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Solid solutions of hydrogen in complex materials

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I. Introduction

Hydrogen in metals has attracted considerably attention of physicists, chemists, material scientists and engineers for many decades. Most of the exciting properties are related to the small size of the H atom which leads to a high mobility in materials. Namely in metals its diffusivity is very high at room temperature and may reach values which are the same as for ions in aqueous solutions. The physical reasons for the high H-mobility are twofold. On the one hand H-atoms are dissolved interstitially and migrate via a direct interstitial mechanism which at dilute concentrations does not require the formation of vacancies. On the other hand a site exchange may occur via quantum mechanical tunneling.

The consequences of the high H-mobility are manifold:

- (i) Thermal equilibrium is established in rather short times at room temperature between the H-dissolved in the metal and either hydrogen gas or protons in aqueous solutions. Thus thermodynamic properties, especially the chemical potential of hydrogen can be obtained simply by measuring the partial pressure or the electrochemical potential.
- (ii) Hydrogen storage in metals and its use as an energy carrier becomes possible at room temperature.
- (iii) Hydrogen can easily redistribute and segregate at defects produced during plastic deformation, i.e. dislocations, crack tips etc.. This interaction gives rise to hydrogen embrittlement.

The small size of the H-atom allows a large packing density in those metals which have a high affinity, i.e. large negative heat of solution, for hydrogen. In other metals H-concentrations at reasonable H_2 -pressures may be very low despite the same number density and size of interstitial sites in these metals. In metal hydrides the atomic density can be even larger than in liquid hydrogen. This property of the hydrides is advantageous when using hydrogen as a fuel although the energy storage per weight is still too low for many applications. At present conventional storage alloys contain 2 wt.-% H whereas for their use in vehicles figures above 3 wt.-% are required. However in rechargeable batteries metal hydrides are widely used nowadays. It will not be the purpose of this review to discuss issues related to hydrogen economy in general or the special role of hydrides. Research results in this area are published elsewhere [1, 2, 3, 4, 5].

Besides hydrogen storage hydrogen embrittlement is a technological subject of major concern, where the negative role of hydrogen is played at much lower concentrations, i.e. in iron base alloys embrittlement effects are observed at contents as low as a few ppm. Here the interaction of H-atoms with lattice defects and its effect on plasticity has to be studied in detail. Again the high mobility of H-atoms is crucial for the phenomena, because hydrogen has to reach or to follow moving dislocations and or crack tips. It appears as if the quantum mechanical diffusion plays a role as well. Especially for adjacent tetrahedral sites in body-centered cubic metals, which are only a very short distance apart, this effect is strongly pronounced and leads to the result that ferritic steels (bcc-lattice) are more susceptible to hydrogen embrittlement than austenitic steels (fcc-lattice). Topics of embrittlement phenomena are treated in conferences [6, 7, 8] which seldom overlap with the ones on hydrogen storage.

Metal-hydrogen systems are often used as model systems to study physical or chemical properties and how they change with composition. This is often very easy because hydrogen can be doped in a controlled way by either measuring changes of the H_2 -pressure in closed systems or by electrochemical deposition on a metal electrode applying Faraday's Law,. This

advantage of easy alloying is supported by the possibility of obtaining the chemical potential of hydrogen by measuring partial pressures and/or electrode potentials. Cases where metal-hydrogen served as model systems are

- (i) solute-solute interaction measured and interpreted in the framework of a quasi chemical approach for the first time in the Pd-H system by Lacher [9],
- (ii) tunneling as a diffusion mechanism for atoms in solids was discovered and discussed for hydrogen in metals [10, 11, 12],
- (iii) the behavior of hydrogen in systems with reduced dimensions can be studied nicely in metals [13],
- (vi) hydrogen interaction with defects in metals is representative for other solute/solvent systems and has been studied extensively [14]. After knowing the basic features of the interaction H-atoms can be used as probes for the defects [15, 16]. By gradually increasing the H-concentration the sites of increasing energy within the defects are saturated successively and, therefore, a kind of spectroscopic method will be available (examples will be discussed throughout this study).

Another peculiarity of the lightest element is the large mass difference of its isotopes which gives rise to pronounced isotope effects in most of its properties. The different scattering length for neutrons which even changes sign from H to D gave rise to an extensive use of neutron scattering and diffraction techniques in the area of metal-hydrogen systems [17].

Hydrogen at high concentrations may change the physical properties of a material remarkably. Examples are changes of the magnetic coupling between ferromagnetic layers [18, 19] or even more exciting a metals-insulator transition in yttrium going from the dihydride to the trihydride [20]. In addition microstructural changes have been observed during alloying a metal with hydrogen. Examples are the generation of abundant vacancies [21] and dislocations [22, 23, 24], the decomposition of miscible alloys [25, 26] and the improvement of mechanical properties of Ti-alloys by decreasing the grain size [27] or by variation of the α to β volume fraction [28]. Thus hydrogen can be used as a temporary alloying element, in order to set up a desired microstructure. In other materials like semiconductors hydrogen is used as a permanent alloying addition for the purpose of saturating deep impurity levels or dangling bonds at the Si/SiO₂ interface as well as in amorphous silicon [29].

As the present study will focus on solid solutions of hydrogen in metals, the properties of hydrides will be omitted and the reader is referred to monographs including these subjects [30, 31, 32, 33]. The major topic will be the behavior of hydrogen in disordered and amorphous systems including the interaction with defects. The experimental and theoretical findings are relevant for other materials like polymers, oxidic glasses or amorphous silicon which will be treated in a special chapter of this study.

II. Fundamental properties of hydrogen

1. EQUILIBRIUM PRESSURE AND SOLUBILITY

a) Solubility

Hydrogen molecules interacting with a metal are dissociating on the surface and dissolved as atoms within the metal according to the following reaction

Evidence for this reaction is provided for instance by measuring pressure composition isotherms (pc-isotherms) and showing that Sieverts' Law

$$c_H = K \sqrt{p_{H_2}} \quad (1.2)$$

is valid, where c_H is the H-concentration within the metal, p_{H_2} is the partial pressure of hydrogen and K is Sieverts' constant. In rubbery polymers for instance the molecules are not dissociated during sorption and proportionality between concentration and pressure arises. Eq. (1.2) is derived by assuming thermodynamic equilibrium between gaseous and dissolved hydrogen which requires that the chemical potentials in the two phases are the same. H-atoms are occupying interstitial sites in the metal lattice which are mostly tetrahedral or octahedral sites. This can be proven directly experimentally by ion channelling experiments using single crystals of the metal [34]. Then the configurational entropy s_{cf} is given by

$$s_{cf} = -k_B \ln \frac{N_H}{N_i} = -k_B \ln \frac{N_H}{\beta N_{Me}} , \quad (1.3)$$

where k_B is Boltzmann's constant, N_H , N_i , N_{Me} are the numbers of H atoms, interstices and metal atoms respectively. Thus β is the ratio of interstitial sites to metal atoms being 6 for tetrahedral sites in bcc lattices and 1 for octahedral sites in fcc lattices. Then the chemical potential of ideally dissolved H-atoms is expressed as

$$\mu_H = \mu_H^o + k_B T \ln \frac{N_H}{\beta N_{Me}} \equiv \mu_H^o + k_B T \ln \frac{r_H}{\beta} , \quad (1.4)$$

where μ_H^o is a standard value of the chemical potential. As a measure of hydrogen concentration the ratio r_H of hydrogen and metal atoms is used mostly. The chemical potential of the molecules in the gas phase is

$$\mu_{H_2} = \mu_{H_2}^o + k_B T \ln p_{H_2} . \quad (1.5)$$

Eq. (1.1) and equilibrium require

$$\mu_H = \frac{1}{2} \mu_{H_2} . \quad (1.6)$$

Inserting Eqs. (1.4) and (1.5) into the last one yields Sieverts' Law

$$r_H = \beta \sqrt{p_{H_2}} \exp \left(\frac{\mu_{H_2}^o - 2\mu_H^o}{2k_B T} \right) , \quad (1.7)$$

because the relation between r_H and the H-concentration c_H which is usually defined as the number of moles of H per unit volume is proportional. Often the H-concentration at a given hydrogen pressure and temperature is called solubility. This has to be distinguished from the maximum or terminal solubility of hydrogen in a metal for those case where a hydride is formed.

The difference of the standard values of the chemical potentials in Eq. (1.7) is equal to the Gibbs free energy of the reaction given in Eq. (1.1) or the Gibbs free energy of absorption (dissolution), respectively, i.e.

$$\Delta G^o = \Delta H^o - T\Delta S^o = 2\mu_H^o - \mu_{H_2}^o . \quad (1.8)$$

The major contribution to the entropy change of dissolution stems from the lost degrees of freedom the free H_2 molecules have in the gas phase. Thus ΔS^o is about equal to the standard entropy of gaseous hydrogen at room temperature [35]

$$\Delta S^o \approx S_{295}^o = 131 J / K / mol \quad (1.9)$$

Because of this rather high and positive entropic contribution to the Gibbs free energy of dissolution hydrogen can be desorbed at high temperatures.

The enthalpy of dissolution in metals is very negative at the left hand side of the periodic table and increases to very positive values going to the right via the transition metals [32, 36]. An atomistic interpretation is rather involved as elastic and electronic contribution play an important role. As the metal expands during dissolution of hydrogen (see II.C) elastic energy has to be paid. Assuming no changes of the electronic structure the additional electron of the hydrogen atom has to be placed in states above the Fermi level which gives rise to a positive contribution to the enthalpy of dissolution. However, it has been shown [32, 37] that by the incorporation of H-atoms new energy levels below the Fermi-level are generated yielding negative contributions to ΔH^o .

The Gibbs free energies of hydride formation per H-atom or molecule are defined as the free energy change during the following reaction

Values of ΔG_f^o are very close to the Gibbs free energy of dissolution [36] which has been defined via the reaction in Eq. (1.1). The similarity of the corresponding entropy changes arises from the fact that in both reactions the major contribution to it stems from the loss of translational freedom of gaseous hydrogen. The similarity of the enthalpy changes means that contributions of solute solute interaction in the hydride are small in comparison with the elastic and electronic contributions to the enthalpy of dissolution.

2. DIFFUSIVITY

Diffusion of hydrogen in metals occurs via the direct interstitial mechanism with a diffusion coefficient given by [38]

$$D^* = \frac{l^2 \Gamma}{2d} f \left(1 - \frac{r_H}{\beta}\right) \quad (2.1)$$

where Γ is the jump frequency, l the jump distance and d the dimensionality of the lattice (which is mostly 3 but for diffusion along grain boundaries we have $d=2$). The quantities r_H and β have been defined after Eqs. (1.3) and (1.4) and f is a correlation factor which is unity for $r_H \rightarrow 0$ but will be smaller than unity for $r_H/\beta \rightarrow 1$ where the interstitial lattice becomes filled [39] and the direct interstitial mechanism of diffusion changes gradually to a vacancy mechanism. Then blocking of sites comes into play as well which is accounted for by the factor in brackets. A tacit assumption for the validity of Eq. (2.1) is that all sites visited during a random walk of the H-atom have the same average jump frequency, i.e. the same site and saddle point energy for the case of thermally activated hopping or the same transition probability for tunneling through the potential barrier.

Very often the chemical diffusion coefficient of hydrogen D_H is measured via the flux of hydrogen J_H in a concentration gradient according to Fick's First Law

$$J_H = -D_H \frac{\partial C_H}{\partial x}. \quad (2.2)$$

Using the gradient of the chemical potential of hydrogen as the driving force for diffusion it can be shown [40] that

$$D = \frac{C_H}{k_B T} \frac{\partial \mu_H}{\partial C_H} D^* = \frac{\partial \ln a_H}{\partial \ln C_H} D^* = \left[1 + \frac{\partial \ln \gamma_H}{\partial \ln C_H} \right] D^*, \quad (2.3)$$

where a_H is the thermodynamic activity of H and γ_H the activity coefficient ($a_H = \gamma_H C_H$).

The experimental techniques of measuring diffusion coefficients of hydrogen in metals are manifold [30, 31, 32, 33]. The ones which were used to obtain most of the data presented in this study are described in the following

(i) Electrochemical techniques:

The metal sample is immersed in an electrolyte and a current is passed from a counter electrode. Then the amount of hydrogen deposited on the sample surface is simply calculated from Faraday's Law. Whether this hydrogen produced in *statu nascendi*, i.e. in the atomic form is absorbed by the sample or whether it recombines to H_2 molecules and escapes by dissolution in the electrolyte or as gas bubbles, depends on the H-solubility of the metal, the current density and the permeability of surface oxides [14]. Natural oxides can be removed by sputtering and replaced by a palladium layer as shown for niobium and tantalum [41]. Hydrogen can be also desorbed from a sample by reversing the direction of the current. The H-activity on the surface or the chemical potential, respectively can be obtained by measuring the voltage between sample and a reference electrode. Depending on the boundary conditions with respect to either current or electrochemical potential, transient, changes of these parameters can be evaluated in order to obtain a value for the chemical diffusion coefficient [42]. If the sample is mounted in a double cell as suggested in [43], the values of the diffusion coefficient are more reliable [44]. As diffusion occurs in a concentration gradient, values of the chemical diffusion coefficient are obtained. The main advantages of electrochemical techniques are applicability at low H-concentrations (down to a few at-ppm), simplicity of equipment, ease of doping and the possibility of getting values of the (electro-)chemical potential. Drawbacks are a limited temperature range between freezing and boiling point of the electrolyte and non-permeable surface barriers. Because of the latter most measurements were made with palladium and its alloys.

(ii) Gorsky-Effect [30]:

Here the hydrogen containing sample is bend producing both expanded and compressed regions. This way a gradient of the chemical potential of hydrogen is set up and hydrogen having a positive molar volume migrates from compressed to expanded regions until an equilibrium concentration profile has established. The corresponding strain in the sample remains in the sample after the bending stress is released, i.e. the sample is still bend. Then the concentration gradient is no longer in equilibrium and vanishes by diffusion. The associated strain gradient vanishes too and can be measured by monitoring the decreasing bending of the sample. In order to get measurable strains the H-concentration has to be at least few tenth of one at.-%. This condition sets a lower limit for the temperature range, because by lowering the temperature the concomitantly decreasing terminal solubility will finally be higher than the H-concentration and hydride precipitation occurs. Contrary to the electrochemical technique surface oxides are advantageous for Gorsky-effect measurements, because they prevent desorption of hydrogen and/or an equilibration via the gas phase. At higher temperatures a limit is set by the increasing permeability of hydrogen through the oxide or the dissolution of oxygen within the metal and the destruction of the barrier.

(iii) Permeation:

Here a pressure difference is set up across a metallic membrane separating two closed compartments and the hydrogen flux through the membrane is measured, i.e. by monitoring pressure changes. Transient and steady state behavior yield the chemical diffusion coefficient and the permeability (product of diffusion coefficient and difference of H-concentrations between entrance and exit surface of the membrane). The technique requires rather high permeabilities (high temperatures, diffusivities and solubilities) and may be dominated at the lower temperatures by rate-controlling reactions at the interface.

(vi) Internal friction (mechanical spectroscopy) [45]:

Damping of vibrations in a vibrating reed or in a torsional pendulum is often caused by jumping atoms, if their strain field interacts with the externally applied stress field which excites the vibrations. If the frequency of vibration and the jump frequency are highest, damping reaches its maximum. Thus measuring damping as a function of sample frequency yields a damping peak which is called Snoek peak [45] and which has its maximum at a value which is equal to the jump frequency. The frequencies of sample vibrations can be changed by changing the sample dimensions or by exciting various modes of vibration. Experimentally it is easier to change the temperature and, therefore, changing the jump frequency of the atoms while keeping the frequency of vibration constant. Then the Snoek peak occurs in a damping versus temperature plot. H-atoms incorporated in octahedral sites of an fcc lattice (for instance Pd or Ni) cause a strain in the lattice which has cubic symmetry and, therefore, does not cause any damping. However, H-atoms in tetrahedral sites of a bcc lattice (for instance Nb and Ta) give rise to a tetragonal distortion and a Snoek relaxation is expected. It has not been observed so far which may be due to a relaxation strength being smaller than the detection limit of the technique or due to the very rapid tunneling of H-atoms between the 4 adjacent tetrahedral sites may smear out the tetragonal distortion. However, for hydrogen in amorphous alloys an internal friction peak has been discovered [46, 47, 48, 49] and it was shown that the jump frequency is in agreement with the one calculated from diffusion coefficients via Eq. (2.1). In addition hydrogen atoms being trapped in the neighborhood of a foreign solute atom, i.e. at a substitutionally dissolved titanium atom in a niobium lattice [50] give rise to a Snoek peak.

The diffusion coefficients usually obey an Arrhenius Law when they are measured in a limited temperature range. However, the values obtained from Gorsky effect measurements over a large range down to very low temperatures revealed for the Vb metals vanadium, niobium and tantalum a pronounced curvature when presented in an Arrhenius plot [11, 30]. The curvature corresponds to a decreasing activation energy of diffusion with decreasing temperature which is in accordance with a quantum mechanical tunneling of the H-atom through a potential barrier between two adjacent sites. Thus values as large as $1 \cdot 10^{-5} \text{ cm}^2/\text{s}$ have been measured in α -Fe and V at room temperature which correspond to diffusion length of about 1 cm in one day.

3. PARTIAL MOLAR VOLUME AND INTERACTION WITH STRESS AND STRAIN FIELDS

Partial molar volumes of hydrogen in metals are usually obtained by measuring changes of the lattice parameter as a function of H-concentration [51]. Because hydrogen is mostly dissolved in interstitial sites with a smaller volume, the lattice parameter increases with increasing H-concentration. For many metals and their alloys the partial molar volume is 2.9

$\text{\AA}^3$ per H-atom or $1.7 \text{ cm}^3/\text{mol}$, respectively [32, 51, 52]. Details of the lattice distortion in the neighborhood of the H-atom can be revealed by Huang scattering [51].

For high H-concentrations measurements of the density of the sample yield the partial molar volume, whereas at low concentrations in-situ dilatometry is more appropriate. An example for the latter case is shown in Fig. 1 [53], where results obtained by electrochemical doping of one sample of polycrystalline palladium and one of an amorphous Pd-Si alloy are presented. Increasing the H-concentration step by step and measuring the length change of the ribbon-shaped samples gave the same partial molar volume for the crystalline Pd, whereas large variations were observed for the amorphous alloy. The volume contraction being observed for the first 40 atppm of hydrogen were explained by trapping of H-atoms in vacancy-like defects [53]. At higher concentrations the expected volume change of about $1.5 \text{ cm}^3/\text{mol}$ for hydrogen being dissolved in interstitial-like sites was measured. In this concentration range there is a tendency of increasing partial molar volume with increasing H-concentration which is indicative of filling larger interstices in the amorphous structure first [54]. In order to provide additional experimental evidence for the unusual negative volume change, the partial molar volume was also measured by measuring changes of the chemical potential under tensile stress as explained in the following.

For a solute atom which leads to an isotropic strain of insertion the chemical potential changes if an arbitrary stress state σ_{ik} is present according to the relation [55, 56]

$$\mu(\sigma) = \mu(\sigma = 0) - \frac{\sigma_{ik} V_s}{3} \quad (3.1)$$

where V_s is the partial molar volume of the solute. For uniaxial tensile stress ($\sigma_{11}=\sigma$ and $\sigma_{ik}=0$ otherwise), hydrogen as a solute and measuring changes of the electromotive force ΔE the last equation becomes

$$\Delta E = \frac{\sigma V_H}{3F} \quad (3.2)$$

where F is Faraday's Constant. By measuring changes of the electrochemical potential of metal-hydrogen systems as a function of the applied stress the partial molar volume V_H was determined via Eq. (3.2) in an independent way when compared with the dilatometric studies [53]. Namely, the negative changes shown in Fig. 1 could be reproduced.

Besides allowing a determination of V_H Eq. (3.1) is much more important in the context of H-embrittlement as discussed in section 12.

III. Behavior of hydrogen in defective and disordered metals

The behavior of hydrogen in single crystalline metals or polycrystalline metals with a small density of lattice defects has been studied fundamentally and extensively during the 1960ies 70ies and 80ies. In the 1990ies the metal hydride batteries replaced the nickel cadmium batteries gradually and the focus of researchers was directed toward metal hydrides and their application. In order to extend the application of hydrogen storage materials to vehicles driven directly with hydrogen or indirectly via a fuel cell the density of metallic materials or the storage capacity in terms of hydrogen per unit of mass is a matter of serious concern. In addition, the theoretical storage capacity of an alloy is often not reached because of crystalline defects, namely dislocations [57, 58]. They are present from the very beginning, or even more, they are formed during loading and unloading of the alloy. Besides effecting storage capacity grain boundaries play an important role, because they increase the kinetics of uptake and release of hydrogen. Thus nanocrystalline alloys are favorable storage alloys [59].

The interaction of hydrogen with crystalline defects is even more important in the context of hydrogen embrittlement. There are various mechanisms leading to hydrogen embrittlement but they are all related to hydrogen/defect interaction. The most prominent one is the direct action of hydrogen at the crack tip by either a decohesion mechanism [60] or the formation of a brittle hydride [61]. In the first case a single hydrogen atom migrating with the propagating crack tip will be sufficient whereas in the latter higher H-concentrations are required. For ductility being part of the failure mechanism, the interaction of hydrogen with dislocation becomes important. In general, the “storage” of hydrogen in crystal defects and/or the trapping by the defects determines how much of “mobile” hydrogen will be available to reach a critical value for embrittlement. As this is a rather complex problem, it has been treated qualitatively only at the beginning of research in this area. The present study will provide a quantitative result by defining a density of site energies (DOSE) or an energy landscape, respectively, and filling the various sites according to Fermi Dirac Statistics (FD-Statistics).

It will be shown in chapter VI that the concept of a DOSE and FD-Statistics is useful for other interstitials in other materials besides metallic ones. It also provides the basis for a fundamental study of the interaction of solute atoms with the microstructure of a material. Hydrogen systems are especially suited for these fundamental experiments because of the ease of doping and the ease of measuring its chemical potential which is of central importance in FD-Statistics. As the system can be studied around room temperature the crystal defects will not be annihilated, i.e. the microstructure remains the same during experimentation.

4. DENSITY OF SITE ENERGIES (DOSE) AND FERMI-DIRAC STATISTICS (FD-STATISTICS)

The DOSE is defined as usual in solid state physics as the normalized number of sites $n(E)$ in a given energy window $E, E+dE$ with

$$\int_{-\infty}^{\infty} n(E) dE = 1 . \quad (4.1)$$

This definition is equivalent with the density of states (DOS) function used for electrons or other particles in quantum mechanics. For electrons in solids the distribution of energy states in reciprocal space is considered, whereas here we are interested in sites in real space. However, the DOSE does not contain any information about the localization of the sites and spatial correlations between low and/or high energy sites are not accessible. For the energy

scale the standard state of gaseous hydrogen at one bar and 298 K is used. In the following a few relevant example of a DOSE of hydrogen in metals will be presented (cf. Fig. 2).

Because of the translational symmetry all the interstitial sites in a single crystal have the same energy and, therefore, the site energy for hydrogen atoms is the same. In other words, the system is totally degenerate. This simple picture has to be modified, because in a crystalline lattice different interstices are available among which the tetrahedral and octahedral sites are the most prominent ones. The situation becomes even more complex, if the single crystal contains different constituents, i.e. a solid solution or an intermetallic compound. Then the degeneracy of the system is partly lifted and a discrete number of site energies have to be considered. Nevertheless, for dilute solutions of hydrogen and single component crystals the simplification of one interstitial site is usually fulfilled because the site energies of other interstices are too high to be occupied. The mathematical representation of the corresponding DOSE will be a Dirac delta function.

From the one level system of a single crystal we come to a two level system by introducing isolated point defects like substitutionally dissolved foreign atoms or vacancies, by restricting the interaction with hydrogen to the nearest interstices. As spatial correlation does not play a role all the foreign atoms may be combined to a layer in between the host metal and by neglecting the interface this becomes a two level system, too.

Going from zero to one and two dimensional defects of the lattice, it is more convenient to introduce continuous functions instead of discrete energy levels. This will be discussed in more detail in the following sections dealing with dislocations and grain boundaries. And finally in a perfect amorphous structure all sites may be considered to be different from each other representing a system without degeneracy.

The various sites of a DOSE compete for the occupancy with hydrogen. By occupying the sites of lowest energy the system reduces its total energy whereas distribution among sites being present in large numbers increases the configurational entropy both effects reduce the Gibbs free energy. If we allow a site to be occupied by one H-atom only, the corresponding minimization can be treated in the framework of the Fermi-Dirac Statistics (FD-Statistics) [62]. Here the configurational entropy in each energy window of the DOSE is calculated under the assumption of single occupancy. During this procedure it does not matter whether electrons are distributed among energy states in reciprocal space or particles among sites in real space. The minimum of Gibbs free energy for all energy windows yields the following result for the thermal occupancy of energy level E_i or the corresponding site, respectively

$$o(E_i) = \frac{1}{1 + \exp[(E_i - \mu) / k_B T]} \quad (4.2)$$

where μ is the derivative of Gibbs free energy with respect to particle concentration and, therefore, it is the chemical potential of the particles despite being called Fermi energy in this context.

