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Gorsky effect study of H and D diffusion in V and Ti at high H(D) concentrations

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Abstract

The chemical diffusion coefficient of D in V and of H and D in Ti were determined by Gorsky effect measurements at high H(D) concentrations. On V, data were taken between 22 and 70 °C for D/V ratios from 0.73 to 0.82 (pure bcc α phase). The diffusion coefficients follow Arrhenius laws with activation energies of ~120 meV. They are extremely high, exceed in part 10^{-4} cm^2/s, and are up to four (two) times larger than the diffusion coefficients of D(H) in V at low concentrations. With the possible exception of Fe, they are the highest diffusion coefficients reported so far for H(D) in any metal in the considered temperature range, and probably also for any solid state diffusion process. The thermodynamic reason for the high diffusion coefficients is discussed. The measurements on Ti were performed between 160 and 310 °C for H(D)/Ti atom ratios between 1.5 and 1.71 (pure fcc γ phase). The diffusion coefficients are practically independent of concentration and follow Arrhenius laws with activation energies of 520 and 530 meV for H and D, respectively. H diffuses about 1.5 times faster than D. For the same concentration and isotope (H), the chemical diffusion coefficients in Ti are ten to fifty times larger than new and literature data for the self diffusion coefficient determined by field-gradient nuclear magnetic resonance and quasielastic neutron spectroscopy. These large differences result mainly from high values of the concentration derivative of the chemical potential of H in Ti.

Keywords: Metal–hydrogen systems; Metal hydrides; Hydrogen diffusion; Gorsky effect

1. Introduction

This paper reports Gorsky effect results for the chemical diffusion coefficient of H and D interstitials in VD_x, TiH_x and TiD_x at high H(D) concentrations x. The chemical diffusion coefficient D describes the hydrogen flux j according to Fick's law, $j = -D \operatorname{grad} n$, where n is the number of hydrogen interstitials per unit volume (hydrogen stands for both isotopes, H and D). The value of D depends on hydrogen–hydrogen interaction effects characterized by the chemical potential μ of the hydrogen interstitials [1–3]. This dependence is demonstrated by the present data.

As a second important quantity, the self (or tracer) diffusion coefficient D_{self} describes diffusion of a single (tagged) hydrogen. It can be defined by [2,3] $D_{\mathrm{self}} = \lim_{t\to\infty} \langle r^2\rangle/(6t)$, where $\langle r^2\rangle$ is the expectation value of the squared distance a hydrogen diffuses in time t. D_{self} is directly determined by quasielastic neutron scattering and field-gradient nuclear magnetic resonance [2–5]. The ratio between the two diffusion coefficients above is given by [2,3]

$$\frac{D}{D_{\mathrm{self}}} = \frac{x\,\partial\mu/\partial x}{k_B T}\,\frac{1}{f_{\mathrm{cor}}}, \tag{1}$$

where $x\ \partial\mu/\partial x$ expresses the concentration dependence of the chemical potential μ, $k_B T$ is the thermal energy and f_{cor} is the correlation factor (or Haven's ratio). f_{cor} describes the correlation between consecutive diffusive jumps of a given hydrogen ([2–4] and references therein). Specifically for the TiH_x system, an approximate theoretical expression for f_{cor} is given in [4]. In the low-concentration limit, i.e. in the absence of hydrogen–hydrogen interaction effects, $(n\ \partial\mu/\partial n)/k_B T$ and f_{cor} are 1, so that D and D_{self} are identical. With increasing concentrations, f_{cor} becomes

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smaller and reaches typically lowest values between 0.5 and 0.8 for the highest possible concentrations ([2,4] and references therein). In discussing our TiH_x results, we shall compare, with the help of Eq. (1), our data for D with new field-gradient nuclear magnetic resonance measurements of D_{self} and with literature data for this quantity [4,5].

2. Experimental

The Gorsky effect data were taken from quasi-static anelasticity measurements [2,6,7] on foil-shaped samples with thicknesses d between 0.05 and 1 mm, lengths between 30 and 75 mm and widths of 5 mm. The VD_x samples had concentrations x from 0.73 to 0.82 and were studied between 22 and 70 °C, so that they were in the α-phase where the D atoms occupy tetrahedral interstitial sites in a bcc V lattice [8]. VD_x has the same structure at low concentrations ($x < \sim 0.04$), which allows a meaningful comparison of present results with low-concentration literature data [1–3]. The V-hydrogen phase diagram exhibits a large isotope effect so that the structure of VH_x samples in the temperature and concentration range of the present measurements would differ from that at low x, a fact that would not have allowed a meaningful comparison of data for small and large x.

