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., $Z^* = K/\rho$, with $K \approx -60$ 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 interconnects 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 $F_d = Z_d e E$ due to the field $E$ 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 $F_{\text{wind}} = Z_{\text{wind}} e E$ due to a net momentum transfer by scattering charge carriers. The theory of the wind force is well established and in general one finds $Z_{\text{wind}} = K/\rho$, where $\rho$ is the total resistivity and $K$ is approximately constant. Experimentally, one determines the quantity $Z^* = Z_d + Z_{\text{wind}}$, so that any information on $Z_d$ and $Z_{\text{wind}}$ is to be found from the dependence of $Z^*$ on $\rho$.

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 ($0 < Z_d \lesssim 1$), while $K$ is typically between 10 and 100 $\mu$Ω 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 $\alpha$-phase (YH$_{x<0.21}$) and fcc $\beta$-phase (YH$_{1.8<x<2.1}$) are metallic, whereas the hcp $\gamma$-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 Broder 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 ($T_{\text{sub}} = 293$ K, $p_{\text{base}} = 5 \times 10^{-9}$ 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 $p_{\text{H}_2}$), staying well above the $\beta$–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 $T_{\text{opt}}$ of YH$_{3-\delta}$ decreases when H is taken out, the
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
\[
c = xN_A/V_y,\]
where \( N_A \) is Avogadro’s number and \( V_y \) is the \( y \)-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
\[
J_H = -L(\nabla \mu - Z^* eE),
\]
where \( L \) is related to the Fickian diffusion coefficient by
\[
D = L \cdot \mu / \partial c,
\]
and \( \mu \) 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:
\[
\frac{\partial c}{\partial t} = \frac{\partial}{\partial z} \left[ D \frac{\partial c}{\partial z} \right] - \frac{\partial}{\partial c} \left[ \frac{D}{\partial \mu / \partial c} \left( Z_d + \frac{K}{\rho} \right) e \rho j \right] \frac{\partial c}{\partial z},
\]
(1)
where \( z \) is the lateral distance from the Pd-strip edge (see Fig. 1). Note that \( D \), \( \partial \mu / \partial c \), and \( \rho \) are in principle dependent on \( c \). The concentration dependence of \( D \) can be deduced explicitly from Fig. 2, using
\[
\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial z^2} - v(c) \frac{\partial c}{\partial z},
\]
with
\[
v(c) = D e j \left[ \frac{(\rho Z_d + K)}{\partial \mu / \partial c} \right].
\]
(3)
Although \( \mu(c) \) for YH\(_{3-\delta}\) deviates markedly from ideal lattice gas behavior [12], and \( \rho \) 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 \( c(z = 0, t) = c_j \), \( c(z = \infty, t) = c_{\text{max}} = 2.82 \) [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 \( c(z, t > 0) \) are well reproduced using \( v_0 = 19.5 \) nm/s and \( D = 1.85 \times 10^{-9} \) cm\(^2\)/s.

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. [23].

We proceed by showing that the velocity \( v(c) \) is dominated by the \( K \) term. For this we rewrite Eq. (3) as
\[
v_0 / D e j = Z_d \xi(c) + K \xi(c),
\]
defining
\[
\xi(c) = \frac{\partial}{\partial c} \left[ \frac{\rho \cdot \partial \mu / \partial c}{\partial c / \partial c} \right] \text{ and } \xi(c) = \frac{\partial}{\partial c} \left[ \frac{\partial \mu / \partial c}{\partial c / \partial c} \right].
\]
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 $\zeta$ and $\nu_0/Dej$ is smaller than 0.16 for all temperatures. As $|Z_d| \ll 1$ for H, we can neglect the $\zeta$ term in Eq. (3), so that $K\xi = \nu_0/Dej$. In Fig. 3b, $K$ is shown for the temperature range considered here. Typically, $K \sim -60$ m$\Omega$ 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 $c(z = 0, t) = c(z = \infty, t) \equiv c_{\text{max}}$, we have $\langle J_H \rangle = L Z^* eE \approx -L K e^2 \langle J_e \rangle$, where $\langle J_e \rangle = J_e = j/(\varepsilon e)$. Using $\nu_0 = D K e j \xi$, $D = L \partial \mu/\partial c$ and the definition of $\xi$, we determine the ratio of both fluxes:

$$\frac{\langle J_H \rangle}{\langle J_e \rangle} = \frac{D Z^* e^2 \rho}{\partial \mu/\partial c} \approx \frac{\nu_0}{f} \cdot \alpha(c),$$

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 $k_B T > E_a$. 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 $\mu$. 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 $\delta_d$ needed for a metal-insulator transition is anomalously high ($\approx 0.2$ for YH$_{3-\delta}$ cf. $\approx 10^{-3}$ 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 $E_{\text{gap}} = 0.4$ eV, consistent with the large value of $\delta_d$ [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 results 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 $Z_{\text{wind}} = K/\rho \approx -n l \sigma_{\text{cross}} = -p_F \sigma_{\text{cross}}/\rho e^2$, where $n$, $l$, and $\sigma_{\text{cross}}$ represent the charge carrier density, mean free path, and impurity scattering cross section, respectively [1,2,27]. Using the free electron expression $p_F = -k(3\pi^2 n)^{1/3}$ with $n \sim 10^{26}$ m$^{-3}$ [25,26], and $\sigma_{\text{cross}} \sim 3$ Å$^2$, we obtain $K \sim 10$ $\mu$Ω 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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[24] Den Broeder et al. anticipated $Z_{\text{wind}}$ to be negligible and concluded $Z_d < 0$. Our results show that $Z^*$ is dominated by $K/p$ so much, that a conclusion on $Z_d$ is not possible.
[29] For all experiments, $p(c) \leq p(c_{\text{max}}(T)) < 15$ mΩ cm.
[31] Note that within this picture, it is not appropriate to call $K/p$ the wind force term; $K$ is just the coefficient connecting electron and H fluxes.