Integration over the DOSE with the correspondent thermal occupancy yields the total fraction N/N_o of sites occupied with particles, where N is the number of dissolved particles and N_o is the total number of available sites:

$$\frac{N}{N_o} = \int_{-\infty}^{\infty} \frac{n(E)dE}{1 + \exp\left(\frac{E - \mu}{k_B T}\right)} \quad (4.3)$$

The term particle instead of hydrogen atoms has been used before, in order to stress the fact that the concept of a DOSE and FD-Statistics is rather general and not restricted to hydrogen in metals. It has been applied before in the framework of heterogeneous adsorption [62] and the interaction of solute atoms with dislocations [63, 64].

a. Solubility

The relation between hydrogen concentration in the metal expressed as the ratio $r_H = N_H/N_{Me}$ and its partial pressure in the gas phase is obtained by using Eq. (1.5)

$$\frac{r_H}{\beta} = \frac{N_H}{\beta N_{Me}} = \int_{-\infty}^{\infty} \frac{n(E)dE}{1 + \frac{1}{\sqrt{p}} \exp\left(\frac{E - (\mu_{H_2}^o / 2)}{k_B T}\right)} . \quad (4.4)$$

For a single crystal with $n(E) = \delta(E - E^o)$ and dilute concentrations ($r_H \ll 1$) the well known result (cf. Eq. (1.7))

$$r_H = \sqrt{p} \beta \exp\left(\frac{\mu_{H_2}^o - 2E^o}{2k_B T}\right) \quad (4.5)$$

is obtained. A closed solution of the integral in Eq. (4.4) will be possible for simple forms of $n(E)$ only. In order to understand the competition between energy decrease and entropy gain the following approximation based on the step or $T=0$ approximation of the Fermi-Dirac function (i.e. $o(E) \approx 1$ for $E < \mu$ and $o(E) \approx \exp[(\mu - E)/kT]$ for $E > \mu$) will be applied

$$c = \int_{-\infty}^{\mu} n(E)dE + \int_{\mu}^{\infty} \frac{n(E)dE}{\exp[(E - \mu)/kT]} \equiv c_1 + c_2 \quad (4.6)$$

where c will be used for the concentration instead of r_H , in order to be consistent with previous publications of the author and to refer to the general validity of the equations. Thus c refers to the fraction of interstices occupied by particles. The first term c_1 on the right hand side of the equation is that part of the total concentration c arising from particles below the Fermi level and c_2 corresponds to sites above μ . Occupying sites below the Fermi level the system decreases its energy whereas for the sites above it increases its configurational entropy. Thus for $c_1 > c_2$ energy play a more important role than entropy and vice versa.

For $c_2 \ll c_1 \approx c$ which is always fulfilled at low temperatures because of the step-type behavior of the Fermi-Dirac function, we get from the last equation

$$\frac{\partial c}{\partial \mu} = n(\mu) . \quad (4.7)$$

The last equation can be used to get the DOSE from measured values of μ as a function of c (for instance by the electrochemical method).

b. Validity of Henry's Law

For $c \ll 1$ or $\mu \ll 0$, respectively, and $c_1 \ll c_2 \approx c$ we obtain from the last equation

$$c \approx \int_{-\infty}^{\infty} \frac{n(E)dE}{\exp[(E - \mu)/kT]} = \exp\left[\frac{\mu}{kT}\right] \int_{-\infty}^{\infty} n(E) \exp\left[-\frac{E}{kT}\right] dE = a\gamma \quad (4.8)$$

Then Henry's Law $a=\gamma c$ is fulfilled with the thermodynamic activity $a=\exp(\mu/kT)$ being proportional to c .

At low concentrations the condition $c_1 \ll c_2$ is not fulfilled for all site energy distributions. For a Gaussian distribution it was shown that the condition is valid for $\mu \ll -\sigma^2/kT$, where σ is the width of the distribution [14]. Then $\gamma \rightarrow \exp[\sigma^2/(2kT)^2]$ for $c \rightarrow 0$. However, if we consider a continuous exponential distribution, $n(E) = \sigma^{-1} \exp[E/\sigma]$ for $E \leq 0$ and $n(E)=0$ otherwise, Eq. (4.8) yields

$$c_1 = \exp(\mu/\sigma) \text{ and } c_2 = \frac{\exp(\mu/kT) - \exp(\mu/\sigma)}{1 - \sigma/kT} \quad (4.9)$$

where independent of μ (being negative) c_2 is smaller than c_1 for $\sigma \gg kT$. In this limiting case the system decreases its free energy because it lowers its energy by occupying sites of lowest energy only. Thus we have $c_1 \approx c$ and the activity coefficient becomes

$$\gamma = \exp\left[\frac{\mu}{kT} - \frac{\mu}{\sigma}\right] = c^{\sigma/kT-1}. \quad (4.10)$$

This power law has been derived in a different context as well [65] and it shows that γ approaches 0 for $c \rightarrow 0$. The activity coefficient depends on c and, therefore, Henry's Law is not fulfilled. However, as all the samples have a finite number of sites the exponential DOSE has to have a cut-off at the low energy side and it can be shown that this leads to the validity of Henry's Law again.

Very often a sample contains a small fraction f of crystal defects only. Then the majority of sites is the same as in a single crystal and the DOSE can be written as

$$n(E) = (1-f)\delta(E-E^o) + fn_f(E) \text{ with } f \ll 1, \quad (4.11)$$

If the average energy of $n_f(E)$, i.e. its first moment, is above E^o the defects have a negligible effect and the H-atoms are almost all in sites of the single crystalline region. For the reverse case of the average energy being smaller than E^o integration over the first part of the DOSE in Eq. (4.11) yields the concentration in the single crystalline region

$$c_{fr} = \frac{1-f}{1 + \exp\left(\frac{E^o - \mu}{k_B T}\right)} \approx \exp\left(\frac{\mu - E^o}{k_B T}\right) \approx \sqrt{p} \exp\left(\frac{2E^o - \mu_{H_2}^o}{2k_B T}\right). \quad (4.12)$$

The subscript *fr* refers to these H-atoms as being free and not bound to crystalline defects. Then the activity of hydrogen or its partial pressure, respectively is solely determined by the free hydrogen.

5. DIFFUSIVITY

a. Tracer diffusion

Diffusion of tagged particles in a system with a DOSE and constant concentration can be obtained simply from averaging over the jump frequencies Γ and calculating D^* with the jump distance l via Eq.(2.1) written as

$$D^* = \frac{l^2}{6} \langle \Gamma \rangle = \frac{l^2}{6} \left\langle \Gamma_o \exp\left(-\frac{Q^o + E^o - E_1}{k_B T}\right) [n(E_1)o(E_1)][1 - n(E_2)o(E_2)] \right\rangle \quad (5.1)$$

where $\langle \Gamma \rangle$ is the average jump rate. The jump rate for particles hopping from sites of energy E_1 into sites of energy E_2 is written as the product of

- 1.) a constant prefactor Γ_o which is equal for all sites,
- 2.) a Boltzmann factor $\exp[-(Q^o + E^o - E_1)/k_B T]$ because thermally activated jumps are considered (cf. Fig. 3),
- 3.) the partial concentration in sites of energy E_1 [$= n(E_1)o(E_1)$] and
- 4.) the availability of empty sites of energy E_2 [$= n(E_2)\{1 - o(E_2)\}$].

Note that a constant saddle point energy has been assumed, in order to allow for an uncorrelated random walk. The effect a distribution of saddle point energies has on the diffusion coefficient will be discussed in chapter V. By averaging over E_1 and E_2 one obtains:

$$\langle \Gamma \rangle = \frac{1}{c} \iint \Gamma_o \exp\left(-\frac{Q^o + E^o - E_1}{k_B T}\right) \frac{n(E_1)}{1 + \exp\left(\frac{E_1 - \mu}{k_B T}\right)} \left[n(E_2) - \frac{n(E_2)}{1 + \exp\left(\frac{E_2 - \mu}{k_B T}\right)} \right] dE_1 dE_2 \quad (5.2)$$

Thus Q^o is the activation energy of diffusion in the reference material. Integration of the last term in brackets immediately yields one factor $(1-c)$. By using the identity

$$\frac{n(E) \exp\left(\frac{E}{k_B T}\right)}{1 + \exp\left(\frac{E - \mu}{k_B T}\right)} = \exp\left(\frac{\mu}{k_B T}\right) \left[n(E) - \frac{n(E)}{1 + \exp\left(\frac{E - \mu}{k_B T}\right)} \right] \quad (5.3)$$

integration of Eq. (5.2) with respect to E_1 gives

$$\langle \Gamma \rangle = \frac{\Gamma_o}{c} \exp\left(-\frac{Q^o}{k_B T}\right) \exp\left(\frac{\mu - E^o}{k_B T}\right) (1-c)^2. \quad (5.4)$$

Inserting in Eq. (5.1) yields a simple result

$$D^* = \frac{l^2}{6} \Gamma_o \exp\left(-\frac{Q^o}{k_B T}\right) (1-c)^2 \gamma^o = D^o (1-c)^2 \gamma^o \quad (5.5)$$

with D^o being a tracer diffusion coefficient in a material which contains sites of energy E^o only and γ^o being an activity coefficient with respect to this material as a reference state. One of the factors $(1-c)$ is due to blocking of sites whereas the second factor takes care of the fact that γ^o approaches $(1-c)^{-1}$ for $c \rightarrow 1$ in a single crystal [66].

The temperature dependence of the tracer diffusion coefficient is solely determined by the exponential dependence of the average jump frequency according to Eqs. (5.4) and (5.5). Thus at a given concentration the effective activation energy is $Q^o + E^o - \mu$, which is the energy difference between saddle point energy and Fermi energy. The Fermi energy μ will not change very much with temperature for broad DOSE and, therefore, D^* obeys an Arrhenius Law despite a distribution of site energies or jump rates, respectively. This is a consequence of the step behavior of the FD-function, where the occupancy at low temperatures and a broad DOSE is smeared out around the Fermi energy without changing the latter very much [67].

The concentration dependence of the effective activation energy $Q^o + E^o - \mu$ is very pronounced as μ increases with increasing concentration because of the second derivative of Gibbs free

energy being always positive in equilibrium. Thus an increasing concentration always leads to a decreasing activation energy and an increasing diffusivity, if we neglect the effect of c in the denominator of Eq. (5.4) (cf. section 5.4). Again the atomistic interpretation is very simple. With increasing concentration sites of higher energy have to be occupied and, therefore, the Fermi energy rises and comes closer to the saddle point energy. Thus an increasing number of particles experience a smaller activation barrier.

b. Diffusion in a concentration gradient

In order to derive an expression for the chemical or intrinsic diffusion coefficient D we consider two adjacent lattice planes of distance l (= jump distance). The x -axis is parallel to the normal of the planes and the average concentrations c_1 and c_2 within the planes are different. Thus we have a concentration gradient and D is defined by Fick's First Law:

$$J = -D \frac{\partial c}{\partial x} \frac{\beta}{\Omega} = -D \frac{c_2 - c_1}{l} \frac{\beta}{\Omega}, \quad (5.6)$$

where J is the flux of particles from plane 1 at x to plane 2 at $x+l$, Ω is the atomic volume of the metal and β is the number of interstices per metal atom. The ratio β/Ω on the right hand side of Eq. (5.6) has to be included because c was defined as the fraction of occupied interstices whereas in Fick's Law concentration is defined as particles per volume (cf. Eq. 2.2). The flux J is also obtained by averaging over the jumps in between the planes from sites of energy E_1 in plane 1 to sites of energy E_2 in plane 2 and vice versa.

$$J = \frac{\beta l}{6\Omega} \iint \left[\frac{\Gamma_1(x)n(E_1)}{1 + \exp\left(\frac{E_1 - \mu(x)}{k_B T}\right)} - \frac{\Gamma_2(x+l)n(E_2)}{1 + \exp\left(\frac{E_2 - \mu(x+l)}{k_B T}\right)} \right] dE_1 dE_2 \quad (5.7)$$

where the jumps occur in all directions and only 1/6 of them to the plane under consideration. The first term in brackets corresponds to the jumps of particles in sites of energy E_1 out of plane 1 at x and the second term accounts for particles in sites of energy E_2 in plane 2 at $x+l$, where the jump frequencies Γ_i have to be weighted with the fraction of occupied sites of a given energy $n(E_i)/o(E_i)$. Jump frequencies are calculated as before for thermally activated processes over saddle points of constant energy $E^o + Q^o$ (cf. Fig. 3) including blocking of sites by a factor of $n(E_i)[1 - o(E_i, \mu)]$

$$\Gamma_1 = \Gamma_o n(E_2) [1 - o(E_2, \mu(x+l))] \exp\left(-\frac{Q^o + E^o - E_1}{k_B T}\right) \quad (5.8)$$

$$\Gamma_2 = \Gamma_o n(E_1) [1 - o(E_1, \mu(x))] \exp\left(-\frac{Q^o + E^o - E_2}{k_B T}\right) \quad (5.9)$$

In Ref. [68] similar calculation were presented for the first time and the fact that the occupancy depends on the chemical potential (cf. Eq. (4.2)) which depends on position x was not taken into account properly leading to a slightly different expression for D . Inserting Eqs. (5.8) and (5.9) in Eq. (5.7) and partly integrating yields:

$$J = \frac{\beta \Gamma_o (1-c)}{6\Omega} \exp\left(-\frac{Q^o + E^o}{k_B T}\right) \left[\int \frac{\exp\left(\frac{E_1}{k_B T}\right) n(E_1) dE_1}{1 + \exp\left(\frac{E_1 - \mu(x)}{k_B T}\right)} - \int \frac{\exp\left(\frac{E_2}{k_B T}\right) n(E_2) dE_2}{1 + \exp\left(\frac{E_2 - \mu(x+l)}{k_B T}\right)} \right] \quad (5.10)$$

Using Eq. (5.3) and expanding $\mu(x+l)$ in a Taylor series gives:

$$J = \frac{\beta \Gamma_o (1-c)}{6\Omega} \exp\left(-\frac{Q^o}{k_B T}\right) \exp\left(\frac{\mu - E^o}{k_B T}\right) \left[(1-c) - (1-c) \left(1 + \frac{l}{k_B T} \frac{\partial \mu}{\partial x}\right) \right] \quad (5.11)$$

and

$$J = -\frac{\beta D^o (1-c)^2}{\Omega} \exp\left(\frac{\mu - E^o}{k_B T}\right) \frac{1}{k_B T} \frac{\partial \mu}{\partial x}. \quad (5.12)$$

This way we have derived an expression which is in agreement with irreversible thermodynamics stating that the gradient of the chemical potential is the driving force for diffusion. Using the expression derived for the tracer diffusion coefficient D^* (Eq. (5.4) and (5.5)) gives

$$J = -\frac{D^* C}{k_B T} \frac{\partial \mu}{\partial x} = -D^o (1-c)^2 \frac{\partial a}{\partial x}, \quad (5.13)$$

where C is the concentration as usually defined, i.e. moles per unit volume. Thus the factor in front of the gradient term is the mobility of the particles as expected from the Einstein-Stokes relation [38].

Thus a self consistent derivation is provided for both diffusion coefficients D^* and D . In order to apply the concept to diffusion and permeation of hydrogen through materials, the material and its defects have to be characterized first and described by a DOSE. Then Eq. (4.3) is used to calculate $\mu(c)$ numerically or as a closed solution. This function allows to calculate D^* and D via Eqs. (5.5) and (2.3). With appropriate boundary conditions Fick's Second Law has to be solved with a concentration dependent diffusivity D . Instead of using calculated values of μ measured ones can be inserted in Eqs. (2.3) and (5.5) as well.

c. General random walk

It will be shown in the following that the assumption of constant saddle point energies can be replaced by less restrictive conditions. This has been done for thermally activated hopping in a previous study [14] including a Gaussian distribution of saddle point energies. However, one may argue that thermally activated hopping is not appropriate for H-atoms, because they may migrate via quantum mechanical tunneling (cf. section 2). Therefore we approach the problem of diffusion in an energy landscape from a different perspective.

We consider P particles in N sites of a lattice with a given DOSE. The equilibrium distribution of the particles according to FD-Statistics shall be stationary in space and one tagged particle shall do a random walk on the empty lattice. It might not be really necessary to assume a stationary distribution for the remaining particles. What might be the important effect only is that the moving particle will not be able to occupy all lattice sites as they are differently blocked according to Eq. (4.2). One might call this simplification the one particle approximation resembling the one electron approximation of solid state physics. Further on the walk is uncorrelated besides the few blocking events and, therefore, the mean distance R after Z jumps is given according to simple random walk theory [38, 40]

$$R^2 = Z l^2, \quad (5.14)$$

where l is the jump distance. Then a diffusion coefficient can be defined by [38, 40]

$$D^* \equiv \lim_{t \rightarrow \infty} \frac{R^2}{6t} = \frac{l^2}{6} \lim_{t \rightarrow \infty} \frac{Z}{t}, \quad (5.15)$$

where t is the total time required for the walk. The time t is the sum of all the times of residence τ_m the particle stayed in the various sites visited during the walk, if the time interval required for the site exchange is small compared to τ_m . Thus we get

$$t = \sum_{m=1}^Z \tau_m . \quad (5.16)$$

This way the jump rate as the reciprocal of the residence time has not to be described by a special mechanism like thermally activated hopping for instance. Among the various sites we combine those having the same energy E_i and average over the distribution of empty sites, i.e. sum over all N-P sites. Hereby it is assumed that the Z sites which have to belong to the empty category are as representative for empty sites as are the N-P ones. Thus we obtain

$$t = \sum_{m=1}^Z \tau_m = \sum_i \sum_{E_m=E_i} \tau_m \equiv \frac{Z}{N-P} \sum_{i=1}^{N-P} t_i , \quad (5.17)$$

where t_i is the time the particle spends in sites of energy E_i . It is tacitly assumed that the number of jumps Z and the number of lattice sites N are large enough in order to apply the laws of random walk and statistical mechanics. According to the ergodic hypothesis the fraction of time a particle spends in sites of type i is equal to the fraction of particles in this type of site yielding

$$\frac{t_i}{t} = \frac{n'_i o(E_i)}{P} = \frac{n_i [1 - o(E_i)] o(E_i)}{P} , \quad (5.18)$$

where n'_i is the number of free sites of energy E_i which is obtained from the site energy distribution by multiplying with $[1 - o(E_i)]$. For the dilute solution most of the free sites have a low occupancy $[o(E_i) \ll 1]$ and Eq. (4.2) gives

$$o(E_i) \approx \exp \left[\frac{\mu - E_i}{k_B T} \right] . \quad (5.19)$$

This way FD-Statistics is replaced for the empty sites by Boltzmann statistics. For convenience we choose an arbitrary reference site having energy E^o and a low value of $o(E^o)$. Then the following relation is derived from Eqs. (5.18) and (5.19)

$$\frac{t_i}{t^o} = \frac{n_i [1 - o(E_i)]}{n^o [1 - o(E^o)]} \exp \left[\frac{E^o - E_i}{k_B T} \right] , \quad (5.20)$$

where t^o is the fraction of the total time t particles reside within sites of energy E^o . Inserting Eq. (5.20) in Eq. (5.17) with $[1 - o(E^o)] \approx 1$ and Eq. (4.2) gives

$$t = \frac{Z t^o}{(N-P) n^o} \sum_{i=1}^{N-P} n_i \exp \left[\frac{E^o - E_i}{k_B T} \right] \left[\frac{\exp[(E_i - \mu) / k_B T]}{1 + \exp[(E_i - \mu) / k_B T]} \right] \quad (5.21)$$

or

$$t = \frac{Z t^o \exp[(E^o - \mu) / k_B T]}{N(1-c) n^o} \sum_{i=1}^{N-P} \frac{n_i}{1 + \exp[(E_i - \mu) / k_B T]} \quad (5.22)$$

where the last sum on the right hand side is nothing else than the discrete form of Eq. (4.3) and, therefore, it can be expressed by the concentration c. Then the following simple result is obtained

$$t = \frac{c Z t^o \exp[(E^o - \mu) / k_B T]}{(1-c) n^o} = \frac{Z t^o}{\gamma^o (1-c) n^o} = \frac{Z \tau}{(1-c) \gamma^o} \quad (5.23)$$

where τ is the mean residence time as defined by

$$\tau = \frac{1}{n^o} \sum_{s=1}^{n^o} \tau_s \text{ for } E_s = E^o \quad (5.24)$$

Inserting Eq. (5.23) into Eq. (5.15) yields

$$D^* = \frac{l^2(1-c)}{6\tau} \frac{\exp[(\mu - E^o)/k_B T]}{c} = \frac{l^2(1-c)}{6\tau} \gamma^o \quad (5.25)$$

If we consider the hypothetical material with sites of energy E^o only the residence time τ as defined by Eq. 5.24 is enlarged compared to the empty lattice due to blocking of sites. The dilute residence time is then $\tau^o = \tau(1-c)$ and the diffusion coefficient in the dilute regime of the reference lattice is given by

$$D^o = \frac{l^2}{6\tau^o} = \frac{l^2}{6\tau(1-c)} . \quad (5.26)$$

By combining the last two equations the same result as in Eq. (5.5) is obtained and, therefore, the result is independent of thermally activated hopping. However, the concentration dependence of the diffusion coefficient despite containing the same exponential term $\exp(\mu/k_B T)$ has to be interpreted differently. Independent of the atomistic mechanism of diffusion the occupancy of sites with higher energy at high concentration is accompanied with a decrease of the time of residence (ergodic hypothesis) and a concomitant increase of mobility.

d. Low concentration limit

The previous discussion of solubility at low concentrations is relevant for the diffusion coefficient, too. For those cases where Henry's Law is obeyed the activity coefficient is independent of concentration and so are both the tracer and the chemical diffusion coefficient, if in the dilute regime the $(1-c)$ term is neglected. However, for the academic case of an exponential DOSE discussed in section 4.2 the tracer diffusion coefficient D^* will always decrease with decreasing concentration. More realistic cases of a DOSE like the Gaussian one and experimental results show that Henry's Law is fulfilled and, therefore, D^* becomes independent of c at $c \rightarrow 0$. The obvious contradiction to the discussion at the end of the last section is overcome by realizing that at low concentrations the step behavior of the FD function no longer holds. The step behavior is a consequence of energy minimization, but a very low concentrations maximization of entropy is more important. Thus most of the particles go in sites above the Fermi level without filling these up to saturation and, therefore, gain configurational entropy. For a Gaussian distribution it has been shown that the average energy of the occupied sites becomes independent of concentration at $c \rightarrow 0$ and, therefore, the average time of residence and D^* are independent of c . This delicate balance between energy and entropy is discussed in more detail in Ref. [14, 69].

6. H-H INTERACTION

Although in the framework of this study dilute H-systems are considered only, H-H interaction has to be taken into account for those cases, where segregation at extended defects takes place and, therefore, locally high concentrations occur. Then the chemical potential may be written in a first order approximation as [70]

$$\mu = \mu_{id} + Wc_{loc} , \quad (6.1)$$

where W is an interaction parameter. Again it is reasonable to assume that we have a bimodal DOSE like the one in Eq. (4.11) yielding [70]

$$c_{loc} = f \int_{-\infty}^{\infty} \frac{n_f(E)dE}{1 + \exp\left(\frac{E - \mu - Wc_{loc}}{k_B T}\right)} \quad \text{and} \quad c_{fr} = \exp\left(\frac{\mu - E^o}{k_B T}\right) . \quad (6.2)$$

With the trivial equation $c=c_{\text{fr}}+c_{\text{loc}}$ we can solve, analytically or numerically depending on the form of $n_f(E)$, Eq. (6.2) to get the relation $\mu(c)$.

IV. Interaction of hydrogen with defects

7. INTERACTION WITH OTHER SOLUTES AND VACANCIES

An appropriate DOSE for the interaction of hydrogen with point defects is a two-level system

$$n(E) = n_o(E) + n_t(E) = (1 - c_t)\delta(E - E^o) + c_t\delta(E - E_t) \quad (7.1)$$

which is a special form of the DOSE in Eq. (4.11). The traps provided by the defects are present with a concentration c_t and have all the same binding energy $E_t - E^o$ with respect to the "normal" sites. Hydrogen residing in normal sites will be called free and integration of $n_o(E)$ according to Eq. (4.3) yields the concentration of free hydrogen:

$$c_f = \frac{(1 - c_t)}{1 + \exp\left(\frac{E^o - \mu}{k_B T}\right)} \text{ or } \mu = E^o + k_B T \ln \frac{c_f}{1 - c_t - c_f} \quad (7.2)$$

For the dilute case $c_t \ll 1$ and $c_f \ll 1$ Eq. (5.13) gives the same result as derived by Oriani [60]

$$J = -\frac{\beta D^o}{\Omega} \frac{\partial c_f}{\partial x} \quad (7.3)$$

stating that the flux of hydrogen is proportional to the concentration gradient of free particles. This assumption is valid beyond the two-level case as shown in the following.

The derivation of the last two equations is independent of the functional form of $n_t(E)$ as can be seen by comparing Eq. (4.12) and (7.2).

