Correlated Electromigration of H in the Switchable Mirror $YH_{3-\delta}$

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Electromigration of hydrogen in $YH_{3-\delta}$ is studied by exploiting the H concentration dependence of the optical transmission of $YH_{3-\delta}$. We find the effective valence Z^* of H in $YH_{3-\delta}$ to be negative. Its value is dominated by a huge wind-force-like term, i.e., $Z^* \approx K/\rho$, with $K \sim -60$ mΩ cm. This value is 3 orders of magnitude larger than typical for H in metals. In an Arrhenius plot, the ratio of hydrogen and electron fluxes extrapolates to unity at infinite temperature, suggesting a one-to-one correlation of hydrogen and electron hopping. We discuss our results in the light of strong electron correlation theories which predict each proton to bind two electrons in a sort of Zhang-Rice singlet.

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An electric field applied to a solid causes a diffusive flow of atoms. This process, referred to as electromigration, has been the subject of continuous research for two very different reasons. Concerning technology, electromigration is a serious problem as it causes interconnecting lines in integrated circuits to fail. Concerning theory, there has been a long-lasting controversy about the force experienced by an impurity in a metal carrying an electrical current. Two contributions are usually considered [1]: (i) the "direct" force $\mathbf{F}_d = Z_d e\mathbf{E}$ due to the field $\mathbf{E}$ acting directly on the impurity. The size of Z_d has been under debate ever since it was claimed that the charge of an interstitial impurity in a metal is completely screened [2]; (ii) the "wind" force $\mathbf{F}_{\rm wind} = Z_{\rm wind} e\mathbf{E}$ due to a net momentum transfer by scattering charge carriers. The theory of the wind force is well established and in general one finds $Z_{\rm wind} = K/\rho$, where ρ is the total resistivity and K is approximately constant. Experimentally, one determines the quantity $Z^* = Z_d + Z_{\rm wind}$, so that any information on Z_d and $Z_{\rm wind}$ is to be found from the dependence of Z^* on ρ.

For a fundamental study of electromigration, metal hydrides are model systems as H occupies interstitial sites so that its diffusion process is simple and H is highly mobile [3,4]. In metallic hydrides such as PdH_x, VH_x, NbH_x, and TaH_x, hydrogen behaves as a partially screened proton ($0 < Z_d \lessapprox 1$), while K is typically between 10 and 100 $\mu\Omega$ cm [5–8]. In this study we consider electromigration of H near a metal-insulator (MI) transition using the switchable mirrors recently discovered by Huiberts *et al.* [9]. In these materials [YH_x, LaH_x and the rare earth (RE) hydrides [10]] a spectacular change in optical and electrical properties takes place with increasing H content. In YH_x, both the hcp α-phase ($YH_{x<0.21}$) and fcc β-phase ($YH_{1.8<x<2.1}$) are metallic, whereas the hcp γ-phase ($YH_{x>2.7}$) is transparent with an optical gap of 2.6 eV [11–13]. The precise nature of the insulating ground state has been a subject of recent debate. Two different schools emerged in 1997, one considering a Peierls-like distortion [14] and one assuming strong electron correlations [15,16]. Very recently, calculations in the GW approximation were performed, yielding an insulating ground state for $YH_{3-\delta}$ [17]. It is of special interest to investigate electromigration of H in $YH_{3-\delta}$, not only because future devices will be electrically switched [18], but also because strong correlation effects are expected to be important.

In this Letter we extend the optical method of Den Broeder *et al.* [19] to study migration of hydrogen vacancies in $YH_{3-\delta}$. Our samples are prepared as follows. First, a 200 nm, polycrystalline Y film is e-gun evaporated on a sapphire substrate ($T_{\rm sub} = 293$ K, $p_{\rm base} = 5 \times 10^{-9}$ mbar). Subsequently, a 30 nm Pd strip is deposited, covering the Y only partly. The uncovered Y is superficially oxidized in air, resulting in a thin oxide layer, which inhibits H_2 dissociation and recombination [19,20]. The sample is mounted in a chamber equipped with optical windows, temperature control, and electrical leads. The chamber is placed onto the positioning table of an optical microscope (Olympus BX60F5) and 1 bar of H_2 gas is introduced. Using a method described elsewhere, we hydrogenate the entire film to the γ phase via the Pd strip [21]. To study migration, some H is removed from the film, either by lowering the H_2 pressure (at constant temperature) or by increasing the temperature (at constant p_{H_2}), staying well above the β-γ plateau [11,12]. In both cases H leaves the oxide-covered part of the sample by migrating laterally towards the Pd-covered region, where it recombines to form H_2. This results in a small, vacancy-rich region beneath the oxide top layer. Our experiment starts when the initial temperature and H_2 pressure are restored. Within a few seconds, the Pd-covered part of the film returns to its original H concentration, but there is still an area beneath the oxide cap that contains extra vacancies. It serves as the initial distribution of our study of lateral electromigration of H vacancies (see Fig. 1a). Since the optical transmission $T_{\rm opt}$ of $YH_{3-\delta}$ decreases when H is taken out, the