The TiH_x and TiD_x samples had x values between 1.5 and 1.71, were investigated between 160 and 310 °C and were in the pure γ phase in which H(D) occupies tetrahedral interstitial sites in a fcc Ti lattice [9]. In this case, a meaningful comparison with low-concentration data, where the Ti lattice is hcp, cannot be made.

The anelasticity experiments were performed under vacuum in a temperature-controlled furnace. One end of the investigated sample was mounted in a clamp, and a small magnet was fixed at the other end so that a nearby magnetic coil could apply a deflecting force. The deflections of the free sample end, which are proportional to the strain, were monitored with a capacitance bridge from the capacitance change between the free sample end and a ~0.1 mm distant counterelectrode. Thus, the set-up probed the relaxation of Young's modulus under constant stress conditions.

3. Results and discussion

Fig. 1 presents sample strain versus time in an experiment on a $TiH_{1.5}$ sample at 233 °C. The figure shows the strain response after application and removal of the deflecting force at 0 and 5260 s, respectively. The insets show enlarged the anelastic part of the two strain responses.

The time-dependence of the anelastic response was fitted to the theoretically expected expression for the present sample geometry [7]. This expression is an infinite sum of time exponentials with time constants τ_j, where the exponential with the longest time constant $\tau_{j=1} = d^2/(\pi^2 \cdot D)$ describes already more than 98% of the total anelastic response.

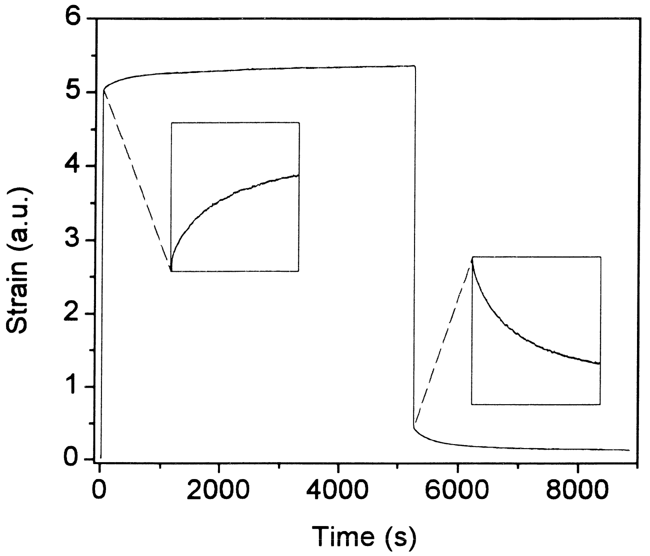

Fig. 1. Sample strain (arbitrary units) versus time of a $TiH_{1.5}$ sample in the course of a measurement. The two insets show the anelastic strain after application and removal of the deflecting force at 0 and 5260 s, respectively.

We discuss our results for the VD_x samples first. Fig. 2 presents an Arrhenius plot of the chemical diffusion coefficients D of D in these samples. The data follow Arrhenius laws with activation energies E of (133±13), (124±16) and (113±8) meV for concentrations $x = 0.73$, 0.76 and 0.78, respectively (E cannot be given for $x = 0.82$ since data were taken at only a single temperature). It can be seen (i) that D is the larger the higher x is and (ii) that E seems to decrease with increasing x. Further, the present D are up to four times larger than the D values in the limit of low D concentrations, indicated by the broken line, and they are still up to two times larger than D values of the isotope H at low x [2,3]. Except for possibly Fe, the present diffusion coefficients are the highest ones ever measured in the considered temperature range for hydrogen in a metal, and probably also for any solid state diffusion process.

