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Brouwer, R.C.; Griessen, R.

published in

Physical Review Letters
1989

DOI (link to publisher)

[10.1103/PhysRevLett.62.1760](https://doi.org/10.1103/PhysRevLett.62.1760)

document version

Publisher's PDF, also known as Version of record

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citation for published version (APA)

Brouwer, R. C., & Griessen, R. (1989). Electromigration of hydrogen in alloys: Evidence of unscreened proton behavior. *Physical Review Letters*, 62(15), 1760-1763. <https://doi.org/10.1103/PhysRevLett.62.1760>

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Electromigration of Hydrogen in Alloys: Evidence of Unscreened Proton Behavior

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(Received 30 January 1989)

In an attempt to resolve the long-lasting controversy about the magnitude of the direct-force valence of impurities in the theory of electromigration, the effective valence, Z^* , for interstitial hydrogen has been determined in concentrated disordered $\text{Nb}_{1-y}\text{V}_y$ alloys. Z^* is found to be almost equal to unity independent of temperature and alloy composition. The important implication of these results is that for hydrogen in $\text{Nb}_{1-y}\text{V}_y$ alloys the direct-force valence is $Z_d = +1$, equal to the charge of the unscreened proton, in agreement with the recent theory of Lodder.

PACS numbers: 66.30.Jt, 66.30.Qa

Electromigration is the transport of (impurity) atoms resulting from the application of an electric field to a metal. Interest in electromigration arises from its use in purifying metals, from its deleterious effect on thin conduction paths in (sub)micron electronic devices, and from interesting fundamental questions.¹⁻⁵

In an electromigration experiment the total force on the migrating (impurity) atom is given by $\mathbf{F} = \mathbf{F}_d + \mathbf{F}_w$, with $\mathbf{F}_d$ the direct force due to the electric field, $\mathbf{E}$, and $\mathbf{F}_w$ the so-called "wind force," which is due to the momentum transfer of conduction electrons scattered by the (impurity) atom. Various microscopic models⁵⁻¹⁵ lead to essentially the same general form for the wind force on an impurity atom in a metal. In its simplest form it can be written as $\mathbf{F}_w = K\mathbf{E}/\rho(T)$, with $\rho(T)$ the temperature-dependent specific resistivity and K a parameter depending on the electronic structure of the metal-hydrogen system.

In contrast to the general agreement between the various microscopic theories for the wind force, a long-lasting controversy exists about the magnitude of the direct force $\mathbf{F}_d$. The direct-force valence Z_d , defined by $\mathbf{F}_d = Z_d e \mathbf{E}$, is assumed to consist of two contributions. The bare valence, Z , of the impurity atom, and a contribution, Z_p , arising from the polarization of the conduction electrons around the impurity atoms ($Z_d = Z + Z_p$). A number of workers,⁹⁻¹¹ starting with Bosvieux and Friedel,⁸ arrived at the conclusion that weakly scattering interstitial atoms in a metal are completely screened ($Z_p = -Z$) and therefore do not feel any direct force ($Z_d = 0$). Calculations, however, by a number of other groups^{12-14,16} showed, also for weak scatterers in a free-electron gas, negligible contributions of Z_p to Z_d ($Z_d = 1$). For a strong scatterer in jellium, Landauer¹⁷ and Sorbello,¹⁸ however, found significant contributions of Z_p . Excellent reviews on electromigration have recently been given by Verbruggen.^{19,20}

Several attempts have been made to determine the direct force from electromigration experiments. Hydrogen in metal proved to be an ideal system, due to the high mobility of the hydrogen atoms (even at low tem-

peratures), and the (relatively) simple lattice-gas behavior of interstitial hydrogen in a metal. In electromigration experiments the total force $\mathbf{F} = Z^* e \mathbf{E}$, where Z^* is the so-called effective valence, is usually determined as a function of temperature. The direct valence, Z_d , is then obtained from a fit by

$$Z^* = Z_d + K/\rho(T) \quad (1)$$

in a Z^* vs $1/\rho(T)$ plot.

