficient of H in $\text{Nb}_{0.90}\text{V}_{0.10}$ at 373 K is plotted as a function of the hydrogen concentration (curve c). Its concentration dependence is mainly determined by two competing effects: site filling and attractive H-H interactions. As a result, $D^*(c)$ is a highly non-linear function of c . These two contributions, which are shown separately in Fig. 7, are now briefly discussed.

(a) *Site filling.* A distribution in site energies leads to an increasing diffusion coefficient with increasing H concentration. This is due to the fact that with increasing hydrogen concentration more and more hydrogen atoms occupy NbV_3 sites which have a higher energy than the already filled V_4 sites. The activation energy for jumps out of the NbV_3 sites is lower than that of the trapping V_4 sites and, consequently, D^* increases with c .

(b) *Effective H-H interaction.* To illustrate the role of the inclusion of the effective H-H interaction $f(c)$, we calculated $D^*(c)$ for an average perfect crystal with the same mean activation energy as in $\text{Nb}_{0.90}\text{V}_{0.10}$ at low H

TABLE III. Probability (q_{ij}) of finding a site Nb_iV_j as the nearest-neighbor site of a given site Nb_mV_n in a $\text{Nb}_{1-y}\text{V}_y$ alloy.

Site Nb_mV_n	Nearest-neighbor site: Nb_iV_j				
	V_4	NbV_3	Nb_2V_2	Nb_3V	Nb_4
V_4	y	$1-y$	0	0	0
NbV_3	$\frac{1}{4}y$	$\frac{1}{4} + \frac{1}{2}y$	$\frac{3}{4} - \frac{3}{4}y$	0	0
Nb_2V_2	0	$\frac{1}{2}y$	$\frac{1}{2}$	$\frac{1}{2} - \frac{1}{2}y$	0
Nb_3V	0	0	$\frac{3}{4}y$	$\frac{3}{4} - \frac{1}{2}y$	$\frac{1}{4} - \frac{1}{4}y$
Nb_4	0	0	0	y	$1-y$

TABLE IV. Selective blocking factors s_j for different sites in various $\text{Nb}_{1-y}\text{V}_y$ alloys. The sites below the dashed lines have a low probability of being occupied up to a hydrogen concentration $c=0.03$, i.e., hydrogen-to-metal-atom ratio of 0.18. Details of the calculation of the selective blocking factors are given in the Appendix.

	$\text{Nb}_{0.90}\text{V}_{0.10}$	$\text{Nb}_{0.75}\text{V}_{0.25}$	$\text{Nb}_{0.50}\text{V}_{0.50}$	$\text{Nb}_{0.25}\text{V}_{0.75}$	$\text{Nb}_{0.10}\text{V}_{0.90}$
V_4	1.3	1.75	2.5	3.25	3.7
NbV_3	1.9	2.13	2.5	2.88	3.1
Nb_2V_2	2.5	2.5	2.5	2.5	2.5
Nb_3V	3.1	2.88	2.5	2.13	1.9
Nb_4	3.7	3.25	2.5	1.75	1.3

concentrations. D^* decreases because of the negative contribution of $\partial f/\partial c$, see Eq. (9). Peterson and Herro extrapolated their experimental data to zero hydrogen concentration as indicated by the dashed line in Fig. 7. By means of this extrapolation they find a diffusion coefficient at zero concentration which is systematically too high. The difference between extrapolated and the real diffusion coefficients increases strongly at lower temperatures. Correction of the extrapolated results of PH led to the dotted lines in Fig. 5. The resulting corrected activation energies (Table V) are plotted in Fig. 5 (open diamonds) and are in excellent agreement with the calculated mean activation energies. This is rather remarkable as the model does not involve any fit parameters.

Although there is a good agreement in the mean activation energies of the calculated and experimental diffusion coefficients in Figs. 4 and 5, the experimental (dashed or dotted) lines are all shifted downwards by approximately the same factor for the alloys. The diffusion coefficients of PH for the pure metals Nb and V are also shifted slightly downwards from the calculated and the best literature values. It is not clear at present what the origin of this shift is. It might arise from a systematic experimental error, but could equally well point to a decrease in the attempt frequency ν_i which determines the prefactors D_{ij}^0 . More experimental data will be required to elucidate this point.