The interaction of hydrogen with foreign atoms both substitutional and interstitial is rather weak with a binding energy of about 10 kJ/Mol [29, 71]. This has been determined by a large variety of experimental techniques measuring permeation, internal friction, resistivity and neutron scattering. Because of the small value of the interaction energy it is difficult to decide how much of it is elastic or electronic interaction. However, interaction with vacancies is very strong with measured binding energies between 30 and 100 kJ/Mol. They are in good agreement with calculated values using the effective medium theory [29].

The hydrogen atom is considered to be dissolved within the vacancy although slightly off centre. The metal hydrogen distances are so large that the interaction potential is in the attractive region giving rise to a volume contraction. This is in agreement with experimental findings in heavily deformed Pd, where negative volume changes occurring at low concentrations have been attributed to vacancies formed during plastic deformations [53].

8. INTERACTION WITH DISLOCATIONS

Theoretical models describing the interaction of solute atoms with dislocations [72] are based on an elastic interaction between the stress field around dislocations and the strain caused by a solute atom (cf. II.C). The interaction is strongest for edge dislocations because of the hydrostatic stress field. Thus solute atoms changing the volume during dissolution, i.e. containing a non-vanishing trace in their strain tensor experience a strong elastic interaction with edge dislocations. Hydrogen in metals causes volume expansion and, therefore, interacts strongly with the stress field of edge type dislocations. As stresses of dislocations are

calculated by applying continuum theory they are less reliable within the dislocation core and, therefore, trapping of hydrogen in dislocation cores has to be treated separately. In the following the DOSE is calculated based on these considerations for edge dislocations.

The hydrostatic part of the stress field of an edge dislocation is given by [72]

$$p = \frac{\sigma_{ii}}{3} = \frac{Gb(1+\nu)}{3\pi(1-\nu)} \frac{\sin \theta}{r}, \quad (8.1)$$

where G is the shear modulus, ν Poisson's ratio, b the magnitude of the Burger's vector, θ and r are cylindrical coordinates as defined in Fig. 4 with the z-axis along the dislocation line.

Then the interaction energy with H-atoms on a circle of constant pressure is obtained from

$$pV_H = \frac{Gb(1+\nu)}{6\pi(1-\nu)R} V_H \equiv \frac{AV_H}{R}, \quad (8.2)$$

where R is the radius of the cylinder and A is defined by the last equation.

For H in Pd the number of octahedral sites which are chosen by hydrogen is the same as the number of Pd-atoms. We assume that like in the β -phase of Pd only the fraction α (being ca. 0.6 at room temperature) is occupied. Then in a material containing ρ dislocations per unit area the number of sites, n, in a cylinder of radius R and unit length is $\rho\pi R^2$ and the DOSE becomes

$$n(E) = \alpha\rho \frac{dn}{dE} = \alpha\rho \frac{dn}{dR} \frac{dR}{dE} = \alpha\rho\pi R \frac{AV_H}{E^2} = \frac{\alpha\rho\pi AV_H}{E^3}. \quad (8.3)$$

Inserting this in Eq. (4.3), using the step approximation, i.e. the first part on the right hand side of Eq. (4.6) and solving for μ gives

$$\mu = \sqrt{\frac{\alpha\rho\pi AV_H}{c}}. \quad (8.4)$$

The last equation is checked by plotting in Fig. 5 measured values of μ for H in cold rolled Pd [73] versus the reciprocal square root of concentration.

Different to the theoretical prediction the interaction energy (difference of chemical potentials between deformed and annealed sample) becomes constant at very low concentrations which is explained in terms of a direct interaction with the dislocation core which was not included in Eq. (8.2). The value of about -50 kJ/Mol-H has been also determined for H in Fe [74]. The linear dependence on $1/\sqrt{c}$ in Fig. 5 yields a slope which corresponds to reasonable dislocation densities for heavily deformed metals ($2 \cdot 10^{11} \text{ cm}^{-2}$). Contrary to Eq. (8.4), the straight line corresponding to the interaction with the long range stress field of the dislocation does not intercept the ordinate at 0 but at a value of about -20 kJ/Mol-H. This is attributed to a direct H-H interaction. It can be calculated from the values obtained for this interaction in well annealed Pd at high H-concentrations where the parameter, W, defined in section 6. was measured to be -30 kJ/mol-H [75]. With a maximum local concentration of $\alpha=0.6$ the contribution to μ from H-H interaction becomes -18 kJ/mol-H in good agreement with the intercept in Fig. 5.

During the electrochemical measurements of μ the standard value was defined such that

$$\mu = k_B T \ln c_f, \quad (8.5)$$

where according to Eq. (4.12) $E^0=0$. This is also the chemical potential for the single crystalline metal, where the concentration of free hydrogen c_f is equal to the total concentration. Besides measuring μ for a metal with a high dislocation density in comparison

with a single crystal, the concentration of free hydrogen can be determined also from measurement of the electrical resistance. It has been shown for Pd [76] that hydrogen trapped as a hydride at the dislocation lines contributes to the resistivity to a negligible part only when compared to the same number of H-atoms distributed homogeneously. Thus the resistivity increment ρ_H caused per unit of H-concentration divided by the same increment in a single crystal ρ_H^0 yields the fraction of H-atom being free. The same is true for a dislocated metal and its tracer diffusion coefficient $D^*=D^0\gamma$ (cf. Eq. (5.5) with $c \ll 1$) where D^0 has a well defined operational meaning being the tracer diffusion coefficient in the single crystal. Therefore, we have

$$\gamma = \exp\left(\frac{\mu}{k_B T}\right) = \frac{c_f}{c} = \frac{\rho_H}{\rho_H^0} = \frac{D^*}{D^0} \quad (8.6)$$

It is shown in Fig. 6 that this simple relation holds for hydrogen in strongly deformed palladium. At very low H-concentrations the fraction of free hydrogen is negligible and, therefore, all the hydrogen is trapped at dislocations. At intermediate concentrations hydrogen atoms are partitioned between sites far away from dislocations and those close to them. But sites at dislocations never become saturated because of both the long range elastic interaction and an attractive H-H interaction. Thus the corresponding cylinder being enriched in hydrogen is steadily growing.

The concentration dependence of the chemical diffusion coefficient of H in deformed crystalline Pd is shown in more detail for very low concentrations in Fig. 7. Using measured values of the chemical potential for the same deformed Pd and a diffusion coefficient obtained for a single crystalline Pd the lines in Fig. 7 were calculated by using Eqs. (2.3) and (5.5). Thus without a fitting parameter the concentration dependence of D is obtained in very good agreement with experimental results. Deviations occurring at very low concentrations are either due to an enhancement of diffusion along the dislocation core or they arise because of difficulties measuring chemical potentials at very low H-concentrations.

The pronounced changes of H-activity, diffusivity and resistivity in crystalline Pd which are caused by plastic deformation and arise from the presence of dislocations do not occur after cold rolling of amorphous PdSi-alloys [77]. The absence of a detectable H-trapping in deformed amorphous alloys is considered to reveal the absence of edge dislocation-like defects.

By measuring volume changes caused by dissolved hydrogen in severely deformed crystalline palladium (99% reduction in cross section by cold rolling) it was shown [53] that samples contracted for the first 50 to 100 atppm of H. This was attributed to trapping in vacancies (cf. section 3) which supposedly form during cold-rolling. After saturating the vacancies hydrogen was trapped in dislocation. In this concentration range the molar volume of hydrogen was slightly smaller than in single crystalline Pd. This behavior is in accordance with the assumption of hydrogen being dissolved in the expanded region below the glide plane of edge dislocations. With increasing concentration the dislocations became saturated and additional hydrogen was predominantly dissolved in normal octahedral sites far away from dislocations. As a consequence the hydrogen partial molar volume approached that of the single crystal.

So far the segregation of hydrogen at edge dislocation and the concomitant formation of hydride cylinders below the glide plane have been proven in an indirect way only. Direct evidence can be provided by small angle neutron scattering (SANS). Scattering by randomly oriented cylinders has to be described by the following macroscopic cross section [78]

$$\frac{d\Sigma}{d\Omega} = \frac{2\pi^3 \rho R_0^4 \Delta g^2}{Q} \exp\left[-\frac{1}{4} Q^2 R_0^2\right], \quad (8.7)$$

where ρ is the dislocation density, R_0 the radius of the cylinders, Δg is the difference of scattering length densities and Q is the magnitude of the scattering vector. By plotting the logarithm of the product of Q and measured values of the macroscopic cross section (after appropriate subtraction of background and incoherent scattering) versus Q^2 straight lines are expected according to Eq. (8.7). This is in agreement with experimental findings as shown in Fig. 8. The slope of the straight lines yields the radius of the cylinders and the intercept with the ordinate yields the dislocation density. Similar plots have been evaluated for different H-concentrations and the results are presented in Fig. 9.

However, the natural choice for SANS is deuterium instead of hydrogen because the former has a larger cross section for coherent scattering. In addition, hydrogen gives rise to pronounced incoherent scattering, i.e. raises the background. In agreement with the larger coherent scattering measurements with deuterium lead to larger macroscopic cross section as shown in Fig. 10. However, they are larger by a factor of 1.5 only, whereas Eq. (8.7) predicts a factor of 3.2 corresponding to the squared ratio of scattering length densities. This discrepancy is overcome by taking into account that there are two contributions to the scattering contrast. The first one is due to the H- or D-atoms having a higher concentration at the dislocation lines. The second one is a consequence of this segregation, because both isotopes expand the Pd-lattice and, therefore, reduce the scattering contrast of Pd with respect to the matrix far away from dislocations. H-atoms have a negative scattering length for neutrons and the corresponding negative contrast (difference of scattering length density) is exaggerated by the lattice expansion. For deuterium with a positive scattering length the opposite is true. Thus the peculiar scattering behavior of the hydrogen isotopes yields additional insight into the segregation at dislocations.

The high local concentrations of hydrogen at the dislocations may be treated as suggested in section 6. However, it is simpler to apply a thermodynamic model treating the pronounced segregation as a hydride formation in a hydrostatic stress field. Without stresses ($p=0$) and for equilibrium between the hydride and saturated solid solution, the chemical potentials in the two phases have to be the same, i.e.

$$\mu_{(\text{hydride}, p=0)} = \mu^0 + kT \ln c_{ts} \quad (8.8)$$

where c_{ts} is the terminal solubility of hydrogen in Pd in equilibrium with the β -phase (of composition PdH_α). As the terminal solubility of H is 0.01 H/Pd at room temperature, the ideal solution approach for the configurational entropy (logarithmic term in Eq. (8.8)) is justified. At the border between the cylindrical hydride and the solid solution a constant hydrostatic pressure p (cf. Eq. (8.1)) is present, and the chemical potential is changed to

$$\mu = \mu^0 + kT \ln c_{ts} + pV_H \quad (8.9)$$

Far away from the dislocation where hydrogen is free and where it has a local concentration of c_f , the chemical potential is given by Eq. (8.5) (here with the standard value μ^0). Then Eqs. (8.2), (8.5) and (8.9) yield

$$c_f = c_{ts} \exp\left(-\frac{Gb(1+\nu)V_H}{6\pi(1-\nu)kTR}\right) = c_{ts} \exp\left(-\frac{C}{R}\right) \quad (8.10)$$

where C is 1.0 nm for edge dislocations of $b=0.275$ nm in Pd. Besides c_f , the hydrogen trapped as a cylindrical hydride of composition $\alpha \approx 0.6$, radius R and length ρ_d contributes to the total concentration c_{tot} . Thus we have in terms of H/Pd

$$c_{tot} = \alpha \rho_d \pi R^2 + c_f = \alpha \rho_d \pi R^2 + c_{ts} \exp\left(-\frac{C}{R}\right) \quad (8.11)$$

If we use this implicit function of $R(c_{tot})$ and compare it in Fig. 9 with measured values, a good agreement is obtained by using a dislocation density of $2.2 \cdot 10^{11} \text{ cm}^{-2}$. This is considered to be additional evidence for an extended segregation of hydrogen, which requires taking into account both elastic and solute/solute interaction.

The experimental results presented in this section are in qualitative agreement with a variety of studies by other groups [24, 44, 79, 80].

9. INTERACTION WITH GRAIN BOUNDARIES

Segregation of solute atoms at grain boundaries is often studied by breaking a sample in a UHV-chamber, where in the case of intercrystalline fracture the crack runs along the grain boundaries and the solute atoms are exposed to surface analytical techniques such as AES, XPS and SIMS. For hydrogen this is difficult to achieve as only the latter method is able to detect H. In addition the high H-mobility at room temperature allows surface segregation to be established on the former grain boundary before the measurement of the original grain boundary coverage takes place.

Again the concept of a site energy distribution is useful to study H-segregation at grain boundaries. Similar to dislocations the number of traps provided by the grain boundaries is rather small and, in order to study them by gradually filling, we need a large density of them, i.e. a small grain size. This will be the case for nanocrystalline metals. Electrochemical measurements [81] of the chemical potential μ which were converted into partial pressures are presented in Fig. 11 for a nanocrystalline sample and a single crystal of Pd. In the latter case Sieverts' Law is fulfilled in the solid solution range.

The behavior of the nanocrystalline sample is described by a Gaussian distribution of site energies for sites within the boundaries and a single level for sites within the grains (cf. Fig. 12). With respect to the large variety of grain boundaries in a nanocrystalline material and a variety of structural units within a certain grain boundary the concept of a continuous distribution of segregation energies appears to be more reasonable. For the sake of simplicity the sites within the grains are assumed to have the same energy as sites in a single crystal. This is still a good approximation for higher concentrations, where the interfacial stress affects the site energy within the grains [82]. Thus at a given chemical potential or partial pressure, respectively the concentration in the grains has to be the same as in the single crystal and, therefore, its contribution to the total concentration can be subtracted yielding the amount segregated at the boundaries. Fitting Eq. (4.3) to the experimental results presented in Fig. 11 yields values for E_{seg} and σ . A more detailed description of the procedure and the results is given in Refs. [14] and [81]. For H in nanocrystalline Ni experimental values are not available over the same large range of H-concentration but they can be described within the same framework of a distribution of segregation energies as well [83, 84].

Although two parameters (E_{seg} and σ) are available, experimental results at large H-concentrations cannot be fitted (dashed curve in Fig. 11). The discrepancy arises from neglecting H-H interaction. This can be included via a quasichemical approach without introducing a new fitting parameter (cf. sections 6 and 8), because the interaction parameter W obtained from pressure composition isotherms of coarse grained Pd was used. Then the solid curve in Fig. 11 is obtained in excellent agreement with experimental data. It is

interesting to note that the width of site energies for the grain boundaries $\sigma = 15$ kJ/Mol H is in between the ones obtained from fitting data of liquid quenched and sputtered amorphous Pd-Si alloys, where the width is 11.5 or 17.5 kJ/Mol H, respectively (cf. section 14).

H-Diffusion in nanocrystalline Pd was measured via a time-lag method [14, 81], where the pellet shaped samples were electrochemically charged with hydrogen from one side and the delayed response of the electrochemical potential at the adjacent side was monitored (cf. section 2). The concentration was raised in small steps, in order to minimize errors arising from the concentration dependence of the diffusion coefficient. As the transport of H through the sample is a mixture of grain boundary and bulk diffusion, the numbers evaluated from the time lag were called effective diffusion coefficients (see discussion below). The results are presented in Fig. 13.

For atoms diffusing along grain boundaries being perpendicular to the surface three limiting cases are discussed [85] as shown in Fig. 14. Case (A) corresponds to the condition $D_{gb}t \gg d^2$, where D_g is the diffusion coefficient within the grains, d is the distance of grain boundaries and t is the time. For the results presented in Fig. 13 $D_g = 3 \cdot 10^{-7}$ cm²/s, $d \approx 10$ nm and t is between a few seconds and a few minutes and, therefore, the condition for type A diffusion is always fulfilled. Then the effective diffusion coefficient is given by [85]:

$$D_{eff} = fD_{gb} + (1-f)D_g \quad (9.1)$$

where f is the volume fraction of grain boundaries which (for the case shown in Fig. 14 with additional boundaries running parallel to the drawing plane) is given by:

$$f = \frac{2\delta}{d + 2\delta} \quad (9.2)$$

The case of solute segregation described by a factor $S = c_{gb}/c_g$ can be formally included by replacing δ by $S\delta$ [85]. Then the ratio of the two contributions to the effective diffusion coefficient becomes:

$$\frac{fD_{gb}}{(1-f)D_g} = \frac{2S\delta D_{gb}}{dD_g} \quad (9.3)$$

The contribution of the grain boundaries can be dominant or determine the transport, respectively for two reasons:

- A1: Grain boundary diffusion is much faster than bulk diffusion ($D_{gb} \gg D_g$) but the grains are fed from the grain boundaries because of the short diffusion length $d \ll \sqrt{D_g t}$ and
- A2: Grain boundary diffusion is slower than bulk diffusion ($D_{gb} < D_g$) but the segregation factor S is much larger than unity. The concentration front is moving ahead within the grains but the boundaries act as sinks retarding the transport through the grains.

The latter case A2 applies to the low concentration results presented in Fig. 13, because from the data of Fig. 11 the segregation factor S can be obtained from the trivial relation

$$c_{tot} = fc_{gb} + (1-f)c_g = fSc_g + (1-f)c_g \quad (9.4)$$

and a grain boundary thickness δ of about 0.5 nm. The concentration within the grains c_g is equal to the values of the single crystalline sample at a given chemical potential, because they are assumed to have the same site energies. Thus the ratio S in Eq. (9.4) is much larger than unity and, therefore, the measured H-transport through the nanocrystalline membrane is determined by grain boundary diffusion and $D_{eff} = D_{gb}$.

Case A2 is not discussed in textbooks on diffusion because grain boundary diffusion is always considered to be faster than diffusion through the grains. This judgment is based on the decreased density of atoms in the boundaries which gives rise to a lower formation energy of

vacancies or vacancy like defects as prerequisites for substitutional diffusion. However, interstitial diffusion does not require vacancies and it is slowed down in the presence of a distribution of site energies as the interstitials are trapped in low energy sites at low concentrations. At higher concentrations the traps are gradually saturated and interstitial diffusion takes advantage of the more open structure of the boundary as well.

The concentration dependence of D_{gb} can be calculated via Eq. (2.3) and (5.5) neglecting the contribution from grains, i.e. considering the Gaussian distribution in Fig. 12 only. H-concentration has to be replaced by the grain boundary part c_{gb} and γ' is obtained from the measured chemical potential. Thus only one fitting parameter, the reference diffusivity D^0 , can be changed to obtain agreement with experimental data. With the logarithmic scale used in Fig. 13 the calculated curves are moved up and down in the direction of the ordinate without changing their slope and curvature. The steady increase of D with increasing concentration is equivalent to amorphous materials (cf. chapter VI) because a Gaussian distribution has been used there as well. However, different to the glassy materials concentrations in the boundaries become so large that blocking of sites and H-H interaction has to be taken into account (without additional fitting parameters). The concentration in the boundaries is about 0.25 H/Pd at $c_{tot}=0.01$ for $\delta=0.5$ nm. As the H-H interaction is attractive ($W=-30$ kJ/mol-H) the diffusivity is finally decreased at high H-concentrations. In agreement with the generally accepted wisdom, the average or reference diffusion coefficient D^0 of the grain boundaries is larger than the bulk value due to a lower activation energy for H-atoms arising from the lower metal density in grain boundaries. The concept of interstitial diffusion in grain boundaries used in this study and the interpretation of the concentration dependence have been embedded in a general context [86].

The increased H-solubility in the α -phase of nanocrystalline Pd has been confirmed by other experimental methods, i.e. doping samples from the gas phase and measuring pressure drops [87] and or lattice parameters [82]. Like in Ref. [87] pressure-composition isotherms or lattice parameters were also measured at high hydrogen concentrations using an electrochemical technique [88]. In all studies [82, 87, 88] it was shown that the miscibility gap between α - and β -phase is remarkably reduced in nanocrystalline Pd. The corresponding increase of the terminal solubility in the α -phase is generally accepted to be due to segregation at the grain boundaries, whereas the reduction of the lower limit of H-solubility in the β -phase is interpreted differently. In Ref. [88] it is argued that the composition of the grain boundaries do not change within the miscibility gap, because the chemical potential of hydrogen has to be constant in this region. Then all of the grains are transformed into β -phase whereas the H-occupancy of the grain boundaries does not change, i.e. remains at a value which is larger than in the α -phase (segregation) but smaller than in the β -phase. Thus an overall decrease of the total H-concentration occurs at the $(\alpha+\beta)/\beta$ -boundary of the miscibility gap. Following this reasoning an average grain boundary thickness of 0.7 to 1 nm can be calculated without data fitting [88]. However, one has to take into account [82] that the inhomogeneous distribution of hydrogen between grains and grain boundaries gives rise to a corresponding inhomogeneous distribution of mechanical stresses which affect the chemical potential. Thus segregation in grain boundaries leads to compressive stresses in these regions whereas the grains go into tension. Hydrogen atoms are redistributed and corresponding changes of the lattice parameter occur. At the $(\alpha+\beta)/\beta$ -boundary of the miscibility gap the stress distribution is reversed because of the higher H-concentrations in grains. These effects do not change the data evaluation presented in this study because at the dilute region the corresponding mechanical stresses are too low to change the chemical potential to a measurable extend.

10. INTERACTION WITH METAL/OXIDE BOUNDARIES

Hydrogen trapping at metal/ceramic interfaces has been studied extensively [89, 90, 91] because of its relevance in the area of hydrogen embrittlement of high strength steels, where hydrogen is trapped at the metal/carbide interface [92]. Due to the large H-solubility and the ease of measuring chemical potentials palladium alloys are used as model alloys again. For some metal/oxide interfaces high resolution electron microscopy and analytical field ion microscopy [93, 94, 95, 96] revealed that most of the terminating layers are dense packed oxygen planes (cf. Fig. 15). As a consequence small oxide precipitates have an excess of oxygen when compared with the stoichiometry resulting from charge neutrality. Thus the negative charge of the excess oxygen at the interface has to be delivered by the surrounding metal as it was shown recently by electron energy loss spectroscopy [97, 98]. In addition, it has been shown [89] that the excess oxygen at the Ag/MgO interface is bound there with an energy which corresponds to the formation energy of Ag₂O in agreement with the structural model of Fig. 15 and electron energy loss spectroscopy for the same [98] and for a similar boundary Cu/MgO [97].

The concept of varying stoichiometry is in agreement with experimental findings, where dependent on the oxygen activity during sample annealing treatments „irreversible“ and reversible trapping of hydrogen was observed [90, 91]. The term irreversible trapping was used because the corresponding part of trapped hydrogen could not be removed by prolonged anodic polarization of the sample, i.e. the binding energy to the traps was so high that the corresponding reduction of H-mobility did not allow a removal of the trapped hydrogen. Raising the temperature above 300 °C finally leads to a depletion of these traps.

The amount of irreversibly trapped H corresponds to about one monolayer at the phase boundary and can be ascribed to the formation of O-H bonds at the interface according to the following relation:

where the oxygen of the PdO corresponds to the excess oxygen within the structural vacancies of the terminating O²⁻-layer of the precipitate (cf. Fig. 15 for the analogous case of Ag/MgO). Calculating Gibbs free energy of the reaction and the volume change yields data for the trapping energy and partial molar volume of H which are in agreement with experimental findings [90, 91]. Thus the formation of a Mg(OH)₂ layer at the interface gives rise to a remarkable volume change which is about two times as much as for H-atoms dissolved in octahedral sites of Pd. Although a higher elastic energy for lattice distortion has to be paid by segregation at the oxide/metal interface, it takes place, because the gain of chemical energy by forming the OH bonds is much larger than the corresponding elastic energy. It is interesting to note that the crude approximation of the chemistry at the interface by bulk behavior gives reasonable results.

Because of the higher hydrogen mobility in silver it was possible to internally oxidize an Ag-1at.-% Mg at rather low temperatures leading to very small precipitates of MgO (1.6 to 5 nm in diameter). These were analyzed using a tomographic atom probe [99]. The results confirmed an excess of oxygen at the interface with the metal. However, an analysis of hydrogen turned out to be difficult because of the residual hydrogen in the vacuum chamber. Therefore, small angle neutron scattering (SANS) was applied, in order to get additional information about segregation of both excess oxygen and hydrogen or deuterium, respectively. Again the Ag/MgO samples were advantageous because of the smallness of their precipitates.

As the solubility of hydrogen in silver is very low, a temperature of 400 °C was chosen, in order to have a sufficient flux of hydrogen which is necessary to fill all the traps at the oxide/metal interfaces. This way it was possible to do SANS experiments with 3 types of samples: (i) samples after internal oxidation, (ii) internally oxidized plus doping with hydrogen and (iii) internally oxidized plus doping with deuterium [100]. The macroscopic cross section $d\Sigma/d\Omega$ obtained for these samples is presented in Fig. 16. After the background and the incoherent scattering were subtracted, three different regimes can be distinguished for all samples. At very low values of the scattering vector Q large MgO precipitates at the grain boundaries give rise to a steep decrease of $d\Sigma/d\Omega$. Then a plateau region follows which describes the scattering of the small precipitates within the grains at low Q -values. The plateau is followed for $Q > R^{-1}$ by a Guinier regime which allows the evaluation of the average radius R of the oxide particles assuming a spherical shape [100].