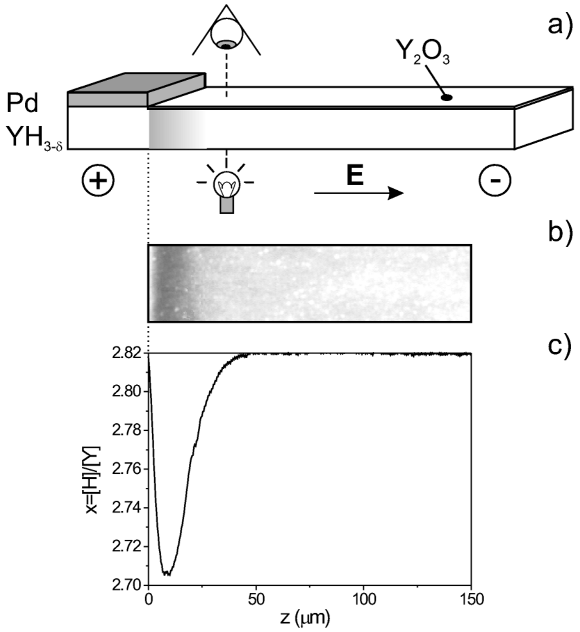

FIG. 1. Experimental procedure. (a) Sample configuration. In a 200-nm $YH_{3-\delta}$ film covered on the left by a 30-nm Pd strip, a small amount of H is removed from the oxide-capped region. In 1 bar H_2 the H deficient region (darker in optical transmission) serves as initial distribution in an electromigration experiment. Note that H can enter or leave the sample only via the Pd strip. An electric field pointing to the right is applied. (b) Optical transmission photograph of the initial ($t_0 \equiv 0$) vacancy distribution in sample 1 at 70 °C. For clarity, the contrast is enhanced and the Pd-covered part is not shown. (c) Local H concentration $x \equiv [H]/[Y]$ vs distance from the Pd edge z, as inferred from (b) and Ref. [12].

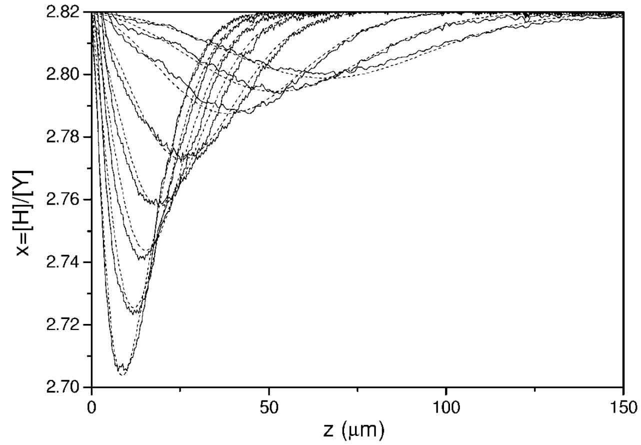

FIG. 2. Evolution of the local H concentration at 70 °C and with $j = 2.5 \times 10^3$ A/cm^2 (sample 1). The experimental curves (solid) are taken at $t_i = 0$, 62, 155, 279, 527, 1085, 1705, and 2387 s, for $i = 0, \ldots, 7$. The dashed curves are fits to the data based on Eq. (2), using constant parameters $D = 1.85 \times 10^{-9}$ cm^2/s and $v_0 = 19.5$ nm/s.

vacancy-rich region is observed as a somewhat darker area of the sample (see Fig. 1b). This allows us to determine the *local* H concentration in the film from the *local* reduction of the transmission (see Fig. 1c) [11,12]. The actual H concentration c is related to x in YH_x by $c = xN_A/V_m^\gamma$ where N_A is Avogadro's number and V_m^γ is the γ-phase molar volume. In Fig. 2 we show the evolution of the hydrogen distribution in Fig. 1c in the presence of an electric field (sample 1, current density $j = 2.5 \times 10^3$ A/cm^2, $T = 343$ K). We observe that: (i) the perturbation moves towards the $(-)$ pole and (ii) the distribution spreads out as a result of diffusion.

