# Existence of Superdiffusion of Hydrogen in Vanadium

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Using an electromigration-relaxation method, we determined the diffusion coefficient $D$ of interstitial hydrogen in homogeneously strained monocrystalline and polycrystalline vanadium samples. In sharp contrast to Suzuki *et al.*, who claimed to have observed superdiffusion due to stress-induced delocalization of hydrogen, we find that within experimental error $D$ remains constant for uniaxial stresses in the [111] direction up to 115 MPa. The "superdiffusion" of Suzaki *et al.* is probably due to an inadequate analysis of their experimental data.

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A few years ago Suzuki *et al.*[1,2] reported on the observation of superdiffusion of hydrogen in vanadium single crystals stressed in the [111] direction. A 25-fold increase in the diffusion coefficient occurred above a critical stress $\sigma_c \cong 35$ MPa at room temperature. According to Suziki *et al.*, superdiffusion results from a delocalization of hydrogen over four neighboring tetrahedral ($4T$) sites. If the stress is applied in the [111] direction a three-dimensional network of delocalized $4T$ states is formed. Without any quantitative evaluation the authors conclude that tunneling of hydrogen atoms along this network results in a strongly enhanced diffusion.

In two Comments, one by Metzger[3] on the evaluation of the x-ray data, and another by Schober and Golczewski[4] on the diffusion data, the results of Suzaki *et al.* were questioned. Although Schober and Golczewski carried out Gorsky-relaxation measurements on vanadium crystals subjected to a longitudinal strain in addition to the bending strain required for this type of measurements, their results neither confirmed nor completely excluded the existence of superdiffusion.[5]

The controversy around the existence of superdiffusion stimulated various workers to investigate the behavior of hydrogen in strained vanadium single crystals. Yagi *et al.*[6] observed in channeling experiments a stress-induced displacement of hydrogen in V from the tetrahedral site, possibly leading to a $4T$ configuration. Matsui, Kubota, and Koiwa[7] studied the effect of stress on hydrogen solubility. Takakusaki, Kajitani, and Hirabayashi[8] observed a redistribution of deuterium atoms in V single crystals under stress by neutron diffraction. Theoretical work was done by Birnbaum and Flynn,[9] who described hydrogen tunneling states within the framework of the theory of diffusion developed by Flynn and Stoneham.[10] A quantum-mechanical treatment of the delocalization of hydrogen in bcc metals has been developed by Fukai and Sugimoto in various papers.[11-13]

Despite these various activities the existence of superdiffusion has remained in dispute until now.

The purpose of our work was to design an experiment that would lead to an unambiguous answer to the existence of hydrogen superdiffusion in vanadium. The experimental method used by Suzuki *et al.*[1,2] suffered from the disadvantage that both the driving force for migration of hydrogen *and* the diffusion enhancement were caused by the *same* parameter: the applied mechanical stress along the [111] axis. As the driving force is directly proportional to the applied stress, they were therefore not able to perform experiments at low strain levels. To evade this disadvantage we use an electric current to create a hydrogen-concentration gradient in a homogeneously strained vanadium crystal. After reaching the steady state, we monitor the relaxation of the hydrogen distribution by resistometric and dilatometric methods and determine the diffusion coefficient of hydrogen in four different sections of the crystal.[14] The measurements can be done at any strain level. At zero stress the reliability of the results obtained by means of our electromigration-relaxation method can be checked on diffusion coefficients obtained from other techniques.

The sample holder shown in Fig. 1(a) is constructed in order to prevent the application of any stress other than in the [111] direction parallel to the sample length. One end of the crystal is clamped in the fixed part of the sample holder; the other end, in the movable part. Two beryllium-copper ring springs allow us to align the fixed and movable part of the sample holder and guarantee a parallel and free movement of the movable part. A reference sample not loaded with hydrogen is used for the compensation of small variations in current ($< 0.1\%$) and temperature ($< 0.02\,°\mathrm{C}/24$ h) in both the resistometric and dilatometric measurements. The temperature is measured with a Pt thermometer. Two current leads and five voltage leads are spot welded to