Both H- and D-doping change $d\Sigma/d\Omega$ considerably. MgO has a higher scattering length density than Ag and, therefore, segregated hydrogen (deuterium) having a negative (positive) scattering length decreases (increases) the macroscopic cross section. The observation that hydrogen has a much more pronounced effect than deuterium cannot be explained by the difference of the scattering lengths but is due to Ag-atoms being repelled from the interface. The corresponding decrease of scattering length density is exaggerated by H with its negative scattering length, whereas the positive contribution of deuterium is compensated this way. This is in accordance with the observation for dislocations, where the contrast variation for H and D were smaller than expected because of a decrease of the packing density of Pd-atoms.

At first sight the changes presented in Fig. 16 are astonishing, because they are assumed to be caused by the segregation of one monolayer of H-atoms at the interface only. However, one has to take into account that the number of H-atoms on the surface of an oxide particle as small as 3 nm corresponds to about 50% of all the ions in the oxide. In addition, the decreasing macroscopic cross section in the Guinier regime is determined by the radius of gyration with respect to scattering contrast and, therefore, any changes of contrast in the periphery of an oxide particle is exaggerated. Besides the changes observed for H and D segregation it is also possible to detect desorption of the excess oxygen with SANS [101].

A quantitative analysis of the SANS data was performed for a set of samples with different average radii and different coverages at the interface [100, 101]. The results yield particle radii which are in agreement with measurements made with the tomographic atom probe [99]. The coverage of the interface with excess oxygen is half of the coverage with hydrogen or deuterium, respectively. This experimental finding supports the model proposed in Fig. 15 or the corresponding reaction described by Eq. (10.1). However, the total values of coverage are about half of what the model predicts for a (111) surface of the MgO. These crystallographic planes of the oxide are adjacent to the (111)-planes of Ag [93, 95] and, therefore, the oxide precipitates should have octahedral shape. However, as a consequence of minimization of interfacial area the actual shapes are truncated octahedra with (100) planes. For these planes the rock salt structure of MgO predicts 50% Mg- and 50% O-ions, i.e. no structural vacancies on the oxygen sublattice. Thus the fraction of (111) planes is reduced and so is the average coverage with excess oxygen or hydrogen, respectively. For more results and a detailed analysis see Ref. [101].

11. DEFECT FORMATION ENERGY

It is well known for surfaces and grain boundaries that their energy γ can be reduced by solute segregation leading to an excess concentration Γ_A at the interface. The corresponding change of energy is expressed by the Gibbs Adsorption Equation [102]

$$\left. \frac{\partial \gamma}{\partial \mu_A} \right|_{T, \mu_B} = -\Gamma_A, \quad (11.1)$$

where μ_A is the chemical potential of solute A and μ_B the one for solvent B. In a related study Carl Wagner [103] defined the excess Γ_A by the amount of solute dn_A one has to add or remove from a system were the interfacial area changed by da with a constant chemical potential of A and a constant number of moles of the solvent B. Thus we have

$$\Gamma_A = \left. \frac{\partial n_A}{\partial a} \right|_{T, P, V, n_B}. \quad (11.2)$$

According to the system being partly open (for A) and partly closed (for B) a new characteristic function was introduced [103]

$$F - n_A \mu_A \quad (11.3)$$

using the free energy F. The differential of the new function is

$$d(F - n_A \mu_A) = -SdT - PdV + \gamma da + \mu_B dn_B - n_A d\mu_A. \quad (11.4)$$

Upon differentiating $F - n_A \mu_A$ once with respect to a , once with respect to μ_A one obtains

$$\frac{\partial^2 (F - n_A \mu_A)}{\partial a \partial \mu_A} = - \left. \frac{\partial n_A}{\partial a} \right|_{T, V, \mu_A, n_B} = \left. \frac{\partial \gamma}{\partial \mu_A} \right|_{T, V, n_B, \mu_A}, \quad (11.5)$$

which yields the classical Gibbs Adsorption Equation via Eq. (11.2).

In the present study this procedure is generalized, in order to include other defects as well. For the sake of the same formalism we introduce an appropriate defect density ρ , i.e. grain boundary area, dislocation length or number of vacancies per volume etc. and the specific energy γ now being the energy of formation of the defect per area, length or number, respectively. Then Eq. (11.4) becomes

$$d(F - n_A \mu_A) = -SdT - PdV + \gamma d(\rho V) + \mu_B dn_B - n_A d\mu_A \quad (11.6)$$

The equivalent definition of solute excess at the defect is defined in analogy to Eq. (11.2) as

$$\Gamma_A^{(\rho)} = \frac{1}{V} \left. \frac{\partial n_A}{\partial \rho} \right|_{T, P, V, n_B}. \quad (11.7)$$

Since n_A is proportional to ρ , it follows from the last equation that

$$\Gamma_A^{(\rho)} = \frac{1}{V} \frac{\Delta n_A}{\rho}, \quad (11.8)$$

where Δn_A is the total excess due to all the defects in volume V. A generalized adsorption equation is derived by following the same lines of derivation as before

$$\left. \frac{\partial \gamma}{\partial \mu_A} \right|_{T, \mu_B} = -\Gamma_A^{(\rho)}. \quad (11.9)$$

With measurements of the chemical potential of hydrogen and measurements of the excess amount of hydrogen at dislocation and grain boundaries as presented in sections 8 and 9 the change of the formation energy of these two types of defects can be calculated. Fig. 17 shows the changes of concentration as a function of the hydrogen pressure for nanocrystalline Pd at room temperature. The following relations have been used to obtain the appropriate quantities

$$\Delta c = \left(\frac{n_H}{n_{Pd}} \right)_{nano} - \left(\frac{n_H}{n_{Pd}} \right)_{single} = \frac{a \Gamma_H}{n_{Pd}} = \frac{a \Gamma_H \Omega_{Pd}}{V} = \frac{3 \Gamma_H \Omega_{Pd}}{g} \quad (11.10)$$

with the last equation being valid for spherically shaped grains and g being the grain size and Ω_{Pd} the atomic volume of Pd. Numerical integration of the Gibbs Adsorption Equation for the data in Fig. 17 yields

$$\Delta\gamma = \int_{-3}^3 \Gamma_H d\left(\frac{2.3k_B T \log p}{2}\right) = -0.89 \text{ J/m}^2 . \quad (11.11)$$

This value is of the order of the energy of the grain boundaries meaning that segregation may finally lead to zero formation energy. Then no driving force for grain growth would be present. This phenomenon of zero grain boundary energies is discussed in more detail in Ref. [104].

In order to estimate the effect hydrogen has on the reduction of the line energy of dislocations the simple relation of Eq. (8.11) derived in section 8 for the hydride cylinder formed in the expanded region below the glide plane of an edge dislocation will be used.

$$\Delta c = \alpha \rho 4\pi r^2 = \frac{\rho \Gamma_H^{(\rho)} \Omega_{Pd}}{V} . \quad (11.12)$$

Then integration of Eq. (11.9) yields

$$\begin{aligned} \Delta\gamma &= - \int_{\mu_1}^{\mu_2} \frac{\alpha 4\pi r^2}{\Omega_{Pd}} d\mu_H = - \int_{c_1}^{c_2} \frac{\alpha 4\pi r^2}{\Omega_{Pd}} k_B T d \ln c_f = \int_{r_1}^{r_2} \frac{\alpha 4\pi r^2}{\Omega_{Pd}} k_B T d \frac{1.1nm}{r} \\ &= - \int_0^r \frac{\alpha 4\pi}{\Omega_{Pd}} k_B T (1.1nm) dr = - \frac{\alpha 4\pi k_B T r}{\Omega_{Pd}} (1.1nm) \end{aligned} \quad (11.13)$$

For a radius of $r=1$ nm as determined experimentally (cf. section 8 and Fig. 9) the last equation gives $\Delta\gamma=2 \cdot 10^{-9}$ J/m. This is about three times the line energy of a dislocation, if we calculate this value from the empirical relation $\gamma b \approx 1 \text{ eV}$ (b =burger's vector=0.275 nm for Pd) [105]. The reduction of the line energy by hydrogen segregation may be overestimated because of the various approximations made during the derivation of Eq. (11.9). Nevertheless, a reduction of the energy of dislocation formation is expected and it may be the reason why higher dislocation densities can be produced by cycling palladium between the α and β phase when compared with severe cold rolling [106]. Crossing the α/β phase boundary dislocation rings are punched out, in order to accommodate the misfit between β and α phase [22, 23]. This occurs at a high chemical potential, i.e. a high excess concentration and, therefore, a reduced energy of dislocation formation.

For a hydride the situation is different, because the local concentration in the expanded region around an edge dislocation is saturated and, therefore, it is the same as far away from a dislocation. The formation of an edge dislocation leads to a negative H-excess because hydrogen is now repelled from the compressed region above the glide plane. Therefore, the energy of dislocation formation is increased leading to a loss of ductility. This may explain the extreme brittleness of metal hydrides. The commonly accepted theory that solute drag decreases dislocation mobility may not apply to hydrogen at room temperature being highly mobile even in hydride phases.

Finally we discuss the effect hydrogen has on the formation energy of vacancies. In this case the defect density is the number of vacancies per unit of volume. Then the excess defined by Eq. (11.7) has the simple meaning of number of H-atoms trapped around one vacancy N_{HV} . Assuming that this number is constant over a certain pressure range Eq. (11.9) yields

$$\Delta\gamma = -N_{HV}\Delta\mu_H = -N_{HV} \frac{k_B T}{2} \Delta \ln p_{H_2} . \quad (11.14)$$

As the interaction energies of hydrogen with vacancies in metals are rather high (ca. 1 eV [14]) hydrogen atoms may be all trapped at low concentrations (i.e. 10 atppm). Up to the terminal solubility in Pd at room temperature (ca. 10^{-2}) three orders of magnitude in concentration are covered which corresponds to 6 orders with respect to pressure (cf. Eq. (2.2)). With an excess of 1 H-atom per vacancy ($N_{HV}=1$) Eq. (11.14) leads to $\Delta\gamma=-0.18$ eV. By increasing temperature and pressure and a possible higher excess, N_{HV} , it is easily concluded that the formation energy becomes zero. This is in agreement with high pressure experiments by Fukai et al. [21], where abundant vacancies have been detected in Pd.

By discussing the effect solute atoms have on the formation energy of a defect it is demonstrated again how useful the knowledge of the chemical potential is. And again hydrogen metal systems are model systems because it is rather easy to measure μ for them.

12. INTERACTION WITH CRACK TIPS AND HYDROGEN EMBRITTLEMENT

First of all a crack tip in a sample which is under external stress according to mode I, i.e. tensile load perpendicular to the crack surface, attracts H-atoms. The hydrostatic stress in front of the crack tip is enhanced and, therefore, H-atoms can lower their chemical potential according to Eq. (3.1). A quantitative treatment of this elastic interaction in terms of a DOSE is presented in Ref. [107]. However, the strength of the interaction is rather weak and the corresponding concentration enhancement is small. Nevertheless, the presence of hydrogen at the crack tip gives rise to the following effects:

- (i) For atoms right at the crack tip a small fraction of H-atoms is sufficient to occupy and weaken the stretched metal-metal bonds at the tip. After rupture of these bonds hydrogen migrates to adjacent bonds and continues to weaken these bonds, too. Under these circumstances the fracture will be a brittle one. This scenario of hydrogen embrittlement is called decohesion [60] and may apply to those metals which have a low H-solubility such as iron.
- (ii) Due to H-H interaction the segregation of hydrogen will be enhanced near the crack tip because of the concentration enhancement stemming from the elastic interaction. When the terminal solubility is reached a hydride forms at the crack tip and the crack can advance through the brittle hydride. Again H-atoms easily redistribute and follow the propagating tip. This mechanism of hydrogen embrittlement is expected to be relevant for metals with a high H-solubility such as group Vb and IVb transition metals. Hydride formation in front of a crack has been observed in-situ in an electron microscope [61].
- (iii) Opening a crack gives rise to the formation of fresh surfaces and, therefore, the work required for crack growth includes a surface energy term. In the presence of hydrogen the surface energy can be reduced by surface segregation of H-atoms [108] like the reduction of grain boundary energy discussed in section 11. This way the energy for propagating a crack tip is reduced.
- (iv) For those cases where ductility plays an important role during fracture the interaction of hydrogen with dislocation has to be taken into account as well. During TEM observations of dislocations it was observed that the motion of these defects was accelerated in the presence of hydrogen [109, 110]. This enhanced local plasticity increases the growth rate of a crack. Therefore, on a macroscopic scale it appears to be an embrittlement phenomenon. The reason for the increased dislocation velocity as suggested by Birnbaum et al. [109, 110] is an elastic interaction between dislocations and the strain field of solute atoms such as carbon. In the light of the decreased line energy of a dislocation by segregated H-atoms as discussed in

section 11 it may also be that the rate of generation of dislocations is increased in the presence of hydrogen because their formation energy is decreased.

Besides the direct interaction of hydrogen with the crack tip there are other hydrogen effects which severely alter the mechanical behavior, too. A recent review is given in Ref. [111]

V. Hydrogen in disordered and amorphous alloys

13. DISORDERED CRYSTALLINE ALLOYS

For a crystalline alloy $A_{1-x}B_x$, where hydrogen occupies tetrahedral sites and A and B atoms are distributed randomly, an appropriate DOSE is

$$n(E) = f \sum_{i=1}^4 \binom{4}{i} x^i (1-x)^{4-i} \delta(E - E_i) , \quad (13.1)$$

where the factor f is equal to the number of tetrahedral sites per metal atom which can be occupied by hydrogen. However, due to the repulsive interaction between nearest hydrogen atoms some of the sites remain empty and, therefore, actual values of f are less than the total number of tetrahedral sites per metal atom. Five different types of tetrahedral sites (A_4 , A_3B , A_2B_2 , AB_3 and B_4) have to be distinguished according to the occupancy of their corners with either A or B atoms. For a random distribution of A and B these five types are present in

concentrations of $\binom{4}{i} x^i (1-x)^{4-i}$. Their site energies for hydrogen are labeled E_i where $i=0, 1, \dots, 4$ is the number of B atoms distributed among the corners of the tetrahedron. For an alloy dilute in B the DOSE of Eq. (13.1) reduces to the one given by Eq. (7.1), because the number of tetrahedra having more than one B atom becomes negligible.

The DOSE proposed for a concentrated alloy has been used by C. Wagner [112] in order to model the thermodynamic activity of interstitial oxygen in liquid iron alloys. Measurements of hydrogen solubility were performed by Feenstra et al. [113] in niobium-vanadium alloys over a wide range of alloy composition and hydrogen concentration. Because of the large data set they were able to show unambiguously that the fraction of the various tetrahedra follows the binominal distribution of a random alloy. Hydrogen prefers tetrahedra having a higher number of V-atoms at their corners in agreement with the vanadium hydride being a stronger hydride former when compared with niobium, i.e. $E_4 < E_3 < \dots < E_0$ where the subscript refers to the number of V-atoms. Besides the expected behavior the site energies with respect to i they also depend on alloy composition, x . This is explained [113] by an overall change of the size of tetrahedral sites following the changes of the lattice parameter. According to the positive partial molar volume of hydrogen the site energy is lowered, when the site volume increases. Therefore, a V_4 -site has a lower site energy in a niobium rich alloy in comparison with a vanadium rich alloy. All of these results are compiled in Fig. 18 as the DOSE of the Nb-V alloy.

14. METAL/NON-METAL GLASSES

A large number of metal/non-metal glasses have a concentration of about 20 at.-% non-metal. Among these amorphous alloys the palladium-silicon alloys were mostly used to measure hydrogen solubility and diffusivity [46, 114, 115, 116]. In some studies it was considered to be appropriate to use for the DOSE of the amorphous alloys a two-level system [114, 116] whereas others preferred a Gaussian distribution

$$n(E) = \frac{1}{\sigma\sqrt{\pi}} \exp \left[- \left(\frac{E - E^0}{\sigma} \right)^2 \right] \quad (14.1)$$

where σ is the width and E^0 the average value of this function. Inserting this DOSE in Eq. (4.3) and application of the step approximation yields

$$c = \frac{1}{2} \operatorname{erfc} \left(\frac{E^0 - \mu}{\sigma} \right). \quad (14.2)$$

Solving the last equation for μ gives

$$\mu = E^0 - \sigma \operatorname{erf}^{-1}(1 - 2c). \quad (14.3)$$

where the inverse error function erf^{-1} was used. By measuring the chemical potential at low concentrations by an electrochemical technique and at high concentrations with a high pressure equipment it was possible to cover a range of hydrogen pressures extending over 18 orders of magnitude [115] as shown in Fig. 19. In this case the concentration was defined as the ratio H/Pd which in crystalline Pd is equivalent with the ratio of the number of H-atoms and the number of sites (octahedral ones in fcc-Pd).

Over the range of pressures shown in Fig. 19 it will be impossible to fit a two level system to the data points. Besides the good agreement between experimental results and a Gaussian DOSE there is also a solid theoretical foundation for this DOSE.

In a first order approximation [14] the DOSE of amorphous PdSi alloys was derived from the distribution of atomic distances which is given by the first peak in the radial distribution function. This distribution of atomic distances may be considered as a distribution of strain. By multiplying the latter with a factor of 3 yields a distribution of the volume of interstices. Its product with the bulk modulus and the partial molar volume of hydrogen results into a distribution of site energies. As the first peak of the metal/non-metal glasses has a Gaussian shape the forgoing simple consideration will lead to a Gaussian DOSE. In a more rigorous treatment P. Richards [117] showed that the assumption of an interaction potential between hydrogen and metal of radial symmetry is sufficient to come to the same conclusion. Then the width σ of the DOSE can be calculated from measurable and known quantities yielding a value which is only about 30% larger than the experimental one.

The pressure composition isotherms shown in Fig. 19 do not show a pressure plateau which is present in crystalline alloys stemming from the constant chemical potential within a miscibility gap or a two phase region of a solid solution and a hydride. The absence of a miscibility gap or the missing hydride formation in amorphous alloys is treated by R. Griessen [70] showing that there is an interesting analogy with ferromagnetism and the Stoner criterion. Thus, if the H-H interaction energy is smaller than the width of the Gaussian DOSE, no hydride formation occurs, i.e. the H-atoms prefer to be distributed among the low energy sites instead of being forced to occupy high energy sites in a concentrated phase, in order to profit from a small H-H interaction energy.

Examples of chemical diffusion coefficients in amorphous $\text{Pd}_{80}\text{Si}_{20}$ measured by an electrochemical technique are presented in Fig. 20. Depending on the methods of preparation of the Pd-Si alloy the values differ by up to two orders of magnitude, although the radial distribution function as measured with X-rays revealed no differences. The chemical diffusion coefficient D of hydrogen in amorphous matrices can be calculated by using Eq. (5.5) and (2.3) in combination with Eq. (14.1). Experimental values are always in good agreement with the calculated ones [14, 46, 118] which is shown for an example in Fig. 20. The different results in Fig. 20 can be explained partly by different distributions of site energies but they are also affected by the distribution of saddle-point energies as discussed in section 17. The latter effect changes the reference diffusivity D^0 . However, the concentration dependence, i.e. the slope and curvature of the calculated curves in Fig. 20 is solely determined by the measured

chemical potentials. The only free fitting parameter D^0 will move the curves up and down, because a logarithmic ordinate has been used in Fig. 20 and because D^0 is a factor in Eq. (5.5).

In Fig. 20 the curve with the steepest slope corresponds to $\text{Pd}_{80}\text{Si}_{20}$ which was prepared by sputtering and had the broadest DOSE as obtained from fitting measured values of the chemical potential. For a broad distribution an incremental change of the concentration dc give rise to larger changes of the Fermi energy $d\mu$ when compared with a narrower DOSE (cf. Eq. (4.7) with $n(\mu)$ being smaller for a broad DOSE). For the extreme case of zero width or a crystalline alloy, respectively D is independent of c as shown in Fig. 20 for a crystallized $\text{Pd}_{80}\text{Si}_{20}$ -alloy [14, 119].

15. EARLY TRANSITION/LATE-TRANSITION METALLIC GLASSES

For an amorphous alloy A_{1-x}B_x the same considerations as in section 13 have to be applied, in order to obtain the fractions of the various A_iB_{4-i} -tetrahedra. However, different to the crystalline case each type of tetrahedral site has a broad distribution of site energies. Assuming a Gaussian one for each of them with an average energy E_i and a width σ_i Eq. (13.1) becomes

$$n(E) = \frac{f}{\sigma_i \sqrt{\pi}} \sum_{i=1}^4 \binom{4}{i} x^i (1-x)^{4-i} \exp\left(-\frac{(E-E_i)^2}{\sigma_i^2}\right). \quad (15.1)$$

Often binary metallic glasses are alloys of an early and a late-transition metal. The affinity of these metals may be obtained from their hydride formation energies. A compilation of these values [36] shows that they in almost all cases increase within the transition series from left to right (Pd being an exception). Thus early transition metals have a high affinity to H whereas the late ones have a much lower one. Then the average site energy E_i for the A_iB_{4-i} -tetrahedron increases with increasing i for A being the late transition component. This expectation is in agreement with experimental findings [120, 121]. By using the step approximation of the FD-Statistics, i.e. Eq. (4.7) the DOSE is obtained directly from measurements of $\mu(c)$ as shown in Fig. 21.

The DOSE for the amorphous Ti-Ni and Zr-Ni alloys shows a structure which arises from the varying composition of the next neighbor atoms around the H-atom. For the sake of simplicity the same width σ was assumed for each type of tetrahedron. The position and the area of the various Gaussian functions yield values for f and E_i . In a first order approximation the average energies are linear combinations of the site energies for A_4 and B_4 and the site energies for the latter are about the same as the hydride formation energies of the crystalline metals A and B. The ratio of the areas of the various Gaussian distributions is independent of f and is determined in agreement with Eq. (15.1) by the alloy composition only. This agreement is considered to be a piece of evidence for a random distribution of Ni and Ti or Zr-atoms, respectively. The situation is totally different for a $\text{Mg}_{50}\text{Ni}_{50}$ alloy, where the pressure composition isotherms resemble those of a crystalline metal, i.e. have rather flat portions like in the ones in the miscibility gap or the two phase region [122]. Thus the majority of sites has to be very similar and according to the composition they are most probably Mg_2Ni_2 -tetrahedra.

The chemical diffusion coefficient of hydrogen in early transition/late-transition metallic glasses is increasing with increasing concentration [120]. However, in the ascending curves of

D vs. c plots there is a dip at those concentrations, where a sub-set of tetrahedra of the type A_iB_{4-i} is filled and the energetically less favorable type $A_{i+1}B_{3-i}$ has to be occupied. Again this feature provides some information about the structure of a metallic glass where H-atoms act as probes. In addition, it is an indication of a correlated random walk through the amorphous structure and, therefore, the concentration dependence of D calculated from measured chemical potentials deviates remarkably from measured data [14].

16. BULK METALLIC GLASSES

Bulk metallic glasses can be quenched into the glassy state with rather low cooling rates [123, 124]. This is achieved - besides other means – by increasing the number of components. In addition a larger variety of atomic radii appears to be favorable for glass formation. There are a few studies on the behavior of hydrogen in bulk metallic glasses only [125, 126, 127]. This may be due to a low H-diffusivity (see below) and the extreme brittleness of hydrogenated samples. Thus electrochemical techniques, where two electrochemical cells are separated by the sample acting as a membrane, fail, because cracks form and hydrogen is permeating quickly along these cracks pretending high diffusivities.

Recently a new technique of measuring H-diffusion has been invented [128], in order to circumvent these problems. Thin film preparation methods were applied in order to produce a multilayer of Pd/bulk-glass/Pd on a substrate (cf. Fig. 22). The covering Pd layer is very thin and serves the purpose to facilitate hydrogen entry. After passing through the bulk metallic glass hydrogen is dissolved in the Pd-layer below. Because of the higher electrical resistance of bulk metallic glass when compared to Pd and because of the thickness of the various layers, the bottom Pd-layer determines the overall resistivity of the package. Then changes of the resistivity as a function of time can be used to calculate the diffusion coefficient of hydrogen, because the rate determining step is diffusion through the bulk metallic glass.

Experimental results of D in a $Zr_{66.8}Al_{17.4}Ni_{7.2}Cu_{8.6}$ glass and the equilibrium pressures are presented in Figs. 23 and 24 as a function of H-concentration. The equilibrium pressures were obtained by electrochemical measurements as well but without the bottom Pd-layer shown in Fig. 22. In agreement with the behavior in other metallic glasses the diffusion coefficient increases with increasing hydrogen content and the increase can be calculated from the measured values of the chemical potential [128].

However, modelling the behavior of the chemical potential or the equilibrium pressures, respectively turned out to be rather complicated. Because of the increased number of components the number of different tetrahedra increases from 5 for a binary alloy to 15 for a ternary and 35 for a quaternary alloy. Assigning different widths and average energies to each of the tetrahedra would result in a corresponding large number of fitting parameters. Thus the measured isotherms were modeled with the smallest reasonable number of parameters by assuming that all Gaussians had the same width $\sigma_i=8$ kJ/mol-H and an average site energy for a tetrahedron obtained from the participating corner atoms and their hydride formation energies E_f as

$$E_k = v_{k1}E_{f1} + v_{k2}E_{f2} + \dots + v_{kn}E_{fn} \quad \text{and} \quad \sum_{j=1}^n v_{kj} = 4 \quad , \quad (16.1)$$

where v_{kj} is the number of j-atoms sitting at the corners of a tetrahedron labeled k and n is the total number of components. The DOSE is given by the sum of Gaussians with these parameters multiplied with the frequency of their occurrence which depends on concentration.