Electromigration experiments for hydrogen in V, Nb, and Ta as a function of temperature by Erckmann and Wipf²¹ and Verbruggen and Griessen,²² and as a function of hydrogen concentration by Maier and Wipf,²³ indicated the existence of a nonvanishing direct force $\mathbf{F}_d$. The exact value of Z_d for H in these pure metals remained, however, uncertain, as Z_d had to be determined by means of a rather extreme extrapolation from the range of $1/\rho(T)$ values covered by experiment to $1/\rho = 0$. As discussed by Verbruggen and Griessen,²² the range of $1/\rho$ values available for experiments in these metals is inherently limited (i) on the high-temperature side by the fact that the surface oxide layer which confines hydrogen in the samples becomes permeable above ~ 550 K, and (ii) on the low-temperature side by the coexistence line in the T - x phase diagram. An attractive way to enter the low- $1/\rho$ regime, or equivalent the weak-wind-force regime, is to increase ρ by alloying.

Until now, to our knowledge, no data on electromigration of hydrogen in concentrated alloys existed. In this paper we report on electromigration experiments of hydrogen in concentrated disordered $\text{Nb}_{1-y}\text{V}_y$ alloys, as a function of temperature and alloy composition. The choice of this alloy system is motivated by the following: (i) There have been an extensive number of investigations on solution, diffusion, and electromigration of hydrogen in the pure metals Nb and V. (ii) Nb and V form a complete series of solid solutions, with a bcc crystal structure. The lattice parameters, the elastic moduli, and the electronic specific-heat coefficients show a weak monotonous variation with composition. (iii) Recently a very detailed study of the pressure-composition isotherms

of $\text{Nb}_{1-y}\text{V}_y\text{H}_x$ alloys has been made by Feenstra *et al.*,²⁴ from which the thermodynamic factor $f = (c/kT)d\mu/dc$ can be determined (μ is the chemical potential of hydrogen in a metal and c is the number of hydrogen atoms per metal atom).

The $\text{Nb}_{1-y}\text{V}_y$ alloys are obtained by levitation melting of the appropriate amounts of 99.9% pure Nb and V in an argon atmosphere, and annealing of the buttons a few hours 100 K below their melting points. Electromicroprobe analysis shows a homogeneous distribution of Nb and V in the alloys, with concentration variations smaller than 1 at.% V, in all alloys. Samples with typical dimensions of $1 \times 1 \times 12 \text{ mm}^3$ are cut from the buttons by spark erosion, and loaded homogeneously with approximately 1.5 at.% H at 800 K. Six potential leads and two current leads are spot welded to the sample. For electrical resistance measurements the samples are placed in an oven under an argon atmosphere with a temperature stability of 0.01 K/(24 h).

A typical run²⁵ carried out at a given temperature 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 five sections of the sample is shown in Fig. 1. In the second phase of the experiment the current is switched off (or is alternated) and the hydrogen atoms diffuse back until a homogeneous concentration is reached in the sample. In the electromigration experiment the particle current density is $\mathbf{J} = -nD \times \text{grad}c + ncM\mathbf{F}$, with n the number of metal atoms per unit volume, D the macroscopic diffusion coefficient, c the hydrogen fraction, and M the mobility. The diffusion coefficient D and the mobility M are related by the generalized Einstein equation, $D = c(d\mu/dc)M$. In the steady state, as the chemical potential μ depends on position x only through the concentration $c(x)$, the

FIG. 1. Electromigration of hydrogen in a $\text{Nb}_{0.50}\text{V}_{0.50}\text{H}_c$ sample ($c = 0.0165$, $T = 370 \text{ K}$, $J = 4.1 \times 10^6 \text{ A/m}^2$), monitored by measuring the local resistivities over five sections, s_i , of the sample.