At present, for the comparison of the calculated concentration dependence of the diffusion coefficients with the experimental data (Fig. 8), we shall simply shift the calculated curves down by a constant factor. These fac-

tors are determined by the differences between the calculated and experimental curves in Figs. 4 and 5 at 460 K ($c=0.001$), because at high temperatures deviations due to extrapolation (as discussed above) of the measured diffusion coefficients are small. The concentration dependence of the diffusion coefficient of the $\text{Nb}_{1-y}\text{V}_y$ alloys at 373 K is displayed in Fig. 8. Solid lines are calculated curves and dashed lines experimental data from PH. The concentration dependence of the diffusion coefficient in $\text{Nb}_{0.10}\text{V}_{0.90}$ is 1 order of magnitude larger than in $\text{Nb}_{0.50}\text{V}_{0.50}$ or $\text{Nb}_{0.90}\text{V}_{0.10}$. The calculated and experimental curves are parallel to each other, indicating that there is probably only a change in the prefactor D_{ij}^0 by a constant factor as a function of temperature and hydrogen concentration.

V. CONCLUSION

The agreement in the temperature and concentration dependence of the calculated and experimental chemical diffusion coefficients D^* indicates that diffusion in the ternary alloy system $\text{Nb}_{1-y}\text{V}_y\text{H}_x$ can be described by single-jump processes with site-dependent activation energies, prefactors, and blocking factors when the interstitial-interstitial interaction is included. Using a constant saddle-point energy of -25.2 kJ/mol H for the various $\text{Nb}_{1-y}\text{V}_y$ alloys, we find a reasonable quantitative agreement between calculated and experimental mean activation energies. The concept of an approximately constant saddle-point energy is supported by calculations of McLellan and Yoshihara for hydrogen diffusion in

TABLE V. Mean activation energies ($c=0.001$) for hydrogen diffusion in the $\text{Nb}_{1-y}\text{V}_y$ alloy system (in kJ/mol H). The calculated values for pure Nb and V are in agreement with the best values from literature (Ref. 2).

	Nb	$\text{Nb}_{0.90}\text{V}_{0.10}$	$\text{Nb}_{0.75}\text{V}_{0.25}$	$\text{Nb}_{0.50}\text{V}_{0.50}$	$\text{Nb}_{0.25}\text{V}_{0.75}$	$\text{Nb}_{0.10}\text{V}_{0.90}$	V
Expt. ^a	7.9±1.2	16.4±0.9	21.9±0.3	20.9±0.5	13.9±1.2	8.8±1.3	4.1±0.6
Expt. ^b	7.9±1.2	20.4±0.9	24.9±0.3	20.9±0.5	13.9±1.2	8.8±1.3	4.1±0.6
Model ^c	10.2	21.6	25.6	20.9	13.4	8.0	4.3

^aActivation energies as determined experimentally in Ref. 26.

^bActivation energies of Ref. 26 corrected for extrapolation to zero hydrogen concentration.

^cCalculated activation energies.

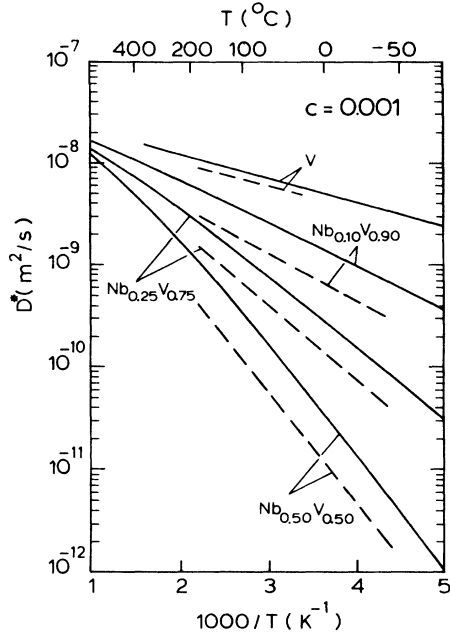


FIG. 4. Chemical diffusion coefficients D^* as a function of temperature for $c=0.001$, with c the number of hydrogen atoms (N) divided by the number of tetrahedral sites (M). [Solid lines, diffusion coefficients calculated by means of Eq. (9)—the solid line for V stands also for the best experimental diffusion coefficients from Ref. 2; dashed lines, experimental diffusion coefficients from Ref. 26.]