Then the only fitting parameter left is the total number of tetrahedra, f (cf. Eq. (15.1)) which moves the calculated pressure composition isotherms in a double logarithmic plot parallel in the direction of the $\log c$ axis but does not affect slope and curvature. Calculating isotherms this way resulted in good agreement with experimental results for the $\text{Zr}_{66.8}\text{Al}_{17.4}\text{Ni}_{7.2}\text{Cu}_{8.6}$ alloy as shown in Fig. 23. However, the agreement was not achieved by this procedure for the $\text{Zr}_{46.8}\text{Ti}_{8.2}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ (Vitalloy 1) alloy. This failure of the simple concept may arise because of two reasons: (i) the atoms of the various components are not distributed randomly but a pronounced short range order exists, and (ii) the distances between a H-atom and the atom of one of the components is very different from the ones in the pure component (H-atoms may actually occupy non-tetrahedral sites). The latter affect then has to be treated in a similar way as in the crystalline Nb-V alloys (cf. section 13).

VI. Other interstitials in amorphous materials

It has been stated several times in chapter III that the concept of a DOSE and FD-Statistics is not applicable to hydrogen alone but to all small particles dissolved interstitially in a defective crystalline or an amorphous material. The term interstitially requires a new definition for an amorphous matrix and an attempt is made in section 18. As a consequence of the generalized treatment Eq. (14.3) can be used successfully for other amorphous materials, too, as shown in Fig. 25. This way the solubility of interstitials in amorphous materials can be treated in a universal way. However, in some cases the solute particles change the DOSE like H in amorphous silicon (see section 19) or alkali ions in oxidic glasses (see section 20) and Eq. (14.3) becomes inapplicable. Before these special systems are considered in more detail a general treatment of interstitial diffusion in amorphous systems is treated first.

17. MODELING DIFFUSION

During the derivation of Eq. (5.5) it had to be assumed that diffusion occurs via an uncorrelated random walk. As Eq. (5.5) has been successfully used in many cases to describe the concentration dependence of measured chemical diffusion coefficients, correlation effects are apparently not changing the concentration dependence in these cases. However, they can change the magnitude of the D-values. Correlation effects can arise in extended defects where solvent particles migrate predominantly within the defect. This can be circumvented as demonstrated for grain boundaries in section 9 by neglecting the material surrounding the defect and considering the DOSE of the defect alone. If this diffusion within the defect is rate determining the overall effective diffusion coefficient is obtained. Besides these spatial correlations there may be energetic correlations as well. It is easy to comprehend that the saddle point energy between two sites of low energy is reduced on the average when compared with the average saddle point energy. If for instance the site energy is reduced because the site volume is large, then atomic distances of the neighboring atoms are larger than the average value. Thus the corresponding distances for the saddle point configuration are large, too, which gives rise to a lower saddle point energy.

Besides attempts to obtain analytical solution [14, 65] for a distribution of saddle point energies, Monte-Carlo (MC) simulation have been conducted [14, 129, 130, 131]. The advantage of studying diffusion by MC-simulations is the freedom of choosing various kinds of DOSE and various kinds of distributions of saddle point energies (DOSPE). The dependence of the simulated tracer diffusion coefficient D^* on concentration, c , and temperature, T , is summarized in a schematic way in Fig. 26.

The following four cases are distinguished:

1) Delta function for both DOSE and DOSPE (first column in Fig. 26)

This simulates the behavior of an interstitial in an ideal single crystal. D^* does not depend upon c unless the lattice becomes filled. For $c \rightarrow 1$ ($\log c = 0$) blocking of sites and vacancy correlation effects (preferred jumps back into the site just left) leads to a decrease of D^* . The temperature dependence follows an Arrhenius Law. These dependencies are shown for comparison as dashed curves in Fig. 26 for the following cases.

2) Delta function for DOSE and Gaussian function for DOSPE (second column in Fig. 26)

For a Gaussian distribution of saddle point energies having the same average value as the constant value in case 1) the tracer diffusion coefficient is increased, because the interstitials prefer jumps over lower barriers. In two and three dimensions there will be always passes

through the lattice having a lower average activation barrier than the mean value. Thus in agreement with MC-simulations the effective activation energy is reduced. At very low temperatures and the concomitant short diffusion lengths the lowest barriers allowing a percolated walk through the lattice are preferred even more giving rise to the convex curvature in an Arrhenius diagram when viewed from the $1/T$ -axis. As there is no DOSE D^* does not depend on c unless $c \rightarrow 1$ and like in case 1) blocking and correlation effects decrease D^* .

3) Delta function for DOSPE and Gaussian function for DOSE (third column in Fig. 26)

As there is no distribution of saddle point energies in this case, there is no correlation between successive jumps and the results derived in chapter III can be used. At very low concentrations D^* is independent of c because Henry's Law is fulfilled and $\gamma^0 = \text{const}(c)$. Here the particle distribution among the sites of the DOSE is controlled by maximizing entropy and, therefore, sites above the Fermi energy are filled predominantly. Then the mean energy of the particles is given by [69]

$$\langle E \rangle = \int_{-\infty}^{\infty} \frac{E \exp[-(E - E^o)^2 / \sigma^2]}{1 + \exp[(E - \mu) / k_B T]} \approx E^o - \frac{\sigma^2}{4k_B T} > \mu \quad \text{for } c \rightarrow 0. \quad (17.1)$$

Then the activation energy is the difference between the constant saddle point energy and this average energy. Because of the temperature dependence of $\langle E \rangle$ given by Eq. (17.1) the D^* values at low concentrations exhibit a concave curvature in an Arrhenius plot when viewed from the abscissa. By increasing c the Fermi energy μ increases and finally becomes larger than $\langle E \rangle$. Then minimizing of energy controls occupancy of sites and the activation energy is the difference between the constant saddle point energy and μ . This activation barrier decreases with c as μ increases and, therefore, D^* increases with c . This increase of D^* is a consequence of FD-Statistics, because low energy sites will be saturated and high energy ones have to be occupied. This way trapping by low energy sites vanishes and the activation barrier is decreased. The c -dependence disappears, if the condition of single occupancy of a site is not taken into account during a MC-simulation. Then FD-Statistics is replaced by Boltzmann Statistics. Finally for $c \rightarrow 1$ D^* starts to decrease because of the same reasons discussed before in case 1) and 2). Increasing temperature in the intermediate concentration range does not change μ very much, despite an increasing spread between full and empty sites of the order of $k_B T$. Thus the activation energy does not depend on temperature and straight lines are obtained for the MC-results in an Arrhenius diagram.

4) Gaussian functions for both DOSE and DOSPE (fourth column in Fig. 26)

The case of having a Gaussian distribution in site and saddle point energies appears to be the one which is the most appropriate for real amorphous materials. Evaluating the MC-results of this case shows that the effects of both distributions can be superimposed according to the relation

$$D^* = f_{sp}(T) f_{st}(c, T) D^o, \quad (17.2)$$

where the various factors are obtained from the limiting cases 1), 2) and 3), i.e. $D^o = D^*$ in case 1), $f_{sp} = D^*/D^o$ calculated from the MC-data of case 2) and $f_{st} = D^*/D^o$ calculated from the MC-data of case 3). There is also theoretical support for the validity of Eq. (17.2) [65]. Thus the c -dependence of D^* in case 4) is the same as in case 3) but the values are increased by the factor $f_{sp} > 1$.

Despite the fact that both activity and diffusivity depend strongly upon c the permeation, P , being the product of both shows a minor c -dependence in defective and amorphous materials only. For the stationary flux through a film of thickness d , a permeation coefficient P is defined according to the following equation:

$$J = P \frac{\Delta a}{d} , \quad (17.3)$$

where d is the membrane thickness and Δa is the activity difference (or partial pressure difference) between entrance and exit side of the film. According to Eq. (5.13) steady state means

$$J = -D^o (1-c)^2 \frac{\Delta a}{d} . \quad (17.4)$$

Thus the permeation becomes $P=D^o(1-c)^2$ which is independent of c at dilute solution. It is astonishing to note that this result, although it is derived for a distribution of site energies, is equivalent with permeation through a matrix which contains sites of energy E^o only. This result is caused by a compensation effect, i.e. any increase or decrease of D is accompanied by a equivalent decrease or increase of the solubility and, therefore, both changes have no effect on the concentration dependence of the permeation coefficient P . An interesting example is a polymer foil which was produced with and without clusters of Pd-atoms. For both samples the permeability of hydrogen was not changed very much although the diffusivity decreased by more than two orders of magnitude within the polymer containing the palladium clusters as trapping centres [132].

18. SMALL MOLECULES IN GLASSY POLYMERS

There are a variety of different applications where the solubility and diffusivity of small molecules plays an important role like penetration of CO_2 through PET beverage bottles, permeation of oxygen through plastic foils used to wrap food, drug release through polymer coatings, diffusion of dye molecules into fibers, separation of gases by polymeric membranes etc.. If molecules are dissolved in the intermolecular space between the macromolecules of a polymer they interact mainly via Van-der-Waals or dipole-dipole forces with the matrix. Contrary to metals the matrix is in the majority of cases an amorphous one.

For polymers above the glass transition (rubbery or liquid state) the elastic constants are orders of magnitude smaller than in the glassy state and, therefore, any size misfit between the intermolecular site and the dissolved molecule is accommodated by a negligible amount of elastic stress which most probably relaxes. As a consequence the volume change per dissolved molecule or its partial molar volume, respectively is equal to the volume of the molecule (in its liquid state). Then the DOSE is represented by a Dirac delta function and for small concentrations Eq. (4.3) yields the well known relation for an ideal dilute solution

$$\mu = E^o + k_B T \ln \frac{N}{N_o} = E^o + k_B T \ln c . \quad (18.1)$$

Where N_o is the total number of sites which is usually not known because of an unknown structure (cf. the factor f in Eq. (15.1)). But N_o can be either estimated [133] or measured by positron annihilation spectroscopy [134, 135]. Expressing μ by the partial pressure of the small molecules in the gas phase via Eq. (1.5) yields the proportionality between concentration and pressure. This is in agreement with experimental findings and it is called Henry's Law because the partial pressure is equivalent to the thermodynamic activity at low pressures.

Small molecules dissolved in polymers below the glass transition temperature behave very different. First of all the partial molar volume of the small molecules is much smaller than the volume of the molecule and it increases with increasing concentration (cf. Fig. 27 and [136]). This is interpreted via a distribution of site volumes belonging to the intermolecular volume.

In accordance with the nomenclature used in polymer science the sites are called holes in the following. Because the polymer structure is frozen in below the glass transition temperature the free volume occupied by small molecules is not regenerated as in the case of rubbery or liquid polymers. For molecules having larger sizes than the holes elastic energy has to be paid during dissolution and, therefore, larger holes are filled first. Increasing the number of dissolved molecules requires filling of the smaller holes as well leading to an increasing volume change with increasing concentration. Assuming spherical shapes for both molecule and hole allows the calculation of the partial molar volume V_p in the framework of continuum mechanics [137]

$$V_p = \gamma(V_i - V_h) \quad (18.2)$$

where V_i is the volume of the interstitially dissolved small molecule and V_h the one of the hole, γ is a factor of about unity taking into account the different elastic constants of the spherical molecule and the matrix [136]. Thus the smaller V_h is the larger is V_p .

The elastic energy E_{el} associated with the incorporation of the molecule is [137]

$$E_{el} = \frac{2\mu_s (V_i - V_h)^2}{3\mathcal{W}_h}, \quad (18.3)$$

where μ_s is the shear modulus of the polymer. Thus a broad distribution of the volume of holes gives rise to a broad DOSE. The distribution of hole sizes is modeled according to Bueche [138] as a Gaussian stemming from volume fluctuations above the glass transition temperature

$$n(V_h) = \frac{1}{\sigma_V \sqrt{\pi}} \exp \left[-\frac{(V_h - V_h^o)^2}{\sigma_V^2} \right] \text{ with } \sigma_V = \sqrt{\frac{2kT_g V_h^o}{B}}, \quad (18.4)$$

where B is the bulk modulus at the glass transition temperature T_g . The original treatment by 138 is modified in as far as the temperature, T , was replaced by T_g assuming that the volume fluctuation are quenched in at the glass transition. For the simplified case of a linear expansion of the elastic energies around the average volume V_h^o the Bueche distribution leads to a Gaussian DOSE [133] with an average energy E^o and a width σ_E given by

$$E^o = E_r + E_{el}^o = E_r + \frac{2\mu_s (V_i - V_h^o)^2}{3\mathcal{W}_h^o} \text{ and } \sigma_E = \frac{2\mu_s (V_i^2 - V_h^{o2})}{3\mathcal{W}_h^{o2}} \sigma_V \text{ for } V_i \geq V_h^o, \quad (18.5)$$

where E_r is that part of the dissolution energy stemming from Van der Waals interactions. Throughout this study site energies were considered, although the formula will not change, if E is replaced by G , i.e. Gibbs free energies. Thus site entropies can be taken into account.

Experimental concentration-pressure isotherms are shown in Fig. 28 and compared with the predictions of a Gaussian DOSE. It can be shown [139] that in a double logarithmic plot the shape of the calculated isotherms is solely determined by the width σ_E whereas the second fitting parameter E^o move the curves in the direction of the abscissa. Straight lines with a slope of unity correspond to Henry's Law which is appropriate for water molecules in polycarbonate (see Fig. 28). This is a consequence of the small size of H_2O molecules being smaller than the holes in polycarbonate. No elastic energy comes into play and the DOSE degenerates to a Dirac-delta function known to lead to Henry's Law.

In text books on polymers [140, 141] the solubility is described by the dual sorption model [142, 143, 144] where the DOSE is a two-level system. It allows fitting of c-p isotherms with three free parameters yielding an agreement with experimental data which is as good as fitting with a Gaussian DOSE. However, the parameters of the dual sorption model do not have a

rigorous physical meaning and they are not related analytically to other physical quantities like the two parameters of the Gaussian distribution as represented by Eqs. (18.4) and (18.5). For a more detailed comparison of the two approaches the reader is referred to Refs. [133, 139, 136, 145]. The quantities used in Eqs. (18.4) and (18.5) are compiled in Ref. [141] or obtained as follows. For the volume of the dissolved molecule the partial molar volume in a rubbery polymer or the one in the liquid state of the small molecules was used. From a comparison of measured partial molar volumes with predicted ones the average hole volume V_h^0 is obtained. Once this value is known the volume change of other small molecules can be calculated without a fitting parameter (cf. Fig. 29).

By knowing values of V_h^0 values of the width of the Gaussian DOSE, σ_E , can be calculated via Eqs. (18.4) and (18.5). They are about 30-50% larger than the ones obtained from fitting c-p isotherms. This is considered to be good agreement in the light of the various crude assumption made during the derivation of Eq. (18.5). The functional relation are fulfilled as well as shown in Fig. 30 and 31, i.e. E^0 plotted vs. E_{el} yields a straight line of slope 1.

Plotting σ_E vs. V_i squared should give a straight line with an intercept $(V_h^0)^2$ on the abscissa. For atoms or molecules like He and H₂O the width is zero because of $V_i < V_h^0$. Very large molecules as ethene and acetone yield smaller values than predicted by the linear relation. This deviation at large V_i may arise because the assumption of an elastic incorporation of the small molecule is no longer valid. A calculation of the stresses within Eshelby's continuum approach [137] yields values which exceed the flow stress of the polymer considerably and, therefore, inelastic relaxation of macromolecules or plastic deformation, respectively will occur. In other words, the larger the molecule gets the more it is incorporated substitutionally. The analogue in a crystalline lattice would be an atom being too large for an interstices which kicks out a neighboring atom from its lattice site and becomes a substitutional solute. By generalizing these considerations a solute atom is incorporated in a material interstitially, if it is straining the matrix elastically only.

Diffusion of small molecules follows the predictions for a broad DOSE as discussed in section 6 and, therefore, the concentration dependence as obtained from measured c-p isotherms (c- μ isotherms, respectively) is in good agreement with experimental data as shown for a few examples in Fig. 32. Again, only the reference diffusion coefficient D^0 has been used as a fitting parameter which in the presentation of Fig. 32 moves the curves in the direction of the ordinate without changing their shape. The concentration dependence is the larger the larger the size of the dissolved molecule is. Fig. 32 also shows that in cases where σ_E is smaller the diffusion coefficient becomes independent of c for $c \rightarrow 0$ in agreement with the expectation for a Gaussian DOSE.

19. HYDROGEN IN AMORPHOUS SILICON AND GERMANIUM

Experiments on H and D solubility and interdiffusion of H and D in amorphous silicon and germanium were conducted by using Secondary Ion Mass Spectrometry (SIMS) [146, 147, 148, 149]. It was shown that the activation energy of diffusion decreased with increasing concentration. This was interpreted using the concept of the chemical potential and a site energy distribution as developed much earlier for metallic glasses [14]. Besides striking similarities there are remarkable differences. Most of the hydrogen atoms are bound to dangling bonds of the silicon because the amorphous semiconductor was prepared by CVD from SiH₄ at elevated temperature. H-concentration was varied by varying the preparation

temperature. This way the site energy distribution or namely its fraction belonging to dangling bonds depends upon H-concentration. This is schematically shown in Fig. 33.

As the DOSE has small values around μ any remarkable increase of the H-concentration requires a large change of μ . Thus the solubility seems to be constant or it is predetermined by the concentration of dangling bonds, respectively. Whereas in metallic glasses or glassy polymers the chemical potential increased because of a filling of a pre-existing distribution of site energies, the situation in amorphous semiconductors is different. In the latter case an increase in concentration is accompanied by changes of the distribution function leading to an increase of the chemical potential as well (cf. Fig. 33).

A peculiar behaviour can be observed, if a sample with a high content of H (or D) called sample B in the following is brought in contact with a sample of low H (or D)-content which is called sample A. The total (H+D)-concentration will not change in the two samples although interdiffusion occurs as observed from the isotope redistribution measured by SIMS depth profiling. A step in the total concentration of H+D remains at the interface. In addition the diffusivity of H (or D) is now much faster in sample A with the low H-content when compared with an experiment without a step in total concentration. This increase of H-diffusivity in sample A stems from an increase of the chemical potential as imposed by sample B (cf. Fig. 33). In order to raise μ in sample A to about the same level as in B, only a negligible amount of H has to be transferred from B to A. Then the diffusion coefficient is about the same in A and B in agreement with experiment [146, 147, 148, 149].

20. IONS IN OXIDIC GLASSES

Mixing an alkali oxide with SiO_2 leads to non-bridging oxygen atoms in the network of SiO_4 -tetrahedra [150, 151, 152]. These oxygen atoms are the centres of negative charge which are immobile far below the glass transition temperature, whereas the alkali cations are still mobile. They migrating via the holes (interstices) of the silicate network (cf. Fig. 34). Due to the strong Coulomb interaction among cations and anions the sites next to the anions have the lowest energy. Because of charge neutrality the concentration of anions and cations has to be equal, in analogy to the equivalence of dangling bonds and H-atoms in amorphous silicon. Therefore, the distribution of site energies is changing also in silicate glasses by changing the alkali concentration.

Different to the materials discussed before a decrease of the diffusion coefficient has been determined for low alkali contents [153] which was explained [69] by the "weak electrolyte" model (cf. Fig. 35). Assuming that sites next to the anions have a much lower energy compared to sites far away leads to a bimodal distribution of site energies where both fractions vary with concentration as shown in Fig. 36. With this distribution the weak electrolyte behaviour could be modelled for this solid material [69]. It is worth noting that a similar concentration dependence at low c is expected for H in amorphous silicon. The decrease of the diffusion coefficient with increasing concentration is in contradiction with the simple minded interpretation of Eq. (5.5) used so far, where an increase of μ by increasing c lowers the activation energy of diffusion. This must not be used in this context, because the DOSE changes with concentration, whereas it has been tacitly assumed in the derivation of Eq. (5.5) that it will not change. The decrease of D for cations in glasses stems from an entropy effect [69]. As the number of anion and cation pairs increases the number of "free" cations increases as well. However, the corresponding enhancement of the effective mobility is more than compensated by the increased trapping efficiency of the "naked" anions.

At high alkali contents the diffusivity increases like in the case of the other amorphous or glassy materials. Besides the interpretation given before either for amorphous metals or silicon another possible cause exists for a decrease of the activation energy and the concomitant increase of D^* . At high alkali concentrations a considerable modification of the network occurs accompanied by a decrease of the O-atom density. Thus the network becomes more open which could lower the activation energy for cation hopping. In addition it increases the mobility of neutral atoms as He, too [154]. Besides changing the mesh size of the silicate network with additions of alkali ions it can be also changed by externally applied hydrostatic pressure. The effect of pressure on cation diffusivity can be easily measured by monitoring changes of the electrical conductivity yielding the activation volume of the cation diffusion coefficient. The average changes of the mesh size or strain, respectively by external pressure can be calculated from continuum elastic theory and can be compared with the changes induced by the addition of alkali oxides [154]. Thus a quantitative treatment of mesh size effects is achieved. If we accept this mesh size effect and include the effect of a DOSE and FD-Statistics, a new and quantitative explanation of the mixed alkali effect can be offered [155, 156].

The mixed alkali effect [151, 152, 153, 155] can be observed as a decrease of ion conductivity or mobility, respectively, by several orders of magnitude when one alkali ion is substituted by another one without changing the total alkali content (cf. Figs. 37 and 38). If we assume that all the alkali ions are distributed over a broad DOSE and that the smaller ones occupy the lower levels (because they come closer to the anions), the addition of smaller cations to a glass with larger ones reduce the mobility of the small ones as they are placed in the lowest energy levels. The mobility of the larger cations is reduced as well, because the mesh size of the network is reduced according to an average reduction of the mean cation size. This behavior can be treated quantitatively, too, yielding agreement with experimental data by fitting one free parameter, the width of the distribution, only [155, 156].

VII. Hydrogen in systems with reduced dimensions

The behavior of hydrogen in samples with reduced dimensions is one of the more recent areas of research in metal-hydrogen systems [20, 158, 159, 160, 161, 162, 163, 164, 165, 166, 167, 168, 169, 170]. The properties of these systems are affected by the proximity of surfaces or interfaces providing additional sites to the DOSE. In this case the surface of the sample or its interface with a different material is just a source of new sites and reduction of dimensions leads to an increasing fraction of the new sites. Thus the interaction of hydrogen with free surfaces falls in the same category (cf. section 9). In addition stresses and strains play an increasing role. On a free surface the normal component of the stress is zero and this boundary condition is important for hydride formation in the elastic regime [171, 158]. Inelastic processes like dislocation emission are also affected by free surfaces as they act as sinks for defects. Reduced dimension inhibit dislocation generation and motion [172] and, therefore, hinder that mechanism of hydride formation which requires dislocation emission. Samples adhering to a substrate or being embedded in a matrix are subject to boundary conditions with respect to their strain at the interface. Again the related stresses may not relax as easy as in the extended bulk sample. It has also been discussed (cf. section 22) whether the proximity of a different material changes the electronic structure in the neighborhood of an interface [159].

21. THIN FILMS

First measurements of hydrogen dissolved in thin films were conducted by H. Zabel et al. [160]. They determined the lattice expansion of niobium films in a hydrogen gas atmosphere of varying partial pressure. As the Nb-film was adhering to a substrate, no expansion in plane can occur and compressive stresses develop. During the dissolution of hydrogen expansion out of plane takes place and it is accompanied by the Poisson effect, i.e. additional expansion due to the increasing compressive stresses. By using H-concentrations from bulk pc-isotherms the lattice expansion per H-atom was found to be much larger than in bulk niobium [160]. However, it was shown later on [166] that the lattice expansion per H-atom was the same as in bulk niobium and the larger values obtained in Ref. [160] were most probably due to less reliable H-concentration values obtained from the isotherms. Strains and stresses developing in thin Nb-films as a function of H-concentration are presented in Figs. 39 and 40.

Within the α -phase of Nb and Pd the out of plane expansion of thin films follows the laws of continuum mechanics. However, the associated compressive stresses are smaller by 10 to 30% when compared with calculated values [166]. This discrepancy may be attributed to some stress relaxation. A much more pronounced stress relaxation takes place when the terminal solubility of the α -phase is reached and a hydride or a high concentration phase is formed. Then the in-plane distance of lattice planes is changing, too. In some cases the pronounced stress relaxation occurs within the α -phase, i.e. before the terminal solubility is reached, because the compressive stresses simply exceed the yield strength of the thin metal film. The terminal solubility increases as the film thickness decreases which may be caused by a lowering of the critical temperature in finite dimensions or a kinetic barrier for the necessary volume expansion.

The plot of stress vs. H-concentration as shown in Fig. 40 may be interpreted as a stress-strain curve, where the strain is internally imposed by H-atoms instead by an external machine. Therefore, similar features known from the deformation of bulk metals can be observed, i.e. single crystalline Nb-films have a much lower yield strength and a lower work hardening rate

than polycrystalline films. After removal of the hydrogen a dislocation network remains in the film and at the subsequent second loading with hydrogen yield strength and work hardening are increased (cf. Figs. 41 to 43).