Theoretically, the hydrogen flux J_H is given by $J_H = -L(\nabla\mu - Z^* eE)$ [5], where L is related to the Fickian diffusion coefficient by $D = L \cdot \partial\mu/\partial c$, and μ is the chemical potential of H in YH_x. Using the continuity equation as well as $Z^* = Z_d + K/\rho$ and $E = \rho j$, we find in one dimension:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial z}\left[D\frac{\partial c}{\partial z}\right] - \frac{\partial}{\partial c}\left[\frac{D}{\partial\mu/\partial c}\left(Z_d + \frac{K}{\rho}\right)e\rho j\right]\frac{\partial c}{\partial z}, \tag{1}$$

where z is the lateral distance from the Pd-strip edge (see Fig. 1). Note that D, $\partial\mu/\partial c$, and ρ are in principle dependent on c. The concentration dependence of D can be deduced explicitly from Fig. 2, using $[\partial c/\partial t]_{z=z(c_{\min})} = D(c_{\min}) \cdot [\partial^2 c/\partial z^2]_{t=t_i}$ at the minimum of every curve. As we find D to be essentially constant, Eq. (1) simplifies to

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial z^2} - v(c)\frac{\partial c}{\partial z}, \tag{2}$$

with

$$v(c) \equiv Dej\frac{\partial}{\partial c}\left[\frac{(\rho Z_d + K)}{\partial\mu/\partial c}\right]. \tag{3}$$

Although $\mu(c)$ for $YH_{3-\delta}$ deviates markedly from ideal lattice gas behavior [12], and ρ is strongly dependent on c due to the MI transition, the curves in Fig. 2 are surprisingly well described by Eq. (2) using *constant* $v(c) \equiv v_0$. To demonstrate this we solve Eq. (2) for constant v_0 and D, using boundary conditions $c(z = 0, t) = c(z = \infty, t) \equiv c_{\max} \approx 2.82$ [12] and an initial distribution $c_0(z)$ which is a fit to the first experimental curve $c(z, t_0)$ [22]. As shown in Fig. 2, all concentration profiles $c(z, t_{i>0})$ are well reproduced using $v_0 = 19.5$ nm/s and $D = 1.85 \cdot 10^{-9}$ cm^2/s. Direct confirmation of the negligible concentration dependence of v is found by applying Eq. (2) at the inflexion point of every curve in Fig. 2.

In total, we performed 11 experiments on two samples at temperatures between 292 and 408 K. Both v_0 and D exhibit Arrhenius behavior, the latter with activation energy $E_a = 0.45 \pm 0.03$ eV (see Fig. 3a), a value comparable to the estimate obtained from NMR measurements by Balbach *et al.* (0.5 ± 0.1 eV) [23].

We proceed by showing that the velocity $v(c)$ is dominated by the K term. For this we rewrite Eq. (3) as $v_0/Dej = Z_d\zeta(c) + K\xi(c)$, defining $\zeta(c) \equiv \partial/\partial c[\rho \cdot (\partial\mu/\partial c)^{-1}]$ and $\xi(c) \equiv \partial/\partial c[(\partial\mu/\partial c)^{-1}]$.