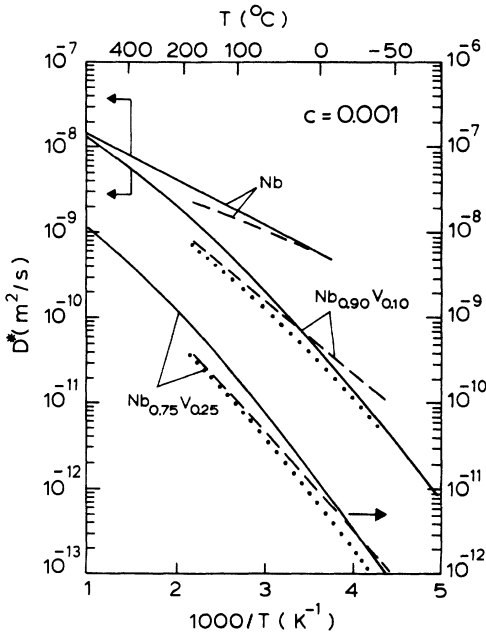


FIG. 5. Chemical diffusion coefficients D^* as a function of temperature for $c=0.001$ (solid lines, diffusion coefficients calculated with the same model as in Fig. 4—the solid line for Nb stands also for the best experimental diffusion coefficients from Ref. 2; dashed lines, experimental diffusion coefficients from Ref. 26.)

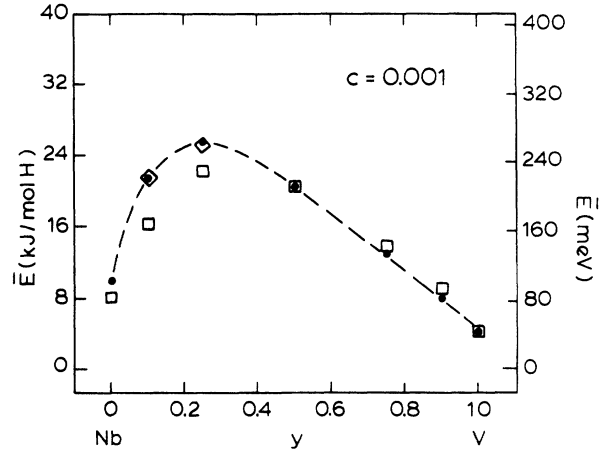


FIG. 6. Mean activation energy \bar{E} for diffusion in the $\text{Nb}_{1-y}\text{V}_y$ alloy system between 225 and 500 K ($c=0.001$). The mean activation energy \bar{E} is the activation energy for diffusion as determined by the slope of the Arrhenius plots of the diffusion coefficients in Figs. 4 and 5. (Solid circles, calculated values; open squares, experimental values of Ref. 26; open diamonds, experimental values corrected as described in the text. The line is a guide to the eye.)

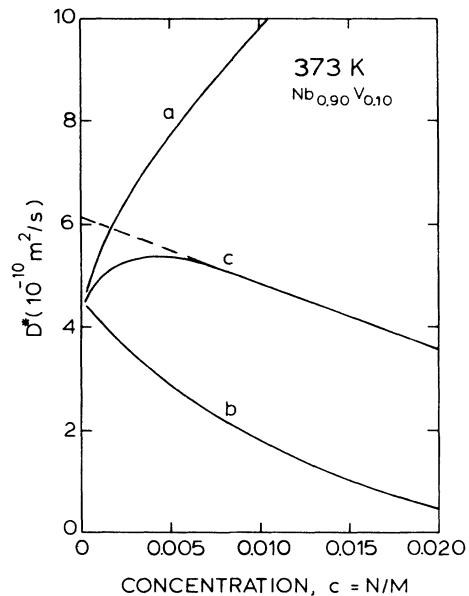


FIG. 7. Chemical diffusion coefficients D^* for H in $\text{Nb}_{0.90}\text{V}_{0.10}$ as a function of hydrogen concentration at 373 K. Curve *a*, diffusion coefficients without H-H interactions, but including the effect of site filling. Sites with low energy ϵ_i and low diffusion coefficients are filled first. Curve *b*, average crystal approximation: diffusion coefficients in a crystal with sites of constant energy ϵ_i and a constant activation energy. No site-filling effects, but including an effective H-H interaction. Curve *c*, calculated diffusion coefficients for $\text{Nb}_{0.90}\text{V}_{0.10}$ including both site-filling and interaction effects. (Dashed line: extrapolation made by Peterson and Herro in Ref. 26.)