Recently thin Y-films have attracted considerable interest [173, 174, 175, 176], because a metal/insulator transition occurs between $H/Y=2$ and $H/Y=3$, i.e. between the di- and trihydride. This transition can be used to build a switchable mirror, if the Y-film is deposited on a transparent substrate. The Y-H system is also peculiar with respect to volume changes. Besides the usual lattice expansion which is observed for $H/Y<2$ a contraction occurs with increasing H-concentration followed by an expansion again. The corresponding tensional and compressive stresses cancel mostly and, therefore, the switching between di- and trihydride is not accompanied by large changes of film stresses [177]. Thus a large number of transitions between a reflecting and a transparent mirror are possible without failure of the device.

If the adhesion between film and substrate is weak, the films start to delaminate from the substrate during hydrogen loading. This has been observed for Nb-films on mica [178] and Pd-films on polycarbonate [179].

22. MULTI LAYERS

With the increasing interest in multilayers, the behavior of hydrogen in these systems has also attracted intensive research. In their pioneering work, Miceli, Zabel, and Cunningham [13, 180] describe critical phenomena in Nb/Ta super-lattices. Hjörvarsson and co-workers [159] emphasized the effect of electron transfer at Mo/V interfaces on the hydrogen solubility in V layers. The influence of hydrogen on the magnetism of Fe/Nb and Fe/Ce multilayers was investigated by Weidinger et al. [162] and Felsch et al. [181]. Actual measurements on strain relaxation and phase separation in Pd/Nb multilayers are presented in Ref. [165]. Transport of hydrogen through thin metallic films is essential for the development of coatings preventing bulk materials from hydrogen uptake. The influence of thin films of Pd, Ni, and Cu on the hydrogen permeation through Fe was investigated by Song and Pyun [182] and Takano et al. [183]. Furthermore, to avoid oxidation and to enable hydrogen charging, thin films are often covered with an additional Pd surface, such that the specimens are multilayered structures (substrate, film, and Pd layer). The influence of Pd coatings on the hydrogen permeation was investigated by Züchner [184]. In the case of thin metallic films prepared on substrates, the hydrogen permeation through the substrate, as well as the influence of the interface and the property of the film has to be taken into account. Assuming defect-free layers, far away from the interfaces, the hydrogen transport should be well described by the known diffusion behavior of the bulk elements. However, deviations from the ideal bulk diffusion can be expected at the interfaces, where possibly high densities of lattice defects, localized misfit strains, or different hydrogen solubility are present. Therefore, it is most important to understand whether the hydrogen transport through a layered specimen is correctly modeled by a layered structure with bulk materials of different hydrogen solubilities or by taking into account additional interface sites of different site energies.

The permeation method, i.e., loading the sample at one side with hydrogen and determining the time dependence of the concentration change at the opposite side, can be used to measure hydrogen diffusivity through multilayers. Depending on the experimental conditions of hydrogen loading, the concentration change at the opposite side appears with a certain time lag [184]. In a single layer the time dependence of the concentration change can be solved

analytically for various boundary conditions [185], whereas in composite systems only the characteristic time lag to reach the steady state has been modeled so far.

Often four different boundary conditions are applied in steady-state permeation experiments: (A) constant current density at the input and output surface, (B) constant concentration at the input and output surface, (C) constant current density at the input and constant concentration at the output surface, and (D) constant concentration at the input and constant current density at the output surface. In their theoretical treatment of diffusion through multi-layers, Ash and co-workers [186, 187] derived the time lag for the permeation using boundary condition B with vanishing concentration at the output side. Their result was applied to interpret hydrogen diffusion in metallic bilayers and triple layers by Züchner [184] and Takano et al. [183] Song and Pyun [182] modified the hydrogen loading conditions by using a constant hydrogen current density at the input side (condition C) and derived the corresponding time lag for a bilayer system. In a recent paper by G. Schmitz et al. [188] solutions for the conditions A and C were provided for the most general case of multilayers including the substrate as one of the layers. For a substrate of thickness s with $2N$ alternating layers of two metals of the thickness a the time lag t_L is for $N \gg 1$:

$$t_L = 3 \frac{s^2}{6D_s} + \frac{1}{6} \frac{N^2 a^2}{kD_1} + \frac{N^2 a^2}{6D_1} + \frac{N^2 a^2}{6D_2}, \quad (22.1)$$

where k is the ratio of H-solubilities in both metals 1 and 2 for the same H_2 partial pressure chosen in a way that $k < 1$ and D are the corresponding diffusion coefficients. The first term on the right hand side of Eq. (22.1) is three times the time lag of the isolated substrate and the third and fourth term are the time lags of the isolated layers of either metal 1 or 2. For nanostructured multilayers on a thick substrate usually $Na \ll s$ applies and the last equation simplifies to

$$t_L = 3 \frac{s^2}{6D_s} + \frac{1}{6} \frac{N^2 a^2}{kD_1} \quad (22.2)$$

The second term on the right hand side of the last equation cannot be neglected because k may be very small. The term can be also used to define an effective diffusion coefficient $D_{eff} = (2Na)^2 / 6t_L = 4kD_1$ for the multilayers. For a different thickness of the two metals the effective diffusion coefficient for a multilayer can be written independently of the boundary conditions as [186, 187, 188, 189]

$$D_{eff} = kv_1v_2D_1 \quad (22.3)$$

where v_1 and v_2 are the volume fractions of metal 1 and metal 2.

In order to comprehend the physics behind Eq. (22.3), the potential trace a migrating H-atom will experience is shown in Fig. 44 for the case of Pd=metal 1 and Nb=metal 2. The site energies E_{Pd} and E_{Nb} correspond to the energies of hydrogen dissolution in Nb and Pd. In agreement with the definition of $k = \exp[(E_{Nb} - E_{Pd})/kT] < 1$ the experimental values correspond to $E_{Pd} > E_{Nb}$.

At room temperature k is as small as about 10^{-4} for Nb/Pd [188] and, therefore, the effective diffusion coefficient is decreased by four orders of magnitude which are in agreement with experimental findings [188]. It is obvious from looking at Fig. 44 that the Nb-layers provide traps for the hydrogen diffusing in Pd whereas Pd-layers act as barriers for H in Nb.

Experimental results of time lag measurements of Pd/Nb-multilayers [188] are shown in Fig. 45 as a function of the partial hydrogen concentration in Nb or Pd, respectively. Due to the lower Gibbs free energy of H dissolution in Nb nearly all of the hydrogen is dissolved in the Nb-layers [36]. The total thickness of the layers was about $0.2 \mu m$ and they were produced on

a Pd substrate of 12.5 μm thickness. With the solubility ratio k in Pd/Nb of about 10^{-4} and a room temperature diffusivity of $3.5 \cdot 10^{-7} \text{ cm}^2/\text{s}$ in Pd the time-lag is calculated to be 0.75 s for the pure substrate and 14 s for the substrate plus multilayers. For H-concentrations of $0.01 < c < 0.04$ experimental data are of the same order of magnitude as this estimated value. Unfortunately, the comparison is approximate only because scatter of data on Gibbs free energy of solution yield data on k which scatter by more than one order of magnitude [188]. It is interesting to note that the high diffusivity of H in Nb with $D = 8 \cdot 10^{-6} \text{ cm}^2/\text{s}$ does not play a role and that despite that value being higher than in Pd the Nb-layers retard the overall transport of H. At very low H-concentrations of $c < 0.01$ or for the smallest double layer thickness the interaction with defects or with the interphase Pd/Nb-boundaries may increase the time lag, i.e. the effective diffusivity.

At a few at.-% of H in Nb the terminating solubility at room temperature is reached and the Nb-layers contain two phases, a solid solution of H in Nb and a hydride phase. Then the time lag can no longer be calculated by Eq. (22.2) which was derived for the single phase case. Experimental values in Fig. 45 show that t_L is reduced in the two phase region. Increasing the total hydrogen content further leads to a total conversion of the Nb-layers into hydride layers, where the k -values are higher because of the higher Gibbs free energies of solution in saturated Nb-hydride. Then the second term on the right hand side of Eq. (22.2) becomes negligible compared to the first one and the time lag reduces to the value of the pure Pd-substrate (0.75 s).

For the Ni/Pd system [190] the Gibbs free energies of H-solution are such that H is enriched in the Pd-layers according to k -values of about 10^{-4} [36] and the diffusion coefficient of H in Ni is $5 \cdot 10^{-10} \text{ cm}^2/\text{s}$ [83]. Inserting these values in Eq. (22.2) yields time lags of the order of thousands of seconds. However, experimental values [190] are about the same as the time lag of the Pd-substrate, i.e. the Ni-layers do not act as barriers for H-diffusion. This discrepancy between experimental findings and theory is overcome by assuming that grain boundary diffusion in the Ni-layers is relevant. The Ni-layers of the samples used were polycrystalline and the concept described in Ref. [188] has to be modified by using an effective diffusion coefficient $D_{gb}\delta/d$, where D_{gb} is the diffusion coefficient of H in grain boundaries of Ni, δ is the thickness of these boundaries and d is the diameter of the grains (about the same as the Ni-layer thickness). The ratio k has to be multiplied by a segregation factor S defined as the ratio of H-concentrations in grain boundaries and grains. Experimental values of S and D_{gb} [83] are so large for the H-concentrations used in the experiment that the second term in Eq. (22.2) is smaller than the first one and in agreement with experimental findings the effective diffusion coefficient is not affected by the presence of the Ni/Pd-layers.

Similar considerations should apply for the case of Pd/Nb-layers where the Pd barrier layers were nanocrystalline, too. However, in this case the product $SD_{gb}\delta/d$ is smaller than the corresponding value of D for the grains. At the H-concentrations expected in the experiments this is mainly caused by a lower diffusivity of H in grain boundaries of Pd when compared with the grains (see chapter IV).

The interface boundaries between different metals produced by either sputtering or electron evaporation are not atomically sharp but an intermixing zone of about 1 nm thickness has been detected by analyzing the multilayers with a tomographic atom probe [191]. This intermixing zone decreases the width of both adjacent layers and it does not absorb hydrogen at a given partial pressure [192], i.e. it acts as a dead layer. This way a different explanation is

offered for the dead layers observed in Refs. [159, 193], where a transport of electrons across the interface was assumed to be responsible for the dead layer.

23. CLUSTERS

In order to study the solubility of hydrogen in metal clusters, a large number of clusters are necessary for the commonly applied techniques. However, clusters tend to agglomerate because of the large cohesion energy of metals. This tendency of forming a polycrystalline metal rather than remaining as isolated clusters is circumvented by stabilizing cluster with a surfactant shell, embedding them in a solid matrix or depositing them on a substrate. Again the Pd-H system is the one first chosen by experimentalists as the nobility of the metal excludes the formation of an oxide layer which otherwise would be an appreciable fraction of the sample. First measurements of pc-isotherms were conducted by Flanagan et al. [194] with Pd-black having a surface area of about $40 \text{ m}^2/\text{g}$ which corresponds to a diameter of about 12 nm. Although changes are small when compared to bulk Pd, a narrowing of the miscibility gap was observed. Griessen et al. [195] observed a much more pronounced narrowing for Pd clusters deposited on an aluminum oxide substrate. However, in this case stresses will develop during hydrogen loading like in thin films and, therefore, the pc-isotherms will be affected by these stresses. The interaction of hydrogen with free palladium clusters of 2 to 6 nm diameter which were stabilized by a surfactant shell has been described in detail in recent studies [164, 168, 169]. The results are summarized as follows.

The preparation of small Pd-clusters is achieved by electrochemical dissolution of Pd and its reduction on a counter electrode to neutral Pd-atoms. If a non-aqueous electrolyte such as tetrahydrofuron with surfactant molecules like octylammonium bromide is used the Pd-atoms agglomerate to clusters which are stabilized by the surfactant [170, 196]. At a certain concentration of clusters they precipitate as a black powder. The diameter of the clusters and the width of its distribution can be varied by changing temperature, electrode distance and current density. Thus clusters are produced with a rather narrow size distribution, i.e. with a variance of the diameter being 10 to 15% of the average diameter.

Detailed investigations of the atomic structure of these cluster by using molecular dynamic simulations, high resolution transmission electron microscopy and X-ray diffraction revealed that they have an icosahedral structure for sizes below 4 nm whereas the larger ones have an fcc structure. All the clusters absorb hydrogen from the gas phase which can be easily shown by monitoring the weight change in a hydrogen atmosphere. However, before hydrogen is reacting with palladium it forms water with oxygen being absorbed on the surface of the clusters. Pumping off the water and the residual hydrogen in the vacuum chamber leads to oxygen and hydrogen free Pd-clusters. After this pre-treatment the clusters can be exposed to hydrogen with a given partial pressure and the absorbed amount is obtained from weight changes or from pressure drops. In the latter case the valves to the pumps and to the hydrogen inlet have to be closed. The absorption is completed in between a few minutes and a few hours. This way pressure composition isotherms are obtained. Some of them are shown in Fig. 46.

At about the same pressure where bulk-Pd decomposes in α - and β -Pd the clusters exhibit a sloped plateau. However, the maximum concentration in the α -phase is larger and the minimum one in the β -phase is smaller, i.e. the width of the miscibility gap is reduced and the reduction is the larger the smaller the clusters are. The increased terminal solubility in the α -phase can be explained by subsurface sites having lower site energies than bulk sites [168]. This is analogous to segregation in grain boundary sites. The surface sites were most probably

occupied during the pre-treatment step where the oxygen was removed with hydrogen. Because of the large binding energies of the order of 100 kJ/mol-H [197] this hydrogen will not be removed at room temperature and high vacuum conditions.

Within the miscibility gap there is a hysteresis between absorption and desorption [168, 170] in analogy with bulk behaviour. However, the hysteresis cannot be explained by the work required to punch out dislocations around the new phases formed [198], because the clusters are too small to allow the formation of dislocations. Thus a coherent phase transformation takes place which leads to a hysteresis as well [199, 200].

Additional evidence for a phase separation in small Pd clusters is provided by X-ray diffraction, where at partial pressure of hydrogen belonging to the plateau region X-ray peaks split into two (cf. Fig. 47). With increasing H-concentration the peaks shift to smaller angles indicating a volume expansion as in bulk Pd. Calculating lattice parameters from the peak positions and plotting them versus the hydrogen pressure yields the results shown in Fig. 48. Within the region of the sloped plateau there is a pronounced change of the lattice parameter according to the transition from the low to the high concentration phase of the Pd-H system. The overall change of the lattice parameter across the miscibility gap decreases with decreasing cluster size in accordance with the corresponding decrease of the width of the miscibility gap.

The change per H-atom is about the same as in bulk Pd. As the changes of the lattice parameter scales with the H-concentration there is also a hysteresis of the lattice parameter between absorption and desorption within the miscibility gap. The hysteresis is not a matter of sluggish kinetics because it is not observed within the one-phase region. Thus the hysteresis is an additional piece of evidence for a phase separation in the Pd-clusters besides the sloped plateau of the pc-isotherms discussed before. Whether a cluster itself contains two phases in coexistence or whether a cluster is either α - or β -phase throughout its volume remains an open question. A piece of evidence for the first case is provided by the hysteresis. If it is caused by the coherent phase transformation as discussed in Refs. [199, 200], high and low concentration phase have to be present in the same cluster. These and other problems are subject of ongoing research, where namely MD-simulation may become a suitable tool to answer part of the remaining questions. Some of the attraction of the cluster research actually stems from the possibility of conducting MD-simulations with “samples” of the same size as one used by the experimentalist.

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References

- [1] International Symposium on Metal-Hydrogen Systems, Fundamentals and Applications, Stuttgart, SEPT 04-09, 1988, R. Oldenburg Verlag, München (1989)
- [2] International Symposium on Metal Hydrogen Systems: Fundamentals and Applications, AUG 25-30, 1996, *J. Alloy Comp.* **253** (1997)
- [3] International Symposium on Metal-Hydrogen Systems, Fundamentals and Applications, OCT 04-09, 1998 *J. Alloy Comp.* **295** (1999)
- [4] International Symposium on Metal-Hydrogen Systems, Fundamentals and Applications (MH2000), OCT 01-06, 2000, *J. Alloy Comp.* **330** (2002)
- [5] L. Schlapbach and A. Züttel, *Nature* **414**, 353 (2001)
- [6] "Hydrogen Effects on Materials Behavior", editors: N.R. Moody and A.W. Thompson, TMS, Warrendale, Pennsylvania, USA (1990)
- [7] Thompson, A.W. and Moody, N.R., „Hydrogen Effects in Materials“ (TMS, Warrendale, PA, (1994)
- [8] International Conference on Hydrogen Effects on Materials Behavior and Corrosion Deformation Interaction, Jackson Lake Lodge, Moran, WY, SEPT 22-26 (2002) to be published
- [9] J.R. Lacher, Proc. Roy. Soc. (London) **A161**, 525 (1937)
- [10] C.P. Flynn and A.M. Stopneham *Phys. Rev.* **B1**, 3966 (1970)
- [11] J. Völkl and G. Alefeld in "Diffusion in Solids", ed. by A.S. Nowick, J.J. Burton, Academic, New York (1979)
- [12] H.K. Birnbaum and C.P. Flynn *Phys. Rev. Lett.* **37**, 25 (1976)
- [13] P.F. Miceli, H. Zabel, and J.E. Cunningham, *Phys. Rev. Lett.* **54**, 917 (1985)
- [14] R. Kirchheim, *Progr. Mat. Sci.* **32**, 262 (1988)
- [15] R. Kirchheim, Encyclopedia of Materials Science, Suppl. Vol. 2, ed. R.W. Cahn, Pergamon Press, Oxford 990 (1990)
- [16] T.B. Flanagan, R. Balasubramaniam and R. Kirchheim, *Platinum Metals Review* **45**, 114 and 166 (2001)
- [17] D.K. Ross in "Hydrogen in Metals III", ed. by H. Wipf, Topics in Applied Physics, Vol. 73, Springer, Berlin, 153 (1997)
- [18] D. Nagengast, C. Rehm, F. Klose, A. Weidinger A, *J. Alloy Comp.* **253**, 347 (1997)
- [19] V. Leiner, K. Westerholt, A.M. Blixt, H. Zabel, B. Hjorvarsson, *Phys. Rev. Lett.* **91**, 037202 (2003)
- [20] J.N. Huiberts, R. Griessen, J.H. Rector, R.J. Wijnaarden, J.P. Dekker, D.G. deGroot, N.J. Koeman, *Nature* **380**, 231 (1996)
- [21] Y. Fukai and N. Okuma, *Phys. Rev. Lett.* **73**, 1640 (1994)
- [22] H. Wenzl and T. Schober in Ref. [31] p. 11
- [23] H.C. Jamieson, G.C. Weatherly and F.D. Manchester, *J. Less Comm. Met.*, **50**, 85 (1976)
- [24] T. Flanagan and J. Lynch, *J. Less-Common Metals* **49**, 25 (1976)
- [25] H. Noh and J.D. Clewley and T.B. Flanagan, *Scripta Mat.* **34**, 665 (1996)
- [26] R. Lüke, G. Schmitz, T.B. Flanagan and R. Kirchheim, *J. Alloy Comp.* **330-332**, 219 (2002)
- [27] J. Nakahigashi and H. Yoshimura, *J. Alloy Comp.* **330-332**, 384 (2002)
- [28] D. Eliezer, N. Eliaz, O.N. Senkov, F.H. Froes, *Mat. Sci. Eng. A-struc.* **280**, 220 (2000)
- [29] S.M. Myers, M.I. Baskes, H.K. Birnbaum, J.W. Corbett, G.G. Deleo, S.K. Estreicher, E.E. Haller, P. Jena, N.M. Johnson, R. Kirchheim, S.J. Pearton and M.J. Stavola, *Reviews of Modern Physics* **64**, 559 (1992)
- [30] J. Völkl and G. Alefeld, „Hydrogen in metals I“ (Springer, Berlin, 1978)
- [31] J. Völkl and G. Alefeld, „Hydrogen in metals II“ (Springer, Berlin, 1978)

- [32] Y. Fukai, "The metal-hydrogen system" (Springer, Berlin) 1993
- [33] H. Wipf, "Hydrogen in Metals III" (Springer, Berlin, 1997)
- [34] H.D. Carstanjen, *phys. status sol. (a)* **59** (1980)
- [35] Lange's Handbook of Chemistry, 15th Edition, by J.A. Dean, McGraw Hills Handbooks, p. 6.93 (1999)
- [36] E. Fromm and E. Gebhardt "Gase und Kohlenstoff in Metallen" (Springer, Berlin, 1976)
- [37] A.C. Switendick in Ref. [30], p. 101
- [38] Th. Heumann, "Diffusion in Metallen", (Springer, Berlin, London, New York, 1992)
- [39] K. Nakazato and K. Kitahara, *Prog. Theor. Phys.* **64**, 2261 (1980)
- [40] P.G. Shewmon, "Diffusion in Solids" McGraw Hill, New York (1963)
- [41] H. Boes and H. Züchner, *Z. Naturforsch.*, **31a**, 754 and 760 (1976)
- [42] R. Kirchheim and R.B. McLellan, *J. Electrochem. Soc.* **127**, 2419 (1980)
- [43] M.A.V. Devanathan and Z. Stachurski, *Proc. Roy. Soc. A* **270**, 90 (1962)
- [44] H. Züchner, *Z. Naturforsch.*, **25a**, 1490 (1970)
- [45] A.S. Nowick and B.S. Berry "Anelastic Relaxation in Crystalline Solids" (Academic Press, New York, 1972)
- [46] B.S. Berry and W.C. Pritchett, *Scripta Metall.*, **15**, 637 (1981)
- [47] U. Stolz, *J. Phys. F Met. Phys.* **17**, 1833 (1987)
- [48] H. Mitzubayashi, Y. Katoh and S. Okuda, *phys. stat. sol. (a)* **104**, 469 (1988)
- [49] H. Mitzubayashi, S. Murayama and H. Tanimoto, *J. Alloys Comp.* **330-332**, 389 (2002)
- [50] A. Cannelli, R. Cantelli and F. Cordero, *J. Phys. F Met. Phys.* **16**, 1153 (1986)
- [51] H. Peisl in Ref. [30], p. 53
- [52] B. Baranowski, S. Majchrzak and T. B. Flanagan, *J. Phys. F*, **1**, 258 (1971)
- [53] R. Kirchheim, *Acta metall.* **34**, 34 (1986)
- [54] U. Stolz, U. Nagorny and R. Kirchheim, *Scripta metall.*, **18**, 347 (1984)
- [55] J. C. M. Li, R. A. Oriani and L. S. Darken, *Z. Phys. Chem.*, **49**, 271 (1966)
- [56] R. Kirchheim and J. P. Hirth, *Acta metall.*, **35**, 2899 (1987)
- [57] H. Inui, T. Yamamoto, H. Hirota and M. Yamaguchi, *J. Alloys Comp.* **330-332**, 117 (2002)
- [58] E. Wu, E. MacA. Gray and Cookson, *J. Alloys Comp.* **330-332**, 229 (2002)
- [59] S. Orimo, H. Fujii and K. Ikeda, *Acta mater.* **45**, 116 (1996)
- [60] R.A. Oriani *Acta metall.* **18**, 147 (1970)
- [61] S. Gahr and H.K. Birnbaum, *Acta metall.*, **26**, 1781 (1978) and D.S. Shih, I.M. Robertson, H.K. Birnbaum, *Acta metall.*, **36**, 111 (1988)
- [62] T.L. Hill, "Introduction to Statistical Thermodynamics" p. 432 (Addison-Wesley, London, 1962)
- [63] D. N. Beshers, *Acta metall.*, **6**, 521 (1958)
- [64] N. Louat, *Proc. Phys. Soc., London*, **B69**, 459 (1956)
- [65] T. Wichmann, K.G. Wang and K.W. Kehr, *J. Phys.* **A27**, L263 (1994)
- [66] J. Gegner, G. Hörz and R. Kirchheim, in Ref. [7] p. 35
- [67] Ch. Kittel, „Introduction to Solid State Physics“ (John Wiley & Sons, New York, 3rd Edition, 1967) p. 204
- [68] R. Kirchheim, *Acta metall.* **30**, 1069 (1982)
- [69] R. Kirchheim and U. Stolz, *J. Non-Cryst. Solids* **70**, 323 (1985)
- [70] R. Griessen, *Phys. Rev. B* **27**, 7575 (1983)
- [71] P. Vargas and H. Kronmüller, *Z. Phys. Chem. N.F.*, **143**, 229 (1985)
- [72] J. P. Hirth and J. Lothe, „Dislocations in Solids“ (McGraw Hill, New York, 1968)
- [73] R. Kirchheim, *Acta metall.* **29**, 835 and 845 (1981)
- [74] A. J. Kummnick H. H. and Johnson, *Acta metall.* **28**, 33 (1980)
- [75] E. Wicke and J. Blaurock, *Ber. Bunsenges. Phys. Chem.* **85**, 1091 (1980)
- [76] J.A. Rodrigues and R. Kirchheim, *Scripta metall.* **17** 159 (1983)