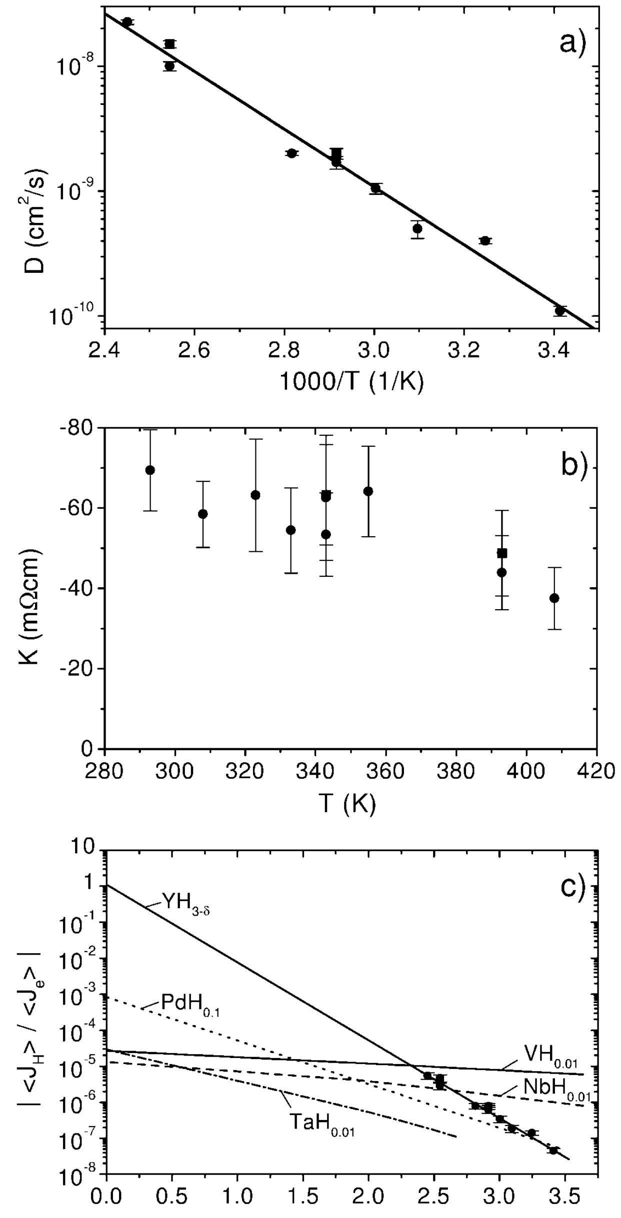

FIG. 3. (a) Arrhenius plot of D from experiments at various temperatures (circles: sample 1, $j = 2.5 \times 10^3$ A/cm^2; squares: sample 2, $j = 5.0 \times 10^3$ A/cm^2). (b) "Wind force" coefficient K vs temperature. (c) Arrhenius plot of $|\langle J_H\rangle/\langle J_e\rangle|$ for electromigration in several MH$_x$ systems. Symbols and line: this work on YH$_{3-\delta}$; dotted line: PdH$_{0.1}$ [6]; solid line: VH$_{\approx 0.01}$ [4,7]; dashed line: NbH$_{\approx 0.01}$ [4,7]; and dash-dotted line: TaH$_{\approx 0.01}$ [4,7].

Extrapolating the room temperature expressions $\rho(c, T_{\text{room}})$ and $\mu(c, T_{\text{room}})$ determined by Kooij *et al.* to the entire temperature range [12], we find that the ratio of ζ and v_0/Dej is smaller than 0.16 for all temperatures. As $|Z_d| \lesssim 1$ for H, we can neglect the ζ term in Eq. (3), so that $K\xi \approx v_0/Dej$. In Fig. 3b, K is shown for the temperature range considered here. Typically, $K \sim -60$ mΩ cm, which is more than 3 orders of magnitude larger than for any other metal-hydrogen system [24].

It is illuminating to view this surprising result from a different perspective. Let us define $\langle J_H\rangle$ and $\langle J_e\rangle$, the sample averaged hydrogen and electron particle flux, respectively. Making use of $Z^* = K/\rho$ and of the boundary conditions $c(z = 0, t) = c(z = \infty, t) \equiv c_{\max}$, we have $\langle J_H\rangle = LZ^*eE \approx -LKe^2\langle J_e\rangle$, where $\langle J_e\rangle = J_e = j/(-e)$. Using $v_0 \approx DKej\xi$, $D = L\partial\mu/\partial c$ and the definition of ξ, we determine the ratio of both fluxes:

$$\left|\frac{\langle J_H\rangle}{\langle J_e\rangle}\right| = \frac{DZ^*e^2\rho}{\partial\mu/\partial c} \approx \frac{ev_0}{j} \cdot \alpha(c), \qquad (4)$$