concentration profile is given by

$$c(x) = c(0) \exp[-(Z^*eE/kTf)x], \quad (2)$$

with f the thermodynamic factor. The concentration $c(x)$ is obtained from resistivity measurements through

$$c(x) = c_0 + [\rho(t=0, x) - \rho(t \rightarrow \infty, x)](d\rho/dc)^{-1},$$

with c_0 the equilibrium hydrogen concentration and $\rho(t, x)$ the specific resistivity at time t and position x along the sample. The increase in the specific resistivity by hydrogen, $d\rho/dc$, in pure Nb is $(63 \pm 5) \times 10^{-8} \Omega \text{ m}/(\text{at.}\% \text{ H})$ and in pure V is $(95 \pm 6) \times 10^{-8} \Omega \text{ m}/(\text{at.}\% \text{ H})$, independently of the hydrogen concentration (for $c < 20 \text{ at.}\% \text{ H}$).²⁶ For $\text{Nb}_{1-y}\text{V}_y$ alloys, however, no data exist. We determined $d\rho/dc$ by means of resistivity measurements on $\text{Nb}_{1-y}\text{V}_y$ alloys, loaded electrolytically with hydrogen ($\sim 2 \text{ at.}\%$). The hydrogen concentration is checked by degassing the samples at high temperatures. The resulting $d\rho/dc$ are plotted in Fig. 2 as a function of alloy composition. In alloying V to Nb the contribution of hydrogen to the specific resistivity decreases, goes through a minimum around $y = 0.35$, and increases again. Interpretation of this interesting behavior will be the subject of a forthcoming publication.

Plots of $\ln[c(x)]$ as a function of position x (or potential) yield the exponent Z^*eE/kTf . The thermodynamical factor $f = (c/kT)d\mu/dc$ is obtained from pressure-composition isotherms of Feenstra *et al.*^{24,27} In pure metals at low hydrogen concentrations f is smaller than 1 and increases to 1 with increasing temperature. However, in a $\text{Nb}_{0.75}\text{V}_{0.25}$ alloy, for example, strong site filling effects are observed, and consequently f is larger than 1 and decreases with temperature.^{27,28}

Knowing $d\rho/dc$ and f for $\text{Nb}_{1-y}\text{V}_y$ alloys, Z^* is

FIG. 2. Resistivity change per hydrogen atom ($d\rho/dc$) at 295 K for $\text{Nb}_{1-y}\text{V}_y$ alloys as a function of alloy composition (for $c \sim 0.02$). Considering that most physical properties interpolate almost linearly between Nb and V, an unexpected minimum is observed around $y = 0.35$.

determined in a straightforward manner. In Fig. 3, Z^* is plotted as a function of temperature, for pure Nb ($c=0.011$), V ($c=0.0115$), $\text{Nb}_{0.11}\text{V}_{0.89}$ ($c=0.0167$), $\text{Nb}_{0.25}\text{V}_{0.75}$ ($c=0.0143$), $\text{Nb}_{0.50}\text{V}_{0.50}$ ($c=0.0165$), and $\text{Nb}_{0.75}\text{V}_{0.25}$ ($c=0.0131$). The effective valence Z^* is 1.05 ± 0.05 for all alloys, and independent of temperature. This shows that the wind force is very effectively quenched in alloys and that Z^* in the pure metals V and Nb is most likely tending asymptotically to $Z^* \approx 1$ in the limit of high temperatures, i.e., in the limit of small $1/\rho$.

To exhibit this remarkable result even more clearly Z^* is plotted in Fig. 4 as a function of $(d\rho/dc)/\rho$, which in the spirit of a ballistic model^{6,7} corresponds to the ratio $\rho_i/n_i\rho$, where n_i is the concentration of defects (H) and ρ_i is the contribution of defects to the total resistivity ρ .

The data in Fig. 4 show that a linear extrapolation of Z^* vs $1/\rho$ data as used so far is not adequate and leads to inaccurate values for the direct-force valence Z_d . In the low-wind-force limit, or equivalently when $(d\rho/dc)/\rho$ tends to zero, Z^* saturates to a value very close to unity. In other words, our data show conclusively that in the low-wind-force limit the direct-force valence of an interstitial impurity is equal to the charge of the *unscreened* impurity, i.e., $Z_d=1$ within experimental uncertainties. This is an important result in view of the long-lasting controversy about the magnitude of the direct-force term in the theory of electromigration.