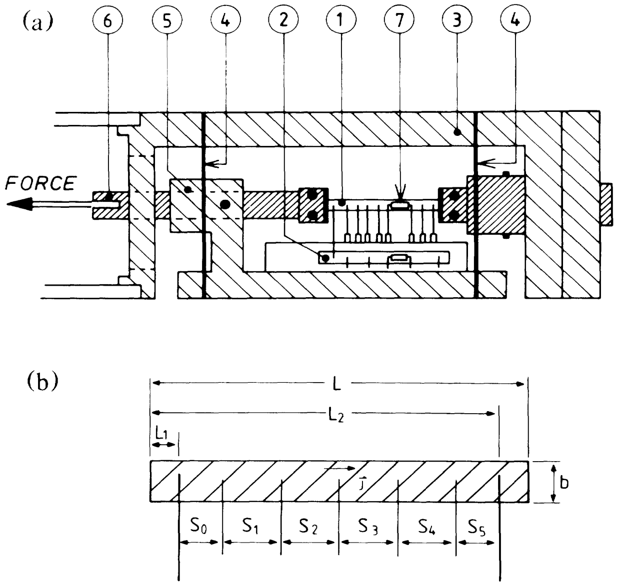

FIG. 1. (a) Experimental assembly consisting of (1) uniformly strained sample with spot-welded contact leads for resistometric measurements over four sections of the sample, (2) reference sample, (3) fixed part of the holder, (4) beryllium-copper ring springs, (5) movable part of the holder, (6) pulling rod, (7) strain gauge. (b) Schematic sample geometry: vanadium crystal with two current and five voltage leads. Typical dimensions for sample V3 are (in mm) $L=21.81$, $L_1=2.98$, $L_2=18.71$, $b=0.92$, $t$ (thickness) $=0.86$, $S_0=2.81$, $S_1=2.68$, $S_2=2.77$, $S_3=2.80$, $S_4=2.49$, $S_5=2.18$.

the crystal [see Fig. 1(b)]. Strain gauges are mounted on both the crystal and the reference sample to measure the (local) dilation induced by the constant force applied from outside the oven or/and by the diffusion of hydrogen.

All samples (designated by V1, V2, and V3) were prepared out of the same polycrystalline rod with a nominal purity of 99.95% by mass. The polycrystalline sample V1 was cut directly out of the rod and had an average grain size of $\sim 5$ $\mu$m. The single crystals V2 and V3 were grown in the [111] direction by the zone-melting technique and cut to the right dimensions by means of spark erosion. V3 was annealed at 1780 K for 70 h in an UHV apparatus at $10^{-8}$ Pa and then cooled down to room temperature in 12 h. Hydrogen loading was done at 720 K in a high-vacuum system. The concentrations of V1, V2, and V3 were 2.26, 2.32, and 0.97 at.% H/V, respectively.

A typical run carried out at a given stress consists of two phases: (i) an electromigration phase and (ii) a diffusion-relaxation phase. In the first phase, hydrogen is driven by electromigration to one end of the sample until a steady state is reached. The time dependence of the resistivity of the four sections of the sample in the electromigration phase is shown in Fig. 2(a). As the effective charge number of H in V is positive,[15,16] the hydrogen atoms move in the direction of the current. In the steady state, the average concentration of hydrogen is 0.77 at.% in section $S_1$ and 1.16 at.% in the section $S_4$ (sample V3, $T=312$ K, $\sigma=0$ MPa, $j=384$ A/cm$^2$). In the second phase of the experiment the electric current is switched off and hydrogen diffuses back until a homogeneous concentration is reached in the sample [see Fig. 2(b)].

An important conclusion which can immediately be drawn without any specific analysis from the curves in Figs. 2(a) and 2(b) is that both processes, i.e., electromigration and diffusion relaxation are *independent* of the applied stress. For a quantitative analysis of our data, we need, however, to consider the electromigration and diffusion-relaxation processes in more detail. In the steady state of the electromigration experiment, assuming a constant electric field $E$ over the sample length, we can write for the chemical potential $\mu$ of hydrogen at positions $x_1$ and $x_2$

$$\mu(x_1)-\mu(x_2)=Z^*eE(x_1-x_2), \tag{1}$$

where $e$ is the positive elementary charge and $Z^*$ the effective charge number of H in vanadium; $\mu$ depends on position through the local hydrogen concentration $c(x)$. For small H concentrations the chemical potential is well described by

$$\mu(x)=-kT\ln[c_m/c(x)-1]+\epsilon c(x)+\epsilon_0, \tag{2}$$

where $\epsilon_0$ is the energy of an isolated hydrogen atom at a tetrahedral site. The blocking factor $c_m$ ($\cong 78$ at.%) takes into account short-range repulsive interactions and $\epsilon$ ($\cong -2.8$ meV/at.%) is a mean interaction energy between the hydrogen atoms. Using Eqs. (1) and (2) we can determine $Z^*$ from the steady-state concentration profile. Once $Z^*$ is known, the diffusion coefficient $D$ can be determined from the time dependence of the diffusion-relaxation experiment.