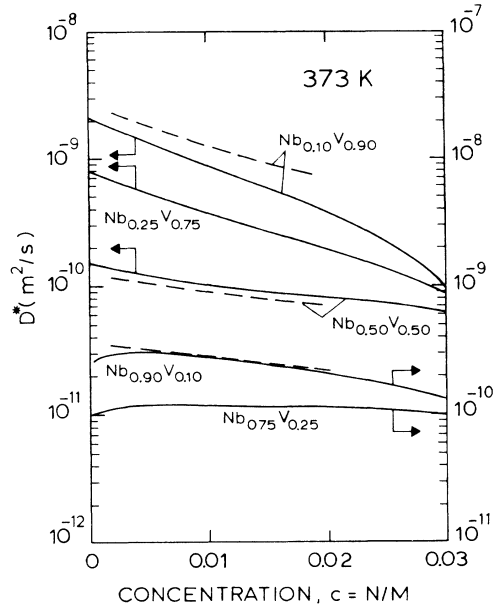


FIG. 8. Chemical diffusion coefficients D^* at 373 K as a function of hydrogen concentration for various alloys. [Solid lines, calculated curve shifted by a constant factor (see text); dashed lines, experimental data from ref. 26.]

$\text{Ti}_{1-y}\text{V}_y$ alloys and by independent measurements on H trapping in $\text{Nb}_{0.95}\text{Mo}_{0.05}$ alloys by Matsumoto *et al.*⁴² The trap energy for hydrogen in $\text{Nb}_{0.95}\text{Mo}_{0.05}$ is found to be ~ 8 kJ/mol H and the increase in the activation energy for diffusion to be ~ 7 kJ/mol H.

The deviation of the experimental data at low temperatures in the Figs. 4 and 5 for the $\text{Nb}_{0.75}\text{V}_{0.25}$ and $\text{Nb}_{0.90}\text{V}_{0.10}$ alloys was shown to be due to an inadequate extrapolation of the experimental data to zero hydrogen concentration. The agreement between corrected experimental values and the calculated values is remarkably good considering the fact that the present model does not involve any further fit parameters.

The most critical test for Eq. (9) is the prediction of the concentration dependence of the hydrogen diffusion coefficients in the $\text{Nb}_{1-y}\text{V}_y$ alloy system (Fig. 8). Figure 7 demonstrates the importance of site filling as well as H-H interactions. Using a constant blocking factor of 4 instead of the variable selective blocking factors would result in a much more nonlinear concentration dependence of curve c , especially at low temperatures. More experimental data at low temperatures as a function of hydrogen concentration are needed to study in detail the importance of variable blocking factors.

The model shows the sensitivity of the interstitial diffusion process to different parameters, such as the site distribution, site energies, blocking factors, and interstitial-interstitial interactions. By comparing calculated and experimental diffusion coefficients as a function of temperature and interstitial concentration, one can obtain information on these parameters and, therefore, on the microscopic chemical and physical structure of an alloy. In this way hydrogen diffusion experiments can be used as a local probe for the alloy structure, sensitive

especially to the number and the energy of trap sites, while pressure-composition measurements are most sensitive to sites with higher densities.

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APPENDIX

Hydrogen atoms on interstitial sites have a short-range repulsive interaction between them due to Coulomb repulsion of the protons. A tetrahedral site has four first-nearest-neighbor sites and two second-nearest-neighbor sites. In V the distance between first-nearest-neighbor sites is 1.07 \AA (1.17 \AA in Nb) and 1.52 \AA between second-nearest-neighbor sites (1.65 \AA in Nb). As shown by comparison of experimental entropies with analytical approximations and Monte Carlo experiments,^{27,39} a hydrogen atom on a tetrahedral site in a bcc metal effectively blocks its first- and second-nearest-neighbor sites, resulting in a blocking factor of $(4+2+1=) 7$. At finite concentrations, however, each Hydrogen atom does not block seven sites, as hydrogen atoms share blocking sites with each other. Boureau²⁷ derived an analytical expression for the concentration dependence of the blocking factor s in a pure metal. The blocking factor changes almost linearly from 7 at low hydrogen concentration ($c=0$) to 4 at high hydrogen concentration ($c=0.25$, with $c=N/M$ the number of hydrogen atoms divided by the total number of interstitial sites). However, a good agreement between calculated and experimental entropies²⁸ is obtained by taking the constant value $s=4$ for all hydrogen concentrations in a pure metal, indicating that the exact value for s at low hydrogen concentrations is not very important.