For a discussion of the large increase of D with x, we consider first a hypothetical ideal hydrogen lattice gas where the actually existing hydrogen–hydrogen interaction effects are absent, except for the fact that a given interstitial site can be occupied only once. We assume further for such an ideal situation that hydrogen jump rates to nearby *unoccupied* sites do not vary with x. In this case, D has a concentration-independent constant value ideal D_{ideal} [10,11] which we can identify with the low-concentration values of D in Fig. 2 since hydrogen–hydrogen interaction becomes negligible in the limit of low x. However, the actual presence of hydrogen interaction effects, in addition

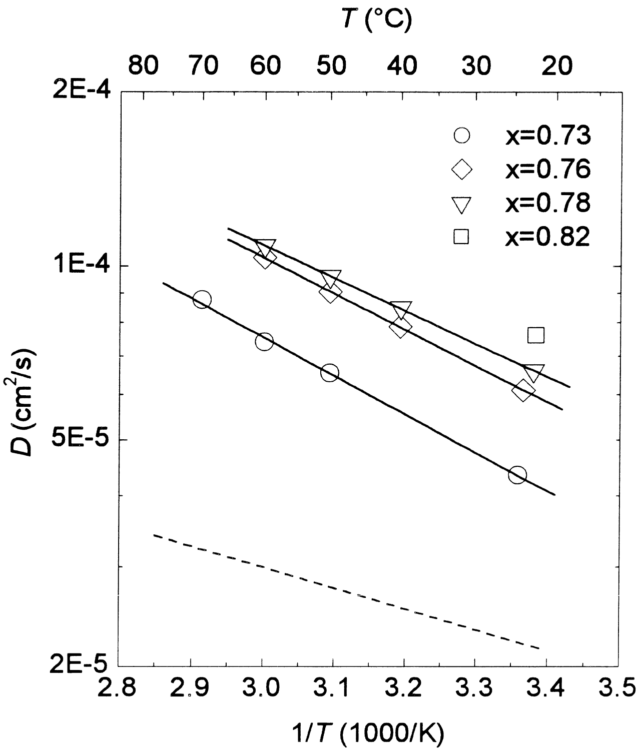

Fig. 2. Arrhenius plot of the chemical diffusion coefficient D of D in V for the indicated D concentrations. The experimental errors are smaller than the size of the data points. The broken line shows the diffusion coefficient of D in V in the limit of low concentrations [2,3].

to a sole blocking of occupied sites, modifies D. Within a mean field approximation, the ratio D/D_{ideal} can be written as

$$\frac{D}{D_{\text{ideal}}} = \frac{x\,\partial\mu/\partial x}{(x\,\partial\mu/\partial x)_{\text{ideal}}} = (1 - x/x_0)\cdot\frac{x\,\partial\mu/\partial x}{k_{\text{B}}T}. \qquad (2)$$

where

$$(x\,\partial\mu/\partial x)_{\text{ideal}} = \frac{k_{\text{B}}T}{(1 - x/x_0)} \qquad (3)$$

holds for an ideal lattice gas [1,2], and $x_0 = 6$ is, for VD$_x$, the concentration at which all the tetrahedral interstitial sites are occupied. Eq. (2) is derived from the generalized Einstein relation $D = M \cdot x\,\partial\mu/\partial x$ [1–3], where the mobility M does, in mean field approximation, not depend on interaction effects beyond those of a sole blocking of occupied sites. The relation expresses the fact that the actual 'force' for a diffusive flux is the gradient of μ, so that D is the larger the stronger μ varies with x.

According to Eq. (2), the present D/D_{ideal} ratios up to four indicate a steep increase of μ with increasing x, a behavior characteristic for a repulsive hydrogen–hydrogen interaction (for the present x, $1 - x/x_0$ does not differ much from 1). This conclusion is supported by neutron diffraction measurements on VD$_{0.75}$ [12] and VD$_{0.81}$ [13] which demonstrate, in agreement with a strong repulsive interaction, that a given D atom blocks nearly completely an occupation of its nearest and second-nearest interstitial sites and reduces significantly the occupation probability of its third-nearest sites.

We present now our TiH(D)$_x$ data, compiled in the Arrhenius plot of Fig. 3. The figure shows the chemical diffusion coefficient D (i) of H in four TiH$_x$ samples with x between 1.5 and 1.71 and (ii) of D in a TiD$_{1.5}$ sample. The D values of the TiH$_x$ samples are indicated by the same symbol since they did, within experimental accuracy, not exhibit any x dependence. The figure shows further the self diffusion coefficient D_{self} of H in TiH$_{1.8}$ [1], measured by field-gradient nuclear magnetic resonance, and literature values for D_{self} obtained by quasielastic neutron scattering [4] and field-gradient nuclear magnetic resonance [5].