Solving the differential equation[17] for free diffusion under the appropriate initial and boundary conditions, we find

$$\begin{aligned} c(x,t)&=\frac{L_1c_1}{L}+\frac{c_1-c_2}{LS}+c_2\left[\frac{L-L_2}{L}\right]+\sum_{n=1}^{\infty}G(n)\cos\left[\frac{n\pi x}{L}\right]e^{-Dn^2\pi^2t/L^2},\\ G(n)&=\frac{2L^2S^2}{n^2\pi^2+L^2S^2}\left[\frac{c_1}{n\pi}\sin\alpha-\frac{c_2}{n\pi}\sin\beta+\frac{c_1}{LS}\cos\alpha-\frac{c_2}{LS}\cos\beta\right].\end{aligned} \tag{3}$$

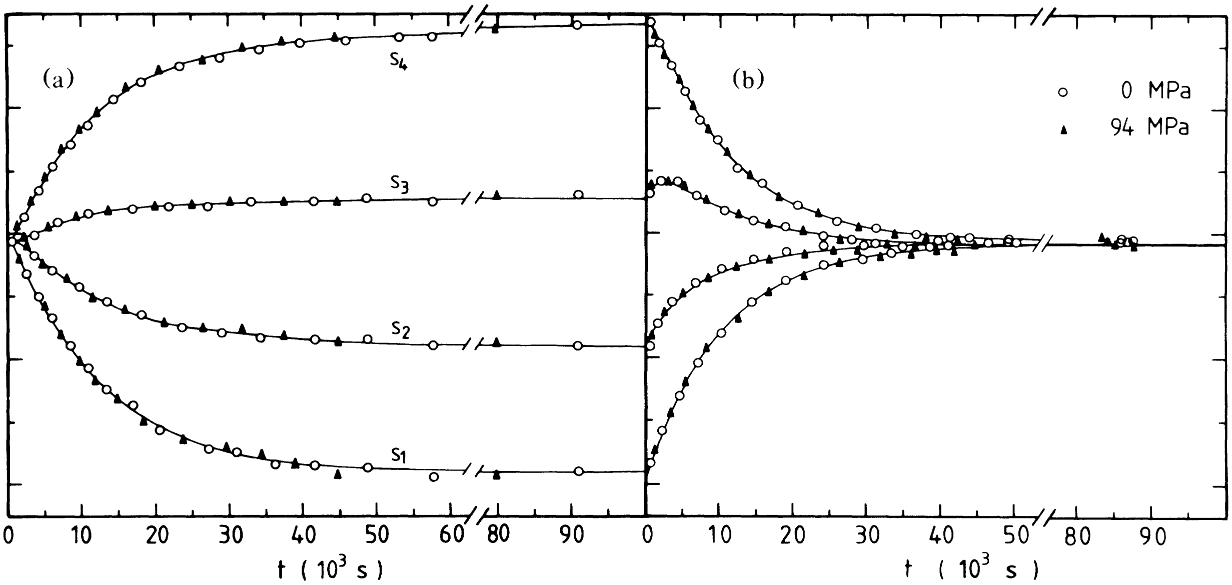

FIG. 2. (a) Electromigration data as a function of time (sample V3, 312 K, $j=384$ A/cm$^2$) for $\sigma=0$ MPa and $\sigma=94$ MPa. The lines are guides to the eye. (b) Diffusion-relaxation data as a function of time (sample V3, 312 K) for $\sigma=0$ MPa and $\sigma=94$ MPa. The lines are fits to the data.