In an alloy the occupation of the different sites is described by Eq. (7). The factor s_i is the number of sites of type i blocked by hydrogen atoms occupying the same type of sites i . In a pure metal the blocking factor s is approximately 4. The number of sites of type i blocked by a hydrogen on a site of type i depends (in an alloy) on the probability of finding a site of type i next to the hydrogen atom. In the limit of a very dilute alloy with a small number of trap sites of type i (e.g., the V_4 site in $\text{Nb}_{1-y}\text{V}_y$), the selective blocking factor $s_i \sim 1$ because the probability of finding two sites of type i (two V_4 sites) as nearest neighbors is negligible. The selective blocking factors in an alloy vary between 1 and 4, depending on the fraction of the sites of type i .

In order to estimate the selective blocking factors, the probability f_i of finding a site of type i not occupied by hydrogen shall be calculated. Taking into account only

TABLE VI. The probability f_i of finding a free site of type i (the index i in f_i, c_i, p_i stands for $1 \equiv V_4$, $2 \equiv NbV_3$, $3 \equiv Nb_2V_2$, $4 \equiv Nb_3V$, $5 \equiv Nb_4$ sites) in Nb_{1-y}V as a function of the alloy composition.

	Nb _{0.90} V _{0.10}	Nb _{0.75} V _{0.25}	Nb _{0.50} V _{0.50}	Nb _{0.25} V _{0.75}	Nb _{0.10} V _{0.90}
V ₄	1 - 1.3(c ₁ /p ₁)	1 - 1.75(c ₁ /p ₁)	1 - 2.5(c ₁ /p ₁)	1 - 3.25(c ₁ /p ₁)	1 - 3.7(c ₁ /p ₁)
NbV ₃	0.94 - 1.9(c ₂ /p ₂)	0.89 - 2.13(c ₂ /p ₂)	0.85 - 2.5(c ₂ /p ₂)	0.83 - 2.88(c ₂ /p ₂)	0.82 - 3.1(c ₂ /p ₂)
Nb ₂ V ₂	0.93 - 2.5(c ₃ /p ₃)	0.84 - 2.5(c ₃ /p ₃)	0.75 - 2.5(c ₃ /p ₃)	0.68 - 2.5(c ₃ /p ₃)	0.65 - 2.5(c ₃ /p ₃)
Nb ₃ V	0.92 - 3.1(c ₄ /p ₄)	0.81 - 2.88(c ₄ /p ₄)	0.66 - 2.5(c ₄ /p ₄)	0.54 - 2.13(c ₄ /p ₄)	0.47 - 1.9(c ₄ /p ₄)
Nb ₄	0.91 - 3.7(c ₅ /p ₅)	0.79 - 3.25(c ₅ /p ₅)	0.60 - 2.5(c ₅ /p ₅)	0.43 - 1.75(c ₅ /p ₅)	0.33 - 1.3(c ₅ /p ₅)

blocking of first-nearest neighbors, the blocking of first-nearest-neighbor sites must be renormalized by a factor 0.75 in order to get the experimentally observed total blocking factor ($4 = 1 + 4 \times 0.75$). In general, there are three contributions to the blocking of sites of type i , e.g., NbV₃ sites: NbV₃ sites are blocked by hydrogen atoms on NbV₃ sites. Secondly, NbV₃ sites are blocked by hydrogen atoms on V₄ sites, and the third contribution is due to blocking from hydrogen on Nb₂V₂ sites. Calculating the probability of finding a free site, we find

$$f_1 = 1 - (1 + 3y) \frac{c_1}{p_1} - \frac{3}{4}y \frac{c_2}{p_1}, \quad (A1)$$

$$f_2 = 1 - \left(\frac{7}{4} + \frac{3}{2}y\right) \frac{c_2}{p_2} - (3 - 3y) \frac{c_1}{p_2} - \frac{3}{2}y \frac{c_3}{p_2}, \quad (A2)$$