where $\alpha(c) \equiv (\partial\mu/\partial c) \cdot (\partial^2\mu/\partial c^2)^{-1}$ is calculated from the data of Kooij *et al.* [12]. Figure 3c shows an Arrhenius plot of $|\langle J_H\rangle/\langle J_e\rangle|$. Remarkably, in the limit of $1/T \to 0$, this ratio is of order unity, suggesting a one-to-one relationship between electron and hydrogen hopping when $k_BT > E_a$. For comparison we also show $|\langle J_H\rangle/\langle J_e\rangle|$ for the archetypical, metallic MH$_x$ systems (PdH$_x$, VH$_x$, NbH$_x$, and TaH$_x$) using the middle part of Eq. (4) and the noninteracting lattice gas expression for μ. The data are obtained from Ref. [6] (PdH$_{0.1}$), and a combination of Ref. [4] [$D(T)$ of H in V, Nb, Ta] and Ref. [7] (K and Z_d in VH$_{0.01}$, NbH$_{0.01}$, TaH$_{0.01}$). As seen in Fig. 3c, the extrapolated values of $|\langle J_H\rangle/\langle J_e\rangle|$ for the metallic MH$_x$ systems never exceed 10^{-3}. We conclude that, concerning electromigration, there is a fundamental difference between metallic hydrides and YH$_{3-\delta}$.

To discuss our results we first examine the properties of H vacancies in YH$_{3-\delta}$. In principle, one expects a vacancy to act as an electron donor. However, comparing YH$_{3-\delta}$ to conventional doped semiconductors (e.g., Si:P), the critical donor concentration δ_c needed for a MI-transition is anomalously high (≈ 0.2 for YH$_{3-\delta}$ cf. $\sim 10^{-3}$ for Si:P). This led Ng *et al.* to investigate the electronic structure of a H vacancy in LaH$_3$. Their calculation yields that an electron is trapped in an s-like vacancy orbital with binding energy $E_{\text{trap}} \approx 0.4$ eV, consistent with the large value of δ_c [15]. Hall measurements, on the other hand, show that the ratio of conduction electrons to H vacancies ($\sim 0.2\%$) is almost independent of temperature [25,26].

As our experiments are done close to the metal-insulator transition, for a discussion we approach the system both from the metallic side and insulating side. First we consider YH$_{3-\delta}$ as a "bad" metal and apply electromigration theory developed for metals. For an estimate of K, we use the first order approximation $Z_{\text{wind}} = K/\rho \approx -nl\sigma_{\text{cross}} = -p_F\sigma_{\text{cross}}/\rho e^2$, where n, l, and σ_{cross} represent the charge carrier density, mean free path, and impurity scattering cross section, respectively [1,2,27]. Using the free electron expression $p_F \approx -\hbar(3\pi^2 n)^{1/3}$ with $n \sim 10^{25}$ m^{-3} [25,26], and $\sigma_{\text{cross}} \sim 3$ Å^2, we obtain $K \sim -10$ μΩ cm. This is in flagrant disagreement with our results.

Next we treat the hypothetical case of $YH_{3-\delta}$ being a purely ionic system with Y^{3+}, Y^{2+}, and H^- ions as well as H vacancies. As Y is virtually immobile, one expects $Z^* = -1$ for H. On the other hand, if electrons are present (via $Y^{2+} \rightarrow e^- + Y^{3+}$), $|Z^*|$ can decrease considerably. This has been demonstrated by Yoo *et al.* for $Co_{1-\delta}O$, in which Co vacancies and electron holes are the mobile species [28]. Since our experiments yield $|Z^*| > 1 \geq |Z_d|$, our results are not consistent with either of these possibilities (for both $|Z^*| \leq 1$) [29].

The inapplicability of the foregoing models is probably related to the peculiarities of the electronic structure of the group III and rare earth trihydrides. From the position of Y and La in the periodic table, it is already evident that YH_3 (and all REH_3) is (are) on the borderline between ionic (e.g., MgH_2, CaH_2, and BaH_2) and metallic compounds (e.g., VH and PdH). This is confirmed by the view of Ng *et al.* and Eder *et al.* in which two electrons are bound by each proton [15,16]. One electron is at approximately 0.5 Å from the proton, while the other is "racetracking" among the nearest neighbor metal atoms. The singlet formed by these two electrons is similar to the Zhang-Rice singlet coupling two holes in the CuO planes of high-T_c superconductors [30]. In this picture, H in Y resembles a negative H ion with a huge ionic radius. It is conceivable that such an entity migrates according to the following two-step scenario: first, the H^- ion donates its outer electron; second, it hops as a neutral entity to a neighboring vacancy where it recaptures an electron. Therefore, the hydrogen and electron particle fluxes are coupled in a natural way, offering a qualitative explanation for Fig. 3c [31]. This highly speculative picture needs, of course, to be confirmed by detailed calculations of the diffusion process within a strong correlation theory.

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