$S=-Z^*eE/(c\,\partial\mu/\partial c)$, $\alpha=n\pi L_1/L$, $\beta=n\pi L_2/L$, $L$ is the sample length, $L_1$ and $L_2$ are the positions of the current leads, $c_1$ is the concentration at $L_1$ and $c_2$ at $L_2$ in the steady state of the electromigration experiment [see Fig. 1(b)]. The parameter $S$ can be determined, because the value of $Z^*$ is known from the electromigration experiment and $\partial\mu/\partial c$ can easily be calculated by means of Eq. (2). The macroscopic diffusion coefficient is obtained by fitting Eq. (3) to experimental curves such as those shown in Fig. 2(b). The quality of the fit is excellent for all four sections. Tracer-diffusion coefficients[18] as a function of the applied stress $\sigma$ for the samples V1, V2, and V3 at different temperatures are plotted in Fig. 3. The diffusion coefficients at $\sigma=0$ are in agreement with values found by Freudenberg.[18] As expected from the direct inspection of the experimental curves, $D$ remains constant up to an applied stress of 115 MPa for three different samples at temperatures between 300 and 400 K. We conclude thus that superdiffusion of hydrogen does not take place in vanadium crystals homogeneously strained in the [111] direction.

There still remains the interesting question of why Suzuki *et al.* arrived at another conclusion and claimed to have discovered superdiffusion. As mentioned above the experimental method of Suzuki *et al.* suffers from some experimental problems. They use a complicated sample geometry and the applied stress serves both to strain the sample *and* to induce diffusion of hydrogen. Their method is inherently inapplicable at low stress levels. Another source of error originates probably from the analysis of their experimental data which is based on the use of the equation

$$\Delta c(x,t)=4kt\{i^2\mathrm{erfc}[x/2(Dt)^{1/2}]\} \tag{4}$$

for the diffusion in a semi-infinite medium with a constant plane source at $x=0$, i.e., $c(0,t)=kt$. The use of this equation is certainly not justified for their experimental configuration and leads to a divergence at $t=\infty$, in disagreement with their data which seem to saturate for $t\gtrsim 2000$ s. As shall be discussed elsewhere[19] the solution of the diffusion equation satisfying the boundary

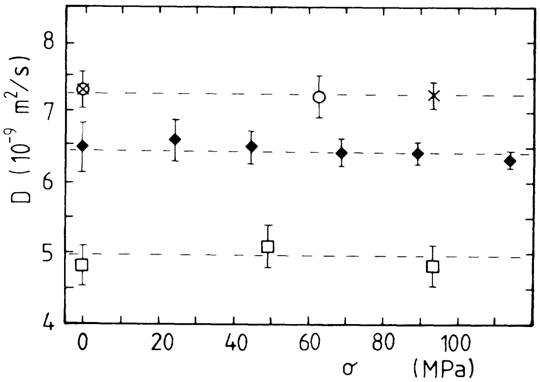

FIG. 3. Tracer-diffusion coefficients as a function of the applied stress. Open circles, polycrystalline vanadium V1 (395 K, 2.26 at.% H/V); closed lozenges, single-crystal V2 (361 K, 2.32 at.% H/V); open squares, single-crystal V3 (312 K, 0.97 at.% H/V); crosses, single-crystal V3 (397 K, 0.97 at.% H/V). The lines are guides to the eye.

and initial conditions appropriate to the experiment of Suzuki *et al.* is given by

$$c(x,t)=c_0\left(1-\frac{\Delta\mu}{kT}\right)+\frac{4c_0\Delta\mu}{\pi kT}\sum_{n=0}^{\infty}\left(\frac{1}{2n+1}\right)\sin\left(\frac{(2n+1)\pi x}{2L}\right)\exp\left[-Dt\left(\frac{(2n+1)\pi}{2L}\right)^2\right], \tag{5}$$

where $\Delta\mu$ is the change in the chemical potential caused by the dilatation of the thin part (of length $L$) of their sample (shown in Fig. 2 of Ref. 1) and $c_0$ is the equilibrium concentration. For $x>0$ a fit of Eq. (5) to their data (Fig. 9, Ref. 2) leads to values for $D$ which agree well with those of Freudenberg and those found in this work.

In conclusion, we have found that electromigration and diffusion experiments on monocrystalline and polycrystalline vanadium at various temperatures, various hydrogen concentrations, and at low and high strain levels do not show any influence of the stress on the diffusion coefficient within 5%. Reanalysis of the results of Suzuki *et al.*[1] by means of an appropriate solution of the diffusion equation of hydrogen in their sample leads to normal values for the diffusion coefficient. We conclude, therefore, that superdiffusion of hydrogen in vanadium strained along the [111] direction does not occur.

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