$$f_3 = 1 - \frac{5}{2} \frac{c_3}{p_3} - \left(\frac{9}{4} - \frac{9}{4}y\right) \frac{c_2}{p_3} - \frac{9}{4}y \frac{c_4}{p_3}, \quad (A3)$$

$$f_4 = 1 - \left(\frac{13}{4} - \frac{3}{2}y\right) \frac{c_4}{p_4} - \left(\frac{3}{2} - \frac{3}{2}y\right) \frac{c_3}{p_4} - 3y \frac{c_5}{p_4}, \quad (A4)$$

$$f_5 = 1 - (4 - 3y) \frac{c_5}{p_5} - \frac{3}{4}(1 - y) \frac{c_4}{p_5}, \quad (A5)$$

with f_1 the probability of finding a free V₄ site in a Nb_{1-y}V_y alloy, p_1 the fraction of V₄ sites, and c_1 the number of hydrogen atoms on V₄ sites divided by the to-

tal number of sites. (The index i in f_i, p_i, c_i stands for $1 \equiv V_4$, $2 \equiv NbV_3$, $3 \equiv Nb_2V_2$, $4 \equiv Nb_3V$, $5 \equiv Nb_4$ sites.) Blocking of a site of type i depends on the alloy concentration y , the hydrogen concentration on sites of type i , and the concentration of hydrogen on two other sites.

The energy difference between different sites in the Nb_{1-y}V_y alloy system is ~ 8 kJ/mol H. It is a reasonable assumption that hydrogen atoms fill up the lowest-energy states and therefore, that, blocking of lower-energy sites by hydrogen on higher-energy sites can be neglected [the last terms in Eqs. (A1)–(A5)]. The probability of finding a free site is now calculated and is shown in Table VI. There are two contributions. A concentration-dependent blocking of sites of type i by hydrogen on sites of type i , and the blocking from hydrogen atoms on lower-energy sites, which effectively reduces the number of free sites of type i by a constant amount. The dashed line in Table VI is the border line between (partly) occupied and (almost) unoccupied sites up to a total hydrogen concentration of 0.03 (and still higher).

The constant blocking by hydrogen atoms on lower energy sites is small because either the number of lower-energy sites is small (for small y) or there are no lower sites filled with hydrogen (large y). The probability f_i of finding a free site of type i can now be approximated by $1 - (c_i/p_i)s_i$, and Eq. (7) can be used to describe the site occupation in the alloy. The factors s_i used in the calculations are tabulated in Table IV.

¹Y. Fukai and H. Sugimoto, Adv. Phys. **34**, 263 (1985).

²J. Völkl and G. Alefeld, in *Hydrogen in Metals I*, Vol. 28 of *Topics in Applied Physics*, edited by G. Alefeld and J. Völkl (Springer-Verlag, Berlin, 1978), pp. 321–348.

³K. W. Kehr, in *Hydrogen in Metals I*, Ref. 2, pp. 197–226.

⁴A. M. Stoneham, Ber. Bunsenges. Gesell. **76**, 816 (1972).

⁵C. P. Flynn and A. M. Stoneham, Phys. Rev. B **1**, 3966 (1970).

⁶C. Morkel, H. Wipf, and K. Neumaier, Phys. Rev. Lett. **40**, 947 (1978).

⁷H. Wipf, A. Magerl, S. M. Shapiro, S. K. Satija, and W. Thomlinson, Phys. Rev. Lett. **46**, 947 (1981).

⁸A. Magerl, J. J. Rush, and J. M. Rowe, Phys. Rev. B **33**, 2093 (1986).

⁹D. Emin, M. I. Baskes, and W. D. Wilson, Phys. Rev. Lett. **42**,

791 (1979).

¹⁰H. Teichler and A. Klamt, Phys. Lett. **108A**, 281 (1985).

¹¹H. Sugimoto and Y. Fukai, Phys. Rev. B **22**, 670 (1980).

¹²H. Sugimoto, J. Phys. Soc. Jpn. **53**, 2592 (1984).

¹³J. Kondo, Physica **124B**, 25 (1984).

¹⁴K. W. Kehr, R. Kutner, and K. Binder, Phys. Rev. B **23**, 4931 (1981).

¹⁵R. Kutner, K. Binder, and K. W. Kehr, Phys. Rev. B **26**, 2967 (1982).

¹⁶R. Kutner, K. Binder, and K. W. Kehr, Phys. Rev. B **28**, 1846 (1983).