The present data for D and D_{self} follow Arrhenius laws. For the chemical diffusion coefficients, the activation

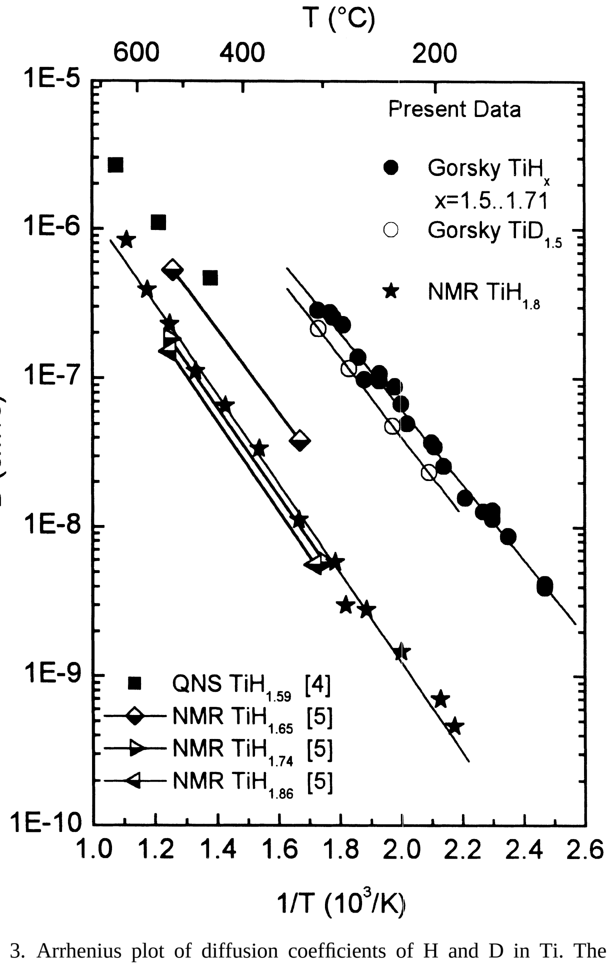

Fig. 3. Arrhenius plot of diffusion coefficients of H and D in Ti. The present data are Gorsky effect results for the chemical diffusion coefficient D and field-gradient nuclear magnetic resonance results for the self diffusion coefficient D_{self}. The scatter of the data characterizes the size of the experimental errors. The other data are literature values for D_{self} obtained by quasielastic neutron scattering (QNS) [4] and field-gradient nuclear magnetic resonance [5].

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[1] Details of these measurements will be presented in a forthcoming publication.

energies are (0.50±0.03) meV for H diffusion in TiH_x and (0.53±0.04) meV for D diffusion in $TiD_{1.5}$. In the investigated temperature range, the D values for H are about 1.5 times larger than those for the isotope D. The activation energy for the present self diffusion coefficient D_{self} of H in $TiH_{1.8}$ is (0.60±0.03) meV, thus being somewhat larger than the activation energy for chemical diffusion.

In contrast to D which is essentially independent of x, the self diffusion coefficient D_{self} decreases with increasing concentration (this statement can be made although the present D_{self} is, for the same x, somewhat higher than those of [5]). Such different concentration dependencies are in fact expected for the present TiH_x system [4,5]. Consider, for example, the most simple situation of an ideal hydrogen lattice gas, in which D is independent of x [10,11]. In this situation, we find from Eqs. (1) and (2)

$$\frac{D}{D_{\mathrm{self}}} = \frac{1}{f_{\mathrm{cor}} \cdot (1 - x/x_0)}, \tag{4}$$

where $x_0 = 2$ since there are two tetrahedral interstitial sites per Ti atom. In essential agreement with experiment [4,5], Eq. (4) predicts a linear decrease of D_{self} with rising x, if we neglect the small influence of f_{cor}, and a vanishing D_{self} for x approaching x_0. For a representative $x = 1.8$ and using $f_{\mathrm{cor}} = 0.7$ [4], Eq. (4) yields a ratio D/D_{self} of about 14. This ratio explains qualitatively the fact that D is much larger than D_{self}. Quantitatively however, it is smaller than the experimental ratio of about 50 that follows from a comparison of the present results for D and D_{self} (for $TiH_{1.8}$). This indicates that the system TiH_x does not completely exhibit an ideal behavior.