- [77] R. Kirchheim, A. Szökefalvi-Nagy, U. Solz and A. Speitling, *Scripta metall.* **19**, 843 (1985)
- [78] M. Maxelon, A. Pundt, W. Pyckhout-Hintzen, J. Barker and R. Kirchheim, *Acta mater.*, **49** 2625 (2001)
- [79] B. J. Heuser, J. S. King, G. S. Summerfield, F. Boué, J. E. Epperson, *Acta metall. mater.*, **39**, 2815 (1991) and B.J. Heuser and J. S. King, *J. Alloys Comp.* **261** 225 (1997)
- [80] D. K. Ross, K. L. Stefanopoulos, *Z. Phys. Chem.*, **183**, 29 (1994)
- [81] T. Mütschele and R. Kirchheim, *Scripta metall.* **21**, 135 (1987)
- [82] J. Weismüller and C. Lemier, *Phys. Rev. Lett.* **82**, 213 (1999)
- [83] D. R. Arantes, X. Y. Huang, C. Marte and R. Kirchheim, *Acta metall. et mater.* **41**, 3215 (1993)
- [84] R. Kirchheim, I. Kownacka and S.M. Filipek, *Scripta metall. et mater.* **28**, 1229 (1993)
- [85] I. Kaur and W. Gust, "Fundamentals of Grain and Interphase Boundary Diffusion" (2nd edition, Ziegler Press, Stuttgart, 1989), p. 77 ff
- [86] A.P. Sutton and R.W. Balluffi, "Interfaces in Crystalline Materials"; (Oxford, 1995), p. 510
- [87] J.A. Eastman, L.J. Thompson and B.J. Kestel, *Phys. Rev.* **B48**, 84 (1993)
- [88] T. Mütschele and R. Kirchheim, *Scripta metall.* **21**, 1101 (1987)
- [89] J. Gegner, G. Hörz and R. Kirchheim, *Interface Science*, **5**, 231 (1997)
- [90] X. Y. Huang, W. Mader and R. Kirchheim, *Acta metall. mater.* **39**, 894 (1991)
- [91] X. Y. Huang, W. Mader, J. A. Eastman and R. Kirchheim, *Scripta metall.* **22**, 1109 (1988)
- [92] B.G. Pound in Ref [7] p. 115
- [93] W. Mader and G. Necker, in "Metal-Ceramic-Interfaces" (ed. M. Rühle, A.G. Evans, M.F. Ashby and J.P. Hirth, *Acta-Scripta Metallurgica Proc. Series*, Vol. 4, Pergamon Press, Oxford, 1990) p. 222
- [94] H. Jang and D. N. Seidman, *Interface Science* **1**, 61 (1993)
- [95] G. Necker and W. Mader, *Phil. Mag. Letters* **58**, 205 (1988)
- [96] H. Jang, D. N. Seidman and K. L. Merkle, *Scripta metall. mater.* **26**, 1493 (1992)
- [97] M. Backhaus-Ricoult and S. Laurent, *Mat. Sci. For.* **294-296**, 325 (1999)
- [98] E. Pippel, J. Woltersdorf, J. Gegner and R. Kirchheim, *Acta mater.* **48**, 2571 (2000)
- [99] C. Kluthe, T. Al-Kassab and R. Kirchheim, *Mater. Sci. Eng.* **A327**, 70-75 (2002)
- [100] R. Kirchheim, A. Pundt, T. Al-Kassab, F. Wang, C. Kluthe, *Z. Metallkd.*, **94**, 266 (2003)
- [101] C. Kluthe, T. Al-Kassab, J. Barker, W. Pyckhout-Hintzen and R. Kirchheim, submitted to *Acta mater.*
- [102] J.W. Gibbs, *Collected works*, Vol. I, Yale University Press, New Haven (1948), pp. 219 ff
- [103] C. Wagner, *Nachrichten der Akademie der Wissenschaften in Göttingen, II. Mathematisch-Physikalische Klasse* **Nr. 3**, 1 (1973)
- [104] R. Kirchheim, *Acta mater.* **50** 413 (2002)
- [105] P. Haasen, "Physical Metallurgy (Springer, Berlin 1994)
- [106] T. Kuji, T. Flanagan, Y. Sakamoto and M. Hasaki, *Scripta metall.*, **19**, 1369 (1985)
- [107] R. Kirchheim and J.P. Hirth, *Scripta metall.* **16**, 475 (1982)
- [108] J. P. Hirth and J. R. Rice, *Metall. Trans. A* **11**, 1502 (1980)
- [109] H.K. Birnbaum, *MRS Bull.* **28**, 479 (2003)
- [110] H.K. Birnbaum and P. Sofronis, *Mat. Sci. Eng. A* **176**, 191 (1994)
- [111] in Ref. [33] p. 215
- [112] C. Wagner, *Acta Metall.*, **21**, 1297 (1973)
- [113] R. Feenstra, R. Brower, R. Griessen, *Europhys. Lett.* **7**, 425 (1988)
- [114] R.S. Finocchiaro, C. L. Tsai and B. C. Giesen, *J. Non-Cryst. Solids*, **61+62**, 661 (1984)

- [115] A. Szökefalvi-Nagy, S. Filipek and R. Kirchheim, *J. Phys. Chem. of Solids* **48** 613 (1987)
- [116] D. Richter, G. Driesen, R. Hempelmann and I.S. Anderson, *Phys. Rev. Lett.*, **57**, 731 (1986)
- [117] P. M. Richards, *Phys. Rev.* **B27**, 2095 (1983)
- [118] M. Hirscher and H. Kronmüller *J. Less-Common Met.* **17**, 658 (1991)
- [119] Y. S. Lee and D. A. Stevenson, *J. Non-Cryst. Solids*, **72**, 249 (1985)
- [120] F. Jaggy, W. Kieninger and R. Kirchheim, *Z. Phys. Chem. N.F.* **163**, 431 (1989)
- [121] J. H. Harris, W. A. Curtin and M. A. Tenhover, *Phys. Rev.* **B36**, 5784 (1987)
- [122] S. Orimo, K. Ikeda, H. Fujii, S. Saruki and T. Fukunaga, *J. Jap. I. Met.*, **63** 959 (1999)
- [123] W. L. Johnson, *JOM-J. Min. Met. Mat.*, **54** 40 (2002)
- [124] A. Inoue and T. Zhang and T. Masumoto, *Mater. Trans.*, **JIM 31**, 425 (1990)
- [125] D. Zander, U. Köster, N. Eliaz and D. Eliezer, *Mat. Sci. Eng.* **294-296**, 112 (2000)
- [126] D. Suh and R.H. Dauskardt, *Met. Trans.*, **42**, 638 (2001)
- [127] N. Ismail, M. Uhlemann, A. Gebert and J. Eckert, *J. alloys comp.*, **198**, 146 (2000)
- [128] J. Bankmann, PhD-thesis, University of Göttingen (2003)
- [129] R. Kirchheim and U. Stolz, *Acta metall.* **35**, 281 (1987)
- [130] A.F. McDowell and R.M. Cotts, *Z. Phys. Chem. NF*, **183**, 65 (1994)
- [131] M. Hirscher, J. Mossinger and H. Kronmüller, *J. Alloys Comp.*, **231**, 267 (1995)
- [132] D. Fritsch and K.-V. Peinemann, *Catalysis Today*, **25**, 277 (1995)
- [133] R. Kirchheim, *Macromolecules*, **25**, 6952 (1992)
- [134] J. Bohlen, J. Wolff and R. Kirchheim, *Macromolecules*, **32**, 3766 (1999)
- [135] J. Bohlen and R. Kirchheim, *Macromolecules*, **34**, 4210 (2001)
- [136] P. Gotthardt, A. Grüger, H.G. Brion, R. Plaetschke and R. Kirchheim, *Macromolecules*, **30**, 8058 (1997)
- [137] J.D. Eshelby, *Solid State Physics*, eds. F. Seitz und D. Turnbull, Academic, New York (1956)
- [138] F. J. Bueche, *J. Chem. Phys.* **1953**, *21*, 1850
- [139] A. Grüger, P. Gotthardt, M. Pönitsch, H.G. Brion and R. Kirchheim, *J. Polym. Sci.: Polym. Phys.* **36**, 483 (1998)
- [140] H. Batzer, "Polymere Werkstoffe" (Georg Thieme Verlag, Stuttgart, 1985)
- [141] D.W Van Krevelen and P.J. Hoftyzer, *Properties of Polymers*, 2nd Ed. (Chap. 4, Elsevier, New York 1980)
- [142] R. M. Barrer, J. A. Barrie and J. Slater, *J. Polym. Sci.*, **23**, 315 (1957)
- [143] A. S. Michaels,; W. R. Vieth; W. R. Barrie, *J. Appl. Phys.*, **34**, 13 (1963)
- [144] D. R. Paul, *Ber. Bunsen-Ges. Phys. Chem.*, **83**, 294 (1979)
- [145] M. Pönitsch, P. Gotthardt, A. Grüger, H.G. Brion and R. Kirchheim, *J. Polym. Sci.: Polym. Phys.* **35**, 2397 (1997)
- [146] R.A. Street, *Physica B* **170**, 69 (1991)
- [147] W. Beyer and U. Zastrow, *J. Non-Cryst. Solids*, **230**, 880 Part B (1998)
- [148] W. Beyer and H. Wagner, *Mat. Res. Soc. Symp. Proc.*, **336**, 323 (1994)
- [149] W. Beyer (2003) *Sol. Ener. Mat. Sol. C*, **78**, 235 (2003)
- [150] K. Hughes and J.O. Isard in „Physics of Electrolytes“, Vol.1, J. Hladik (Ed.), Academic Press, London, 1972
- [151] G.H. Frischat, „Ionic Diffusion in Oxide Glasses“, TransTech, Aedermansdorf (1975) p. 161
- [152] M.D. Ingram, in „Materials Science and Technology“, Vol. 9, eds. R.W. Cahn, P.Haasen, E.J. Kramer, VCH-Verlagsgesellschaft, Weinheim, p. 715
- [153] M. Tomazawa, in "Treatise on Materials Science and Technology, Vol.12, eds. M. Tomazawa and R.H. Doremus (Academic Press, New York, 1977) p. 335
- [154] R. Kirchheim, *Glass Sci. Technol.* **75**, 294 (2002)

- [155] R. Kirchheim, *J. Non-Cryst. Solids* **272**, 85 (2000)
- [156] R. Kirchheim and D. Paulmann, *J. Non-Cryst. Solids*, **286**, 210. (2001)
- [157] H. Jain, N.L. Peterson and H.L. Downing, *J. Non-Cryst. Solids* **283-300**, 55 (1983)
- [158] B. Hjörvarsson, J. Ryden, E. Karlsson, J. Birch, and J.-E. Sundgren, *Phys. Rev. B* **43** 6440 (1991)
- [159] G. Andersson and B. Hjörvarsson and P. Isberg, *Phys. Rev. B* **55**, 1774 (1997)
- [160] G. Song, M. Geitz, A. Abromeit and H. Zabel, *Phys. Rev.*, **B54**, 14093 (1996)
- [161] G. Song, A. Remhof, D. Labergerie and H. Zabel, *Phys. Rev. Lett.*, **79**, 5062 (1997)
- [162] D. Nagengast, J. Erxmeyer, F. Klose, Ch. Rehm, P. Kuschnerus, G. Dortmann, and A. Weidinger, *J. Alloys Compd.* **231**, 307 (1995)
- [163] B. Hjörvarsson, J. A. Dura, P. Isberg, T. Watanabe, T.J. Udovic, G. Anderson and C.F. Majkrzak, *Phys. Rev Lett.*, **79**, 901 (1997)
- [164] A. Züttel, Ch. Nützenagel, G. Schmid, Ch. Emmenegger, P. Sudan and L. Schlapbach, *Appl. Surf. Sci.*, **162**, 571 (2000)
- [165] Q.M. Yang, G. Schmitz, S. Fähler, H.U. Krebs, and R. Kirchheim, *Phys. Rev. B* **54**, 9131 (1996)
- [166] U. Laudahn, A. Pundt, M. Bicker, U.v.Hülsen, U. Geyer, T. Wagner and R. Kirchheim, *J. Alloys Compd.* **293-295**, 490 (1999)
- [167] P. Kesten, A. Pundt, G. Schmitz M. Weisheit, H.U. Krebs and R. Kirchheim, *J. Alloys Compd.* **330-332**, 225 (2002)
- [168] C. Sachs, A. Pundt, R. Kirchheim, M. Winter, M.T. Reetz and D. Fritsch, “Solubility of hydrogen in single-sized palladium clusters”, *Phys. Rev. B* **64** 075408 (2001)
- [169] M. Suleiman, N.M. Jisrawi, O. Dankert, M.T. Reetz, C. Bähitz, R. Kirchheim and A. Pundt, *J. Alloys Compd.* **356-357**, 644 (2003)
- [170] M. Suleiman, PhD-Thesis, University of Göttingen (2003)
- [171] H. Wagner in Ref. [30], p. 5
- [172] W.D. Nix, *Metall. Trans.*, **20**, 2217 (1989)
- [173] E.S. Kooij, A.T.M. van Gogh and R. Griessen, *J. Electrochem. Soc.*, **146**, 2990 (1990)
- [174] J.A. Alford, M.Y. Chou, E.K. Chang and S.G. Louie, *J. Phys. Rev.* **B67**, 125110 (2003)
- [175] S.J. van der Molen, J.W.J. Kerssemakers, J.H. Rector, N.J. Koeman, R. Dam and R. Griessen, *J. Appl. Phys.*, **86**, 6107 (1999)
- [176] P. van der Sluis, M. Ouwerkerk and P. Duine, *Appl. Phys. Lett.*, **70**, 3356 (1997)
- [177] M. Dornheim, S.J. v.d. Molen, E.S. Kooij, J. Kerssemakers, H. Harms, U. Geyer, R. Griessen, R. Kirchheim, A. Pundt, *J. Appl. Phys.* **93**, 8958 (2003)
- [178] G. Song, A. Remhof, D. Labergerie, H. Zabel, private communication
- [179] R. Kirchheim, *Acta mater.*, to be published
- [180] P.F. Miceli and H. Zabel, *Phys. Rev. Lett.* **59**, 1224 (1987)
- [181] F. Klose, J. Thiele, A. Schurian, O. Schulte, M. Steins, O. Bremert, and W. Felsch, *Z. Phys. B* **90**, 82 (1993)
- [182] R.H. Song and S. Pyun, *J. Electrochem. Soc.* **137**, 1051 (1990)
- [183] N. Takano, Y. Murakami, and F. Terasaki, *Scr. Metall. Mater.* **32**, 401 (1995)
- [184] H. Züchner, Proceedings of 2. JIM International Symposium, Hydrogen in Metals JIM, Minakami, Japan, (1979) p. 101.
- [185] J. Crank, “The Mathematics of Diffusion” (Oxford University Press, Oxford, 1975).
- [186] R. Ash, R.M. Barrer, and J.H. Petropoulos, *Br. J. Appl. Phys.* **14**, 854 (1963)
- [187] R. Ash, R.M. Barrer, and D.G. Palmer, *Br. J. Appl. Phys.* **16**, 873 (1965)
- [188] G. Schmitz, P. Kesten, Q.M. Young, *Phys. Rev. B* **58**, 7333 (1998)
- [189] P. Kesten, PhD-Thesis, University of Göttingen (2000)
- [190] P. Kesten, diploma thesis, Univeristy of Göttingen (1996)

- [191] T. Al-Kassab, H. Wollenberger, G. Schmitz and R. Kirchheim in "High-Resolution Imaging and Spectroscopy of Materials", F. Ernst and M. Rühle eds., Springer Verlag (2002) p. 271-320
- [192] P. Kesten, A. Pundt, G. Schmitz M. Weisheit, H.U. Krebs and R. Kirchheim *J. alloys compd.*, **330-332**, 225 (2002)
- [193] B. Hjörvarsson and J. Ryden and E. Karlsson and J. Birch and J.-E. Sundgren, *Phys. Rev. B***43** 6440 (1991)
- [Hjörvarsson3] G. Andersson and B. Hjörvarsson and P. Isberg, *Phys. Rev. B*, **55**, 1774 (1997)
- [194] J. F. Lynch and T. B. Flanagan, *J. Phys. Chem.*, **77**, 2628 (1973)
- [195] E. Salomons, R. Griessen, D.E. de Groot, J.H. Rector and D. Fritsch, *Europhys. Lett.*, **5**, 449 (1988)
- [196] M.T. Reetz and W. Helbig, *J. Am. Chem. Soc.* **116**, 7401 (1994)
- [197] R.J. Behm, V. Penka, M.G. Cattania, K. Christmann, and E. Ertl., *J. Chem. Phys.* **78**, 7486 (1983)
- [198] T.B. Flanagan, B.S. Bowerman, and G.E. Biehl, *Scr. Metall.* **14**, 443 (1980)
- [199] J.W. Cahn and F. Larche, *Acta Metall.*, **32**, 1915 (1984)
- [200] R.B. Schwarz and A.G. Khachaturyan, *Phys. Rev. Lett.* **74**, 2523 (1995)

Figure caption:

Fig. 1:

Partial molar volume of hydrogen in polycrystalline palladium (closed circles) and in a liquid quenched Pd-Si metallic glass. The negative volume changes for the first 40 atppm H are explained by trapping of H-atoms in a corresponding fraction of vacancies [53].

Fig. 2:

Schematic presentation of a distribution of site energies which starts with the most degenerate one, i.e. the single crystal in the top line. In the following lines increasing structural disorder leads to a decreasing degeneracy by increasing the dimensions of lattice defects. For diffusion potential traces or energy landscapes, respectively including the defect are important. For grain boundaries traces within the grain and within the grain boundary are shown separately, where the latter are present with a volume fraction of c_t . The density of site energies (DOSE), $n(E)$, defined as the number of sites within a given energy window is presented both graphically and analytically. The various forms of $n(E)$ are derived in chapters IV and V.

Fig. 3:

Potential trace for an interstitial jumping from site 1 with energy E_1 to site 2 with energy E_2 . E^0 is an average Energy of the DOSE and Q^0 the activation energy with respect to this reference. Thus particles in a material containing sites of energy E^0 only have a jump frequency of $\Gamma = \Gamma^0 \exp[-Q/k_B T]$.

Fig. 4:

Circles of constant hydrostatic stress at an edge dislocation as calculated in continuum mechanics (cf. Eq. (8.1)). The elastic interaction energy with hydrogen is constant at these lines and the corresponding DOSE is the number of sites within the two circles.

Fig. 5:

Electrochemically measured chemical potentials of hydrogen in heavily deformed palladium plotted according to Eq. (8.4) versus $1/\sqrt{c}$. The various regions of the data points represent regions of a predominant interaction mechanism.

Fig. 6:

Hydrogen resistivity increment, hydrogen diffusivity and the concentration of free hydrogen in heavily deformed palladium divided by the corresponding values in well annealed palladium. These ratios are plotted versus H-concentration and in agreement with Eq. (8.6) they are about the same over the whole range of concentrations within the α -phase of Pd.

Fig. 7:

Diffusion coefficient of hydrogen in heavily deformed Pd (closed circles) and well annealed Pd (open circles). The line following the values of deformed Pd was calculated from measured chemical potentials without a fitting parameter (cf. text).

Fig. 8:

A modified Guinier Plot of the macroscopic scattering cross section $d\Sigma/d\Omega$ (cf. Eq. (8.7)) measured by small angle neutron scattering for deformed Pd with 1 at.-% H. The slope of the linear part yields the radius of hydrogen enriched cylinders formed by segregation at the dislocation line.

Fig. 9:

Radii obtained from small angle neutron scattering for a deformed Pd-sample at various H-concentrations. The line is calculated by assuming the formation of a hydride of cylindrical shape in the strain field of dislocations. The dislocation density ($\rho=2 \cdot 10^{11} \text{ cm}^{-2}$) was used as a fitting parameter to obtain agreement with experimental data.

Fig. 10:

Macroscopic cross section for a deformed Pd sample containing 0.8 at.-% hydrogen (closed circles) or deuterium (open circles). The lines are calculated by using Eq. (8.7). The difference of $d\Sigma/d\Omega$ between the two isotopes is less than expected from their scattering length which is evidence for a volume expansion during the “hydride” formation at the dislocation lines (cf. text).

Fig. 11:

H₂-equilibrium pressure versus H-concentration for single crystalline (●) and nanocrystalline Pd (○) [81] at 295 K. The dotted line has a slope of 2 within the α -phase according to Sieverts' Law for $c < 0.01$ and it becomes a plateau within the $\alpha + \beta$ two phase region for $c > 0.015$. The solid and dashed lines for the nanocrystalline sample are calculated assuming a distribution of site energies (cf. Fig. 12) and including or excluding H-H interaction as explained in the text.

Fig. 12:

Site energy distribution for H in nanocrystalline Pd used in order to calculate the line in Fig. 11. The bimodal distribution covers sites within the grains with the same energy $E=0$ by definition and sites with a Gaussian distribution within the grain boundaries. The Gaussian has the average site energy E_{seg} and the width σ .

Fig. 13:

Effective diffusion coefficient of hydrogen at 295 K in nanocrystalline Pd (○) and single crystalline Pd (□) as a function of the total H-concentration. The horizontal line through the single crystalline data corresponds to H-diffusion of non-interacting H-atoms. The curves through the nanocrystalline data are calculated using Eqs. (2.3) and (5.5) and assuming that the effective diffusion coefficient corresponds to the grain boundary diffusion coefficient (cf. text). H-H interaction is included by adding a term Wc_{gb} to the chemical potential, where W equals -30 kJ/Mol as in polycrystalline Pd [75] and c_{gb} is the local concentration in the grain boundaries. Note that grain boundary diffusion of interstitials at low concentrations is slower than in single crystals.

Fig. 14:

Schematic presentation of three limiting cases of grain boundary diffusion with boundaries perpendicular to the surface, where d is the distance of grain boundaries or the grain size, respectively. δ is the thickness of grain boundaries and $c(x,y)$ is the concentration profile. With diffusion coefficients D_g and D_{gb} for grains and grain boundaries and t as the diffusion time the conditions for the three limiting cases are [85]: A1 and A2: $D_g t > d^2$, B: $100\delta < \sqrt{D_g t} < d/20$ and C: $\sqrt{D_g t} > \delta/20$

Fig. 15:

Model of the (111) Ag/MgO interface at low (a) and high (b) partial pressure of oxygen. In a) structural vacancies are formed in the terminating oxygen layer, in order to maintain stoichiometry of MgO (cf. text). At high oxygen pressures the vacancies are filled with excess oxygen which gets its 2 electrons from Ag forming a kind of silver oxide at the interface. In

the presence of excess oxygen strong trapping of hydrogen occurs at the metal/oxide interface.

Fig. 16:

Macroscopic scattering cross section $d\Sigma/d\Omega$ versus scattering vector, Q , for an internally oxidized Ag-1 at.-% Mg alloy (closed circles) and its changes after exposing to hydrogen (open circles) and to deuterium (triangles). The steep decrease at the lowest Q -values is due to large oxide precipitates at grain boundaries. The following plateau and the decrease at large Q -values stems from small oxide particles (average radius ≈ 1.6 nm) within the grains. The pronounced changes caused by hydrogen are caused by both segregation of hydrogen at the metal/oxide interface and displacement of Ag-atoms from the interface (cf. text).

Fig. 17:

Difference of H-concentration between nanocrystalline and single crystalline Pd, Δc , at a given partial pressure of hydrogen, p . The values are obtained from the data set in Fig. 11.

Fig. 18:

Density of site energies for the various $Nb_{1-x}V_x$ tetrahedra in crystalline Nb-V alloys as a function of composition [113].

Fig. 19:

Pressure-concentration isotherms for hydrogen in two amorphous Pd-Si alloys obtained by various experimental techniques at 295 K [115]. The results are plotted in accordance with Eq. (14.3) and the fugacity of hydrogen, f , is used at high chemical potentials instead of the partial pressure. The slope of the straight lines yields a value for the width σ of the Gaussian DOSE.

Fig. 20:

Hydrogen diffusion coefficient as a function of H-concentration in amorphous $Pd_{80}Si_{20}$ alloys prepared by the double piston technique (squares), melt spinning (open circles) and sputtering (triangles). The concentration dependence vanishes after crystallization of the melt spun alloy (closed circles) [14, 119].

Fig. 21 a)

Measured density of site energies $n(E) \approx \partial c / \partial \mu$ (cf. Eq. (4.7)) for an amorphous Ni-Ti alloy (filled circles) and the contributions from different tetrahedral sites (dashed Gaussian curves and their sum as a solid line). The Gaussian curves have about the same width and the ratio of their areas corresponds to the binomial distribution (cf. Eq. (15.1)).

Fig. 21 b) same as a) but for a Ni-Zr alloy

Fig. 22

Bulk metallic glass sandwiched in between two Pd-layers. The top layer allows permeation of gaseous hydrogen into the glass and resistivity changes in the bottom layer are a measure of hydrogen transport through the glass. The transient behavior of this transport yields H-diffusivity [128]

Fig. 23:

Pressure composition isotherms for H in two bulk metallic glasses (Johnson glass: $Zr_{46.8}Ti_{8.2}Cu_{7.5}Ni_{10}Be_{27.5}$, squares for a first run and triangles for a second run and Inoue glass:

Zr_{66.8}Al_{17.4}Ni_{7.2}Cu_{8.6}, circles). The line was calculated for the Inoue glass as described in the text.