We show now that our results are consistent with the predictions of the theory of electromigration proposed recently by Lodder.²⁹ Using a linear-response approach

developed by Kumar and Sorbello,³⁰ Lodder found that the force acting on an impurity of valence Z_i and of arbitrary scattering strength in jellium is exactly given by

$$\mathbf{F} = Z_i e \mathbf{E} + i \sum_{\nu=1}^3 E_{\nu} \int_0^{1/kT} d\lambda N \text{tr} \{ n(h) \mathbf{j}_{\nu} (-i\lambda) \times [1 - n(h)] R \mathbf{f}_1 \}, \quad (3)$$

where ν indicates the vector component of the force $\mathbf{F}$ or electric field $\mathbf{E}$, $\mathbf{j} \equiv ie[\mathbf{r}, h] = -e\mathbf{p}/m$, $\mathbf{f}_1 \equiv -\nabla_{R_1} v_1$, with v_1 the impurity potential, $n(h)$ the one-particle Fermi-Dirac operator, and h the single-electron Hamiltonian. The resolvent R , describing the dissipation, has entered through the time-Fourier transform of the correlation function expression. The interesting point is that the second term in Eq. (3) splits into a Bosvieux-Friedel wind-force term (essentially $e\mathbf{E}K/\rho$) and a term (Eq. 16 in Ref. 29) approximately of the form $-e\mathbf{E}Z_i(1+a\rho)^{-1}$. In a simplified form Eq. (3) can thus be written as

$$\mathbf{F} = e\mathbf{E} \left[Z_i \left(1 - \frac{1}{1+a\rho} \right) + \frac{K}{\rho} \right], \quad (4)$$

and in the low-resistivity limit ($\rho \rightarrow 0$) the direct-force term vanishes. Thus, in this limit one recovers the result of Bosvieux and Friedel: For an interstitial, only the wind force drives electromigration. In the opposite limit of weak wind force, which pertains to our experimental situation, $Z_d \cong Z_i$ which is equal to unity for a proton. In light of this discussion we see that hydrogen in alloys corresponds to the high-resistivity limit of Lodder's

FIG. 3. Effective valence Z^* for $\text{Nb}_{0.11}\text{V}_{0.89}$ ($c=0.0167$, inverted triangles), $\text{Nb}_{0.25}\text{V}_{0.75}$ ($c=0.0143$, closed circles), $\text{Nb}_{0.50}\text{V}_{0.50}$ ($c=0.0165$, open lozenges), and $\text{Nb}_{0.75}\text{V}_{0.25}$ ($c=0.0131$, closed squares) as a function of temperature. The data for Nb ($c=0.011$, open squares) and V ($c=0.0115$, open circles) are obtained from Ref. 5. The lines are guides to the eye.

FIG. 4. Effective valence Z^* for the $\text{Nb}_{1-y}\text{V}_y$ alloys and pure V, Nb, and Ta as a function of $(d\rho/dc)/\rho$. The data for Nb (open squares), V (open circles), and Ta ($c=0.0108$, open triangles; $c=0.0085$, closed triangles) are from Ref. 5. The data point for Nb at high resistivity ($c=0.0103$, cross) is for a sample with a rather small $\rho(295 \text{ K})/\rho(4.2 \text{ K})$ value of 2.6. The lines are guides to the eye.

theory, while hydrogen in pure Nb and V corresponds probably to an intermediate situation.

In conclusion, we have measured accurately for the first time the effective valence, Z^* , for hydrogen in concentrated disordered $\text{Nb}_{1-y}\text{V}_y$ alloys as a function of temperature. In the $\text{Nb}_{1-y}\text{V}_y$ alloys, a temperature-independent $Z^* = 1.05 \pm 0.05$ is found, indicating a direct-force valence, $Z_d = +1$, equal to the valence of the unscreened (bare) proton. The expected and observed quenching of the wind force in the $\text{Nb}_{1-y}\text{V}_y$ alloys is attributed to the lattice disorder, and the minimum in dp/dc as a function of alloy composition. Results on $\text{Ti}_{1-y}\text{V}_y$ alloys, indicating the same trends as the $\text{Nb}_{1-y}\text{V}_y$ alloys, will be published elsewhere.

We are grateful to Professor A. Lodder for interesting discussions, to Dr. R. Feenstra for the preparation, and to N. Koeman and J. Rector for the analysis of the Nb-V samples. This investigation was part of the research program of the Stichting voor Fundamenteel Onderzoek der Materie, which is financially supported by the Nederlandse Organisatie voor Wetenschappelijk Onderzoek.

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