For 464 °C, a temperature above those of the present data for D, the value of $x\ \partial\mu/\partial x/k_B T$ can be derived from a thermodynamic study on TiH_x [9,14]. Considering again $x = 1.8$, the data in [9,14] yield a value of about 16, which is somewhat larger than the value of 10 for a completely ideal lattice gas (Eq. (3)). With $f_{\mathrm{cor}} = 0.7$ [4], a ratio of about 23 is then expected for D/D_{self}. Within experimental accuracy, this ratio is in fact identical to the ratio $D/D_{\mathrm{self}} = 25$ that can be extracted from the present results, if the data for D in Fig. 3 are extrapolated to 464 °C.

Our discussion on the two systems VD_x and TiH_x showed that H in TiH_x seems to approach better an ideal lattice gas behavior than D in VD_x. A likely reason for this is that the closest distance between the interstitial sites occupied by hydrogen in TiH_x is ~2.2 Å [9], and thus about twice as large as the corresponding distance of ~1.1 Å in VD_x [15]. This fact makes it quite understandable that hydrogen–hydrogen interaction effects are less important in TiH_x than in VD_x.

4. Conclusion

The chemical diffusion coefficient D of D in VD_x and of H and D in $TiH(D)_x$ was determined at high H(D) concentrations in Gorsky effect measurements. In the discussion of the results for V, the chief focus was the dependence of D on D concentration. In the case of the $TiH(D)_x$ system, the D values were compared with new and literature data for the self diffusion coefficient D_{self}. For both investigated systems, VD_x and $TiH(D)_x$, the dependence of the chemical potential of H(D) on H(D) concentration was of importance for the values of the experimentally observed diffusion coefficients.

References

[1] H. Wipf, in: G. Alefeld, J. Volkl (Eds.), Topics in Applied Physics, Hydrogen in Metals II, Vol. 29, Springer-Verlag, Berlin, 1978, p. 273.

[2] Y. Fukai, in: Springer Series in Material Science, The Metal–Hydrogen System. Basic Bulk Properties, Vol. 21, Springer, Berlin, 1993.

[3] H. Wipf, in: H. Wipf (Ed.), Topics in applied physics. Hydrogen in metals III, Vol. 73, Springer, Berlin, 1997, p. 51.

[4] U. Stuhr, D. Steinbinder, H. Wipf, B. Frick, Europhys. Lett. 20 (1992) 117.

[5] U. Kaess, G. Majer, M. Stoll, D.T. Peterson, R.G. Barnes, J. Alloys Comp. 259 (1997) 74.

[6] J. Völkl, Ber. Bunsenges. Phys. Chem. 76 (1972) 797.

[7] G. Alefeld, J. Völkl, G. Schaumann, Phys. Stat. Sol. 37 (1970) 337.

[8] T. Schober, H. Wenzl, in: G. Alefeld, J. Volkl (Eds.), Topics in Applied Physics, Hydrogen in metals II, Vol. 29, Springer-Verlag, Berlin, 1978, p. 11.

[9] A. San-Martin, F.D. Manchester, Bull. Alloy Phase Diagrams 8 (1987) 30.

[10] R. Kutner, Phys. Lett. 81A (1981) 239.

[11] J. Haus, K.W. Kehr, Phys. Rep. 150 (1987) 263.

[12] U. Knell, H. Wipf, G. Lautenschläger, R. Hock, H. Weitzel, E. Ressouche, J. Phys.: Condens. Matter 6 (1994) 1461.

[13] Y. Sugizaki, S. Yamaguchi, J. Alloys Comp. 231 (1995) 126.

[14] P. Dantzer, J. Phys. Chem. Solids 44 (1983) 913.

[15] H. Peisl, in: G. Alefeld, J. Völkl (Eds.), Topics in Applied Physics. Hydrogen in Metals I, Vol. 28, Springer, Berlin, 1978, p. 53.