Fig. 24

Diffusion coefficients for hydrogen in the Inoue glass (two samples) as a function of the hydrogen pressure. The straight line is an approximate behavior as expected from the measured chemical potentials [128]

Fig. 25:

Chemical potential or logarithm of the thermodynamic activity, λ , of various small solute molecules or atoms in various amorphous matrices plotted in accordance with Eq. (14.3) versus inverse error function of $(1-2c)$.

Fig. 26:

Schematic presentation of results of Monte-Carlo Simulations for interstitial diffusion in a 3-dimensional energy landscape with and without Gaussian distributions of site and saddle point energies. The concentration and temperature dependence of D in a perfect crystal (first column on the left) is shown in the other columns as a dashed line for the sake of comparison. The temperature dependence for high concentrations is shown as a dotted line in the last two columns. The different dependencies are explained in the text.

Fig. 27:

Measured partial molar volumes of CO₂ in two glassy polycarbonates and in a glassy polyimide (Kapton) as a function of CO₂-concentration and calculated behavior (solid lines) [139]. The partial molar volume increases because with increasing concentration smaller sites with a higher elastic energy have to be occupied. The partial molar volume in the liquid or rubbery state of the polymer as well as in many organic liquids is about 46 cm³/mol. This value is approached at high concentrations of CO₂ (closed circles) because the polycarbonate is swelling and finally transforms into the liquid state due to the strain induced by the dissolved CO₂.

Fig. 28:

Concentration pressure isotherms for various small molecules in polycarbonates [139]. The lines are calculated assuming a Gaussian DOSE and FD-Statistics. A slope of unity corresponds to ideal dilute behavior and the validity of Henry's Law which is the case for water. The width of the Gaussian distribution determines slope and curvature of the isotherms and the smaller the slope the broader the width. Changes of the average energy E^0 result in a parallel movement of the isotherms in the direction of the $\log c$ axis.

Fig. 29:

Relative volume changes of polycarbonate for three different solute molecules (carbon dioxide, ethylene, and acetone). The changes scale with the size of the molecules and the lines are calculated with one fitting parameter for all three curves.

Fig. 30:

Average energy of the DOSE of CO₂ for different glassy polymers obtained from concentration-pressure isotherms plotted versus the elastic energy associated with the incorporation of the molecule into a smaller hole of the polymer and as obtained from Eq. (18.3). The linear relation between the two quantities used as an assumption in Eq. (18.5) appeared to be fulfilled.

Fig. 31:

Widths σ_E of a Gaussian DOSE for various small molecules in bisphenol-A polycarbonate (BPA-PC) plotted versus the squared molar volume of the small molecules. The width was obtained by fitting concentration-pressure isotherms as shown in Fig. 28 and the linear relationship is predicted by Eq. (18.5). The line intercepts the abscissa at V_h^0 , i.e. the average site volume in BPA-PC. For molecules being smaller than V_h^0 no elastic energy has to be provided during dissolution and the Gaussian degenerates to a Dirac-Delta Function.

Fig. 32:

Concentration dependence of the diffusion coefficient (scaled with a factor κ , in order to fit into the diagram) of different small molecules in different polymers [145]. The lines were calculated using measured concentration-pressure isotherms and Eqs. (2.3) and (5.5) and one fitting parameter D^0 (cf. Eq. (5.5)) which like the scaling factor κ moves the curves parallel in the direction of the ordinate only.

Fig. 33:

Schematic presentation [146-149] of the DOSE for hydrogen in amorphous silicon (or germanium). The shown part of the distribution stems mostly from dangling bonds being saturated with H atoms. For high concentrations (sample B with the DOSE shown left) the distribution extends further to the energy E_m of "mobile" hydrogen and, therefore, the energy difference between μ_B and E_m is smaller when compared with the case of low H-concentrations (sample A and distribution on the right). However, if two samples with the distributions shown are in contact, the chemical potential has to be equal. This is achieved by a few H-atoms moving from B to A due to the low density $n(E)$ around μ_A . Thus the activation energy for diffusion in sample A is now much smaller and similar to B.

Fig. 34:

- a) Schematic silicate network containing an alkali oxide.
- b) Cation distribution in a regular lattice containing fixed anions as a model for cation diffusion in oxide glasses.

Fig. 35:

Schematic presentation of the concentration dependence of the tracer diffusion coefficient of alkali ions in oxide glasses. Decreasing D^* in concentration range A and vice versa in B.

Fig. 36:

Bimodal distribution of site energies and occupation according to the shaded area. The total area of the first peak increases proportional with cation concentration. With this distribution the "weak electrolyte behavior" of cation mobility can be derived [69]

Fig. 37:

dc-conductivity of a mixed Na-Cs silicate glass [157] with 25 mol-% alkali oxide at 200, 300 and 400 °C. The lines are calculated using a rectangular DOSE for the exchange energy of Cs and Na [155, 156]

Fig. 38:

Diffusion coefficient of Na^+ (solid circles) and Cs^+ (open circles) at 397 °C in a 25 mol-% alkali oxide silicate glass [157]. The straight lines are fits to the linear behavior for A^+ ions at $y \rightarrow 1$ and R^+ ions at $y \rightarrow 0$, i.e. in regions where the corresponding ions are the majority component [155, 156].

Fig. 39:

Intensity, I , of X-rays in a θ - 2θ scan of a 100 nm thick Niobium film covered with a 10 nm thick Palladium film. The latter protects Nb from oxidation and allows easy electrochemical H-doping. With increasing H-concentration ($c=H/Nb$) the Nb (110) peak moves to smaller angles indicating the out of plane expansion of Nb. The Pd (111) peak at about 40.5 degrees does not move unless saturation of the Nb layer ($c>1$) occurs. Splitting of the Nb-peak into two peaks reveals the decomposition in a low concentration phase of α -Nb and a hydride (β -phase). The formation of the high concentration phase occurs at a higher terminal solubility when compared to bulk Nb.

Fig. 40:

Compressive stresses in a 190 nm thick epitaxial Nb-film on MgO as a function of H-concentration. Stresses are determined from substrate curvature. At low H-concentrations the compressive stresses increase linearly with c . Deviation from this steep increase, i.e. yielding occurs at the decomposition in the two phases α and β . The stress of about 400 MPa where the deflection occurs is much larger than the flow stress of bulk Nb.

Fig. 41:

Same as Fig. 40 but for a 200 nm thick nanocrystalline Nb-film deposited on Silicon by laser ablation. Here stress relaxation or yielding, respectively occurs within the α -phase. The relaxation is increased by entering the two phase region.

Fig. 42:

Same as Fig. 41 but for a 200 nm thick nanocrystalline Nb-film prepared by electron beam evaporation. Here yielding occurs at about 0.6 GPa within the α -phase. Compared to the laser ablated film presented in the previous figure the grain size is larger for the electron deposited film.

Fig. 43:

Same sample as in Fig. 42 after the removal of hydrogen and a second loading with hydrogen. Now stress relaxation starts at a higher stress of about 0.9 GPa.

Fig. 44:

Potential trace for hydrogen atoms in a Nb/Pd multilayer. Site energies E_{Pd} and E_{Nb} are known from solution energies in bulk metals. H-Diffusion through the layers is hindered by Nb-sites acting as traps or by Pd-layers acting as barriers, respectively.

Fig. 45:

Time lag versus H-concentration for diffusion through multilayers on a Pd-substrate of 12.5 μm thickness. The multilayer consists of 4, 8 and 16 alternating double layers of Pd and Nb of the same thickness and a total thickness as given in the inset.

Fig. 46

Pressure composition isotherms of Pd-clusters of 3 nm (circles) and 5.2 nm (triangles) in diameter compared with Pd-powder (crosses) and Pd-bulk (solid line)

Fig. 47:

X-ray diffraction peaks of Pd-clusters of 6 nm in diameter at different partial pressures of hydrogen. At the pressure of $1.8 \cdot 10^3$ Pa which corresponds to the two phase field of α and β bulk Pd (cf. Fig. 46) peaks split into two or broaden at least.

Fig. 48:

Lattice parameter pressure isotherms for various Pd-clusters. The change of the lattice parameter at about 20 mbar is decreasing with decreasing cluster size in accordance with the narrowing of the miscibility gap.

Fig. 1

Partial molar volume of hydrogen in polycrystalline palladium (closed circles) and in a liquid quenched Pd-Si metallic glass. The negative volume changes for the first 40 atppm H are explained by trapping of H-atoms in a corresponding fraction of vacancies [53].

material	structure	potential trace	energy distribution	energy distribution
single crystal				$\delta(E - E^o)$
single crystal + point defect				$(1 - c_t)\delta(E - E^o) + c_t\delta(E - E_t)$
single crystal + dislocation				$\frac{K^2}{(E - E^o)^3}$
single crystals + grain boundary				$(1 - c_t)\delta(E - E^o) + \frac{c_t}{\sigma\sqrt{\pi}} \exp\left[-\frac{(E - E_t)^2}{\sigma^2}\right]$
amorphous state				$\frac{1}{\sigma\sqrt{\pi}} \exp\left[-\frac{(E - E^o)^2}{\sigma^2}\right]$

Fig. 2:

Schematic presentation of a distribution of site energies which starts with the most degenerate one, i.e. the single crystal in the top line. In the following lines increasing structural disorder leads to a decreasing degeneracy by increasing the dimensions of lattice defects. For diffusion potential traces or energy landscapes, respectively including the defect are important. For grain boundaries traces within the grain and within the grain boundary are shown separately, where the latter are present with a volume fraction of c_t . The density of site energies (DOSE), $n(E)$, defined as the number of sites within a given energy window is presented both graphically and analytically. The various forms of $n(E)$ are derived in chapters IV and V.

Fig. 3:
 Potential trace for an interstitial jumping from site 1 with energy E_1 to site 2 with energy E_2 .
 E^0 is an average Energy of the DOSE and Q^0 the activation energy with respect to this
 reference. Thus particles in a material containing sites of energy E^0 only have a jump
 frequency of $\Gamma = \Gamma^0 \exp[-Q/k_B T]$.

Fig. 4
 Circles of constant hydrostatic stress at an edge dislocation as calculated in continuum mechanics (cf. Eq. IV.4). The elastic interaction energy with hydrogen is constant at these lines and the corresponding DOSE is the number of sites within the two circles.

Fig. 5:
Electrochemically measured chemical potentials of hydrogen in heavily deformed palladium plotted according to Eq. IV.7 versus $1/\sqrt{c}$. The various regions of the data points represent regions of a predominant interaction mechanism.

Fig. 6:
Hydrogen resistivity increment, hydrogen diffusivity and the concentration of free hydrogen in heavily deformed palladium divided by the corresponding values in well annealed palladium. These ratios are plotted versus H-concentration and in agreement with Eq. IV.9 they are about the same over the whole range of concentrations with in the α -phase of Pd.

Fig. 7
Diffusion coefficient of hydrogen in heavily deformed Pd (closed circles) and well annealed Pd (open circles). The line following the values of deformed Pd was calculated from measured chemical potentials without a fitting parameter (cf. text).

Fig. 8:

A modified Guinier Plot of the macroscopic scattering cross section $d\Sigma/d\Omega$ (cf. Eq. IV.10) measured by small angle neutron scattering for deformed Pd with 1 at.-% H. The slope of the linear part yields the radius of hydrogen enriched cylinders formed by segregation at the dislocation line.

Fig. 9:
Radii obtained from small angle neutron scattering for a deformed Pd-sample at various H-concentrations. The line is calculated by assuming the formation of a hydride of cylindrical shape in the strain field of dislocations. The dislocation density ($\rho=2 \cdot 10^{11} \text{ cm}^{-2}$) was used as a fitting parameter to obtain agreement with experimental data.

Fig. 10:
Macroscopic cross section for a deformed Pd sample containing 0.8 at.-% hydrogen (closed circles) or deuterium (open circles). The lines are calculated by using Eq. IV.10. The difference of $d\Sigma/d\Omega$ between the two isotopes is less than expected from their scattering length which is evidence for a volume expansion during the “hydride” formation at the dislocation lines (cf. text).

Fig. 11:

H_2 -equilibrium pressure versus H-concentration for single crystalline (●) and nanocrystalline Pd (○) [81] at 295 K. The dotted line has a slope of 2 within the α -phase according to Sieverts' Law for $c < 0.01$ and it becomes a plateau within the $\alpha + \beta$ two phase region for $c > 0.015$. The solid and dashed lines for the nanocrystalline sample are calculated assuming a distribution of site energies (cf. Fig. IV.9) and including or excluding H-H interaction as explained in the text.

Fig. 12:
 Site energy distribution for H in nanocrystalline Pd used in order to calculate the line in Fig. IV.8. The bimodal distribution covers sites within the grains with the same energy $E=0$ by definition and sites with a Gaussian distribution within the grain boundaries. The Gaussian has the average site energy E_{seg} and the width σ .

Fig. 13:

Effective diffusion coefficient of hydrogen at 295 K in nanocrystalline Pd (○) and single crystalline Pd (□) as a function of the total H-concentration. The horizontal line through the single crystalline data corresponds to H-diffusion of non-interacting H-atoms. The curves through the nanocrystalline data are calculated using Eqs. II.13 and III.17 and assuming that the effective diffusion coefficient corresponds to the grain boundary diffusion coefficient (cf. text). H-H interaction is included by adding a term Wc_{gb} to the chemical potential, where W equals -30 kJ/Mol as in polycrystalline Pd [75] and c_{gb} is the local concentration in the grain boundaries. Note that grain boundary diffusion of interstitials at low concentrations is slower than in single crystals.

Fig. 14:
 Schematic presentation of three limiting cases of grain boundary diffusion with boundaries perpendicular to the surface, where d is the distance of grain boundaries or the grain size, respectively. δ is the thickness of grain boundaries and $c(x,y)$ is the concentration profile. With diffusion coefficients D_g and D_{gb} for grains and grain boundaries and t as the diffusion time the conditions for the three limiting cases are [85]: A1 and A2: $D_g t \gg d^2$, B: $100\delta < \sqrt{D_g t} < d/20$ and C: $\sqrt{D_g t} > \delta/20$

Fig. 15:

Model of the (111) Ag/MgO interface at low (a) and high (b) partial pressure of oxygen. In a) structural vacancies are formed in the terminating oxygen layer, in order to maintain stoichiometry of MgO (cf. text). At high oxygen pressures the vacancies are filled with excess oxygen which gets its 2 electrons from Ag forming a kind of silver oxide at the interface. In the presence of excess oxygen strong trapping of hydrogen occurs at the metal/oxide interface.

Fig. 16:

Macroscopic scattering cross section $d\Sigma/d\Omega$ versus scattering vector, Q , for an internally oxidized Ag-1 at.-% Mg alloy (closed circles) and its changes after exposing to hydrogen (open circles) and to deuterium (triangles). The steep decrease at the lowest Q -values is due to large oxide precipitates at grain boundaries. The following plateau and the decrease at large Q -values stems from small oxide particles (average radius ≈ 1.6 nm) within the grains. The pronounced changes caused by hydrogen are caused by both segregation of hydrogen at the metal/oxide interface and displacement of Ag-atoms from the interface (cf. text).

Fig. 17:
Difference of H-concentration between nanocrystalline and single crystalline Pd, Δc , at a given partial pressure of hydrogen, p . The values are obtained from the data set in Fig. IV.8.

Fig. 18:
Density of site energies for the various $\text{Nb}_{1-x}\text{V}_x$ tetrahedra in crystalline Nb-V alloys as a function of composition [113].

Fig. 19:

Pressure-concentration isotherms for hydrogen in two amorphous Pd-Si alloys obtained by various experimental techniques at 295 K [115]. The results are plotted in accordance with Eq. V.4 and the fugacity of hydrogen, f , is used at high chemical potentials instead of the partial pressure. The slope of the straight lines yields a value for the width σ of the Gaussian DOSE.

Fig. 20:

Hydrogen diffusion coefficient as a function of H-concentration in amorphous $\text{Pd}_{80}\text{Si}_{20}$ alloys prepared by the double piston technique (squares), melt spinning (open circles) and sputtering (triangles). The concentration dependence vanishes after crystallization of the melt spun alloy (closed circles) [14, 119].

Fig. 21 a)

Measured density of site energies $n(E) \approx \partial c / \partial \mu$ (cf. Eq. III.7) for an amorphous Ni-Ti alloy (filled circles) and the contributions from different tetrahedral sites (dashed Gaussian curves and their sum as a solid line). The Gaussian curves have about the same width and the ratio of their areas corresponds to the binomial distribution (cf. Eq. V.5).

Fig. 21 b) same as a) but for a Ni-Zr alloy

Fig. 22

Bulk metallic glass sandwiched in between two Pd-layers. The top layer allows permeation of gaseous hydrogen into the glass and resistivity changes in the bottom layer are a measure of hydrogen transport through the glass. The transient behavior of this transport yields H-diffusivity [128]

Fig. 23:
Pressure composition isotherms for H in two bulk metallic glasses [128] (Johnson glass: $\text{Zr}_{46.8}\text{Ti}_{8.2}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$, squares for a first run and triangles for a second run and Inoue glass: $\text{Zr}_{66.8}\text{Al}_{17.4}\text{Ni}_{7.2}\text{Cu}_{8.6}$, circles). The line was calculated for the Inoue glass as described in the text.

Fig. 24
Diffusion coefficients for hydrogen in the Inoue glass (two samples) as a function of the hydrogen pressure. The straight line is an approximate behavior as expected from the measured chemical potentials [128]

Fig. 25:
Chemical potential or logarithm of the thermodynamic activity, λ , of various small solute molecules or atoms in various amorphous matrices plotted in accordance with Eq. V.4 versus inverse error function of $(1-2c)$.

Fig. 26:

Schematic presentation of results of Monte-Carlo Simulations for interstitial diffusion in a 3-dimensional energy landscape with and without Gaussian distributions of site and saddle point energies. The concentration and temperature dependence of D in a perfect crystal (first column on the left) is shown in the other columns as a dashed line for the sake of comparison. The temperature dependence for high concentrations is shown as a dotted line in the last two columns. The different dependencies are explained in the text.

Fig. 27:

Measured partial molar volumes of CO₂ in two glassy polycarbonates and in a glassy polyimide (Kapton) as a function of CO₂-concentration and calculated behavior (solid lines) [139]. The partial molar volume increases because with increasing concentration smaller sites with a higher elastic energy have to be occupied. The partial molar volume in the liquid or rubbery state of the polymer as well as in many organic liquids is about 46 cm³/mol. This value is approached at high concentrations of CO₂ (closed circles) because the polycarbonate is swelling and finally transforms into the liquid state due to the strain induced by the dissolved CO₂.

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Concentration pressure isotherms for various small molecules in polycarbonates [139]. The lines are calculated assuming a Gaussian DOSE and FD-Statistics. A slope of unity corresponds to ideal dilute behavior and the validity of Henry's Law which is the case for water. The width of the Gaussian distribution determines slope and curvature of the isotherms and the smaller the slope the broader the width. Changes of the average energy E^0 result in a parallel movement of the isotherms in the direction of the $\log c$ axis.

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Relative volume changes of polycarbonate for three different solute molecules (carbon dioxide, ethylene, and acetone). The changes scale with the size of the molecules and the lines are calculated with one fitting parameter for all three curves.

Fig. 30:

Average energy of the DOSE of CO_2 for different glassy polymers obtained from concentration-pressure isotherms plotted versus the elastic energy associated with the incorporation of the molecule into a smaller hole of the polymer and as obtained from Eq. VI.7. The linear relation between the two quantities used as an assumption in Eq. VI.7 appeared to be fulfilled.

Fig. 31:

Widths σ_E of a Gaussian DOSE for various small molecules in bisphenol-A polycarbonate (BPA-PC) plotted versus the squared molar volume of the small molecules. The width was obtained by fitting concentration-pressure isotherms as shown in Fig. VI.4 and the linear relationship is predicted by Eq. VI.9. The line intercepts the abscissa at V_h^0 , i.e. the average site volume in BPA-PC. For molecules being smaller than V_h^0 no elastic energy has to be provided during dissolution and the Gaussian degenerates to a Dirac-Delta Function.

Fig. 32:

Concentration dependence of the diffusion coefficient (scaled with a factor κ , in order to fit into the diagram) of different small molecules in different polymers [145]. The lines were calculated using measured concentration-pressure isotherms and Eqs. II.13 and III.17 and one fitting parameter D^0 (cf. Eq. III.17) which like the scaling factor κ moves the curves parallel in the direction of the ordinate only.

Fig. 33:

Schematic presentation [146-149] of the DOSE for hydrogen in amorphous silicon (or germanium). The shown part of the distribution stems mostly from dangling bonds being saturated with H atoms. For high concentrations (sample B with the DOSE shown left) the distribution extends further to the energy E_m of "mobile" hydrogen and, therefore, the energy difference between μ_B and E_m is smaller when compared with the case of low H-concentrations (sample A and distribution on the right). However, if two samples with the distributions shown are in contact, the chemical potential has to be equal. This is achieved by a few H-atoms moving from B to A due to the low density $n(E)$ around μ_A . Thus the activation energy for diffusion in sample A is now much smaller and similar to B.

Fig. 34 a)
Schematic silicate network containing an alkali oxide.

Fig. 34 b)
Cation distribution in a regular lattice containing fixed anions as a model for cation diffusion in oxide glasses.

Fig. 35:
Schematic presentation of the concentration dependence of the tracer diffusion coefficient of alkali ions in oxide glasses. Decreasing D^* in concentration range A and vice versa in B.

Fig. 36:
Bimodal distribution of site energies and occupation according to the shaded area. The total area of the first peak increases proportional with cation concentration. With this distribution the "weak electrolyte behavior" of cation mobility can be derived [69]

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dc-conductivity of a mixed Na-Cs silicate glass [157] with 25 mol-% alkali oxide at 200, 300 and 400 °C. The lines are calculated using a rectangular DOSE for the exchange energy of Cs and Na [155, 156]

Fig. 38:

Diffusion coefficient of Na^+ (solid circles) and Cs^+ (open circles) at 397 °C in a 25 mol-% alkali oxide silicate glass [157]. The straight lines are fits to the linear behavior for A^+ ions at $y \rightarrow 1$ and R^+ ions at $y \rightarrow 0$, i.e. in regions where the corresponding ions are the majority component [155, 156].

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Intensity, I , of X-rays in a θ - 2θ scan of a 100 nm thick Niobium film covered with a 10 nm thick Palladium film. The latter protects Nb from oxidation and allows easy electrochemical H-doping. With increasing H-concentration ($c=H/Nb$) the Nb (110) peak moves to smaller angles indicating the out of plane expansion of Nb. The Pd (111) peak at about 40.5 degrees does not move unless saturation of the Nb layer ($c>1$) occurs. Splitting of the Nb-peak into two peaks reveals the decomposition in a low concentration phase of α -Nb and a hydride (β -phase). The formation of the high concentration phase occurs at a higher terminal solubility when compared to bulk Nb.

Fig. 40:

Compressive stresses in a 190 nm thick epitaxial Nb-film on MgO as a function of H-concentration. Stresses are determined from substrate curvature. At low H-concentrations the compressive stresses increase linearly with c. Deviation from this steep increase, i.e. yielding occurs at the decomposition in the two phases α and β . The stress of about 400 MPa where the deflection occurs is much larger than the flow stress of bulk Nb.

Fig. 41:
Same as Fig. VII.2 but for a 200 nm thick nanocrystalline Nb-film deposited on Silicon by laser ablation. Here stress yielding occurs at about 1.2 GPa within the α -phase. The relaxation is increased by entering the two phase region.

Fig. 42:

Same as Fig. VII.3 but for a 200 nm thick nanocrystalline Nb-film prepared by electron beam evaporation. Here yielding occurs at about 0.6 GPa within the α -phase. Compared to the laser ablated film presented in the previous figure the grain size is larger for the electron deposited film.

Fig. 43:
Same sample as in Fig. VII.4 after the removal of hydrogen and a second loading with hydrogen. Now stress relaxation starts at a higher stress of about 0.9 GPa.

Fig. 44:
Potential trace for hydrogen atoms in a Nb/Pd multilayer. Site energies E_{Pd} and E_{Nb} are known from solution energies in bulk metals. H-Diffusion through the layers is hindered by Nb-sites acting as traps or by Pd-layers acting as barriers, respectively.

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Time lag versus H-concentration for diffusion through multilayers on a Pd-substrate of 12.5 μm thickness. The multilayer consists of 4, 8 and 16 alternating double layers of Pd and Nb of the same thickness and a total thickness as given in the inset.

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Pressure composition isotherms of Pd-clusters of 3 nm (circles) and 5.2 nm (triangles) in diameter compared with Pd-powder (crosses) and Pd-bulk (solid line)

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X-ray diffraction peaks of Pd-clusters of 6 nm in diameter at different partial pressures of hydrogen. At the pressure of $1.8 \cdot 10^3$ Pa which corresponds to the two phase field of α and β bulk Pd (cf. Fig. VII.8) peaks split into two or broaden at least.

Fig. 48:
Lattice parameter pressure isotherms for various Pd-clusters. The change of the lattice parameter at about 20 mbar is decreasing with decreasing cluster size in accordance with the narrowing of the miscibility gap.