¹⁷R. A. Oriani, Acta Metall. **18**, 147 (1970).

¹⁸M. Koiwa, Acta Metall. **22**, 1259 (1974).

¹⁹R. B. McLellan, Acta Metall. **30**, 317 (1982).

- ²⁰M. Yoshihara and R. B. McLellan, *Acta Metall.* **34**, 1359 (1986).
- ²¹R. B. McLellan and M. Yoshihara, *J. Phys. Chem. Solids* **48**, 661 (1987).
- ²²R. Kirchheim, *Acta Metall.* **30**, 1069 (1982).
- ²³R. Kirchheim, F. Sommer, and G. Schluckebier, *Acta Metall.* **30**, 1059 (1982).
- ²⁴R. Kirchheim, *Acta Metall.* **35**, 271 (1987).
- ²⁵R. Kirchheim and U. Stolz, *Acta Metall.* **35**, 281 (1987).
- ²⁶D. T. Peterson and H. M. Herro, *Metall. Trans A* **17**, 645 (1986).
- ²⁷G. Boureau, *J. Phys. Chem. Solids* **42**, 743 (1981).
- ²⁸R. Feenstra, P. Meuffels, B. Bischof, and H. Wenzl (unpublished).
- ²⁹R. Griessen, *Phys. Rev. B* **27**, 7575 (1983).
- ³⁰R. Griessen, in *Hydrogen in Disordered and Amorphous Solids*, edited by G. Bambakidis and R. C. Bowman (Plenum, New York, 1986), p. 153.
- ³¹G. E. Murch, *Atomic Diffusion Theory in Highly Defective Solids*, Vol. 6 of *Diffusion and Defect Monograph Series*, edited by Y. Adda, A. D. le Claire, L. M. Slifkin, and F. H. Wöhlbier (Trans Tech, Aedermannsdorff, 1980).
- ³²In the derivation of Eq. (29) in Ref. 22, an assumption is made which leads to negative diffusion coefficients (for $y > 0.5$) for diffusion in a one-level system (p. 1075 Ref. 22). The applicability of the equation was thus limited to low interstitial concentrations. This is not necessary if one realizes that it is not allowed to take the derivative with respect to x going from Eq. (26) to (27) in Ref. 22 because Eq. (26),

$$J = f \sum_i \sum_k (c_i \Gamma_{ik} l_{ik})_x - (c_i \Gamma_{ik} l_{ik})_{x+dx} ,$$

with $l_{ik} = l$, means, in the limit $dx \rightarrow l$,

$$J = fl \sum_i \sum_k \Gamma_{i0} \{ c_i(x) [c_k^0 - c_k(x+dx)] - c_i(x+dx) [c_k^0 - c_k(x)] \} \times \exp(-G_{ik}/RT) ,$$

which cannot be reduced to Eq. (27) in Ref. 22. After this correction, the analysis in Ref. 22 results in Eq. (9) as derived in this paper, but without selective blocking factors and H-H interactions.

- ³³R. Feenstra, R. C. Brouwer, and R. Griessen (unpublished).
- ³⁴R. Feenstra, P. Sengers, and R. Griessen (unpublished).
- ³⁵W. B. Pearson, *Handbook of Lattice Spacings and Structures of Metals and Alloys*, Vol. 4 of *On Metal Physics and Physical Metallurgy*, edited by G. V. Raynor (Pergamon, New York, 1958).
- ³⁶E. S. Fisher, J. F. Miller, H. L. Alberts, and D. G. Westlake, *J. Phys. F* **11**, 1557 (1981).
- ³⁷J. M. Corsan and A. J. Cook, *Phys. Status Solidi* **40**, 657 (1970).
- ³⁸H. Peisl, in *Hydrogen in Metals I*, Ref. 1, pp. 53–74.
- ³⁹P. Meuffels and W. A. Oates, *J. Less-Common Met.* **130**, 403 (1987).
- ⁴⁰J. E. Kleiner, E. H. Sevilla, and R. M. Cotts, *Phys. Rev. B* **33**, 6662 (1986).
- ⁴¹E. Veleckis and R. K. Edwards, *J. Phys. Chem.* **73**, 683 (1969).
- ⁴²T. Matsumoto, Y. Sasaki, and M. Hihara, *J. Phys. Chem. Solids* **36**, 215 (1975).