Experimental evidence for nonintegral direct-force valence in electromigration

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The effective valence number Z^* of hydrogen in VH_x, NbH_x, and TaH_x (with $x \simeq 0.01$) has been measured by means of a new experimental technique. From the temperature dependence of Z^* it is concluded that the valence associated with the *direct* force in electromigration differs significantly from the bare valence of the migrating ion. The results are discussed on the basis of Landauer's work on the carrier-density modulation effect and the very recent theory of Sorbello on the direct force for a strong scatterer in a free-electron gas.

Electromigration[1,2] is the transport of (impurity) atoms or ions resulting from the application of an electric field to a metal. The renewed interest in electromigration arises both from its importance for submicrometer electronics and from intrinsic interesting fundamental problems.

From a theoretical point of view the basic question concerns the nature of the force $\mathbf{F}$ acting on an impurity imbedded in a metal in the presence of a macroscopic (Ohmic) electric field $\mathbf{E}$. Using the linear response formalism[3] Sham[4] and Rimbey and Sorbello[5] found that $\mathbf{F}$ was made up of three contributions:

$$\mathbf{F} = Ze\mathbf{E} + Z_p e\mathbf{E} + \mathbf{F}_{\text{wind}} \; ; \tag{1}$$

Z is the bare valence of the impurity. The second term is the static polarization-field contribution, parametrized by Z_p. $\mathbf{F}_{\text{wind}}$ is the so-called electron wind term which is proportional to both the electric field and the electron relaxation time τ.

There has been a long-lasting controversy[1,2] about the magnitude of the direct-force valence Z_d, defined by $Z_d = Z + Z_p$, for interstitial impurities. On one hand, a number of French workers[6] claimed that $Z_d = 0$, i.e., $Z_p = - Z$, because of complete screening of the impurity by conduction electrons. On the other hand, calculations by Sham,[4] Schaich,[7] and Sorbello and Dasgupta[8] on weak scatterers in a free-electron gas showed that the contribution of the static polarization term $Z_p e\mathbf{E}$ is negligible as compared to the term $Ze\mathbf{E}$, and thus $Z_d = Z$. The existence of a nonvanishing direct-force valence for interstitial impurities is confirmed experimentally by the discovery of a Hall voltage during the diffusion of hydrogen in palladium in a magnetic field (proton-Hall effect), reported very recently by the present authors,[9] and by the work of Erckmann and Wipf[10] on the electromigration of hydrogen in the group-V transition metals. Unfortunately, the results given in Refs. 9 and 10 were not used to establish that the prediction of the calculations cited above, i.e., $Z_p = 0$, is also valid for systems involving strong scatterers, such as hydrogen, in transition metals.

Landauer[11] was one of the first to point out that there might be a fundamental difference between Z_d and the valence of the ion, and that consequently Z_d is not an integer value as was traditionally assumed. By taking into account the modification of the carrier density in the immediate vicinity of a lattice defect, he found that

$$Z_d = \frac{Z}{1 + \frac{1}{3}\beta \Delta n / n_0} , \tag{2}$$

where Δn is the local increase in electron density due to the impurity, n_0 is the average electron density in the metal, and β is an unspecified parameter of order unity.

In a very recent paper Sorbello[12] derived an exact expression for the total electrostatic force acting on a strong scatterer in a free-electron gas in the presence of an electric current. On the basis of model calculations for hydrogen in metals, he concluded that both positive and negative values for Z_p may occur.

The purpose of this Rapid Communication is to provide experimental data which clearly demonstrate the significance of the static polarization term Z_p in the electromigration of hydrogen in metals. To this end we have measured the effective valence Z^*, defined by $\mathbf{F} = Z^* e\mathbf{E}$, of hydrogen in V, Nb, and Ta as a function of temperature, with a new experimental technique.

The method is based on the explicit dependence of the wind force on the relaxation time, which can be written as $F_{\text{wind}} = Ke\mathbf{E}/\rho(T)$, where $\rho(T)$ is the temperature-dependent specific electric resistivity and K is a constant which depends on the impurity potential and the electronic structure of the metal under consideration. The effective valence is then

$$Z^* = Z_d + K/\rho , \tag{3}$$

and Z_d can simply be obtained from a $Z^*(T)$-vs-$1/\rho(T)$ plot, provided Eq. (3) is indeed well obeyed.

A schematic drawing of the apparatus used for electromigration experiments of H in V, Nb, and Ta is shown in Fig. 1. The sample ① is a thin-walled hollow cylinder of 4.3-cm length, 9-mm outside diameter, and 0.25-mm wall thickness. This sample is initially homogeneously loaded with hydrogen. In the temperature range of our experiments the hydrogen is sealed in the sample, because below 300 °C the group-V transition metals form a hydrogen-impermeable surface oxide layer. As soon as the electrical current, fed to the sample at the points ③, is switched on, there occurs a drift of the hydrogen in a direction along or opposite to the electric field, depending on the sign of Z^*. This leads to a gradient in the hydrogen concentration in the sample. Since hydrogen expands the host-metal matrix, the induced concentration differences can be determined from the local changes in diameter, which in turn are obtained from the change in capacitance between the sample and one of the annular capacitor plates ②. The capacitance changes are measured by means of a General Radio 1621 capacitance bridge with a sensitivity of 10^{-7} pF. This corresponds to a
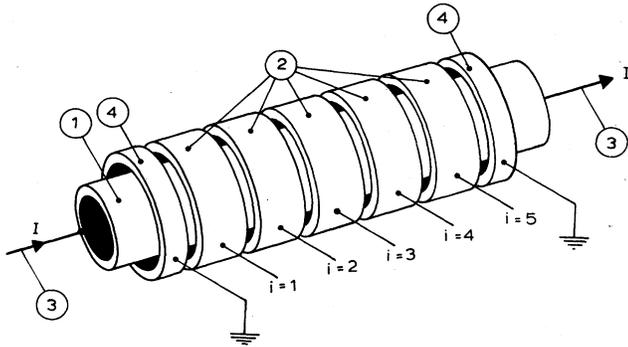
FIG. 1. Schematic scketch of the capacitance multidilatometer for electromigration experiments. ① Thin-walled cylindrical sample, ② annular capacitance electrodes, ③ current leads, and ④ shielding electrodes.

FIG. 2. Plot of $\ln[c(x_i)/c_0]$ vs i for an experiment in $VH_{0.0115}$ at $T = 102.2\,°C$ and $I/S = 158$ A/cm^2. x_i corresponds to the center of the i th capacitance electrode. The distance between the centers of two electrodes is 7.2 mm. c_0 is the initial homogeneous concentration.

few ppm change in local hydrogen concentration. For the conversion of capacitance changes into local hydrogen-concentration changes, we used the values given by Peisl[13] for the relative lattice expansion per atomic percent hydrogen. The lattice expansion varies lineraly with hydrogen content and is independent of temperature. The advantage of dilatation measurements over resistivity measurements is their much smaller sensitivity to temperature fluctuations. A more detailed description of this new multidilatometric technique for electromigration will be given in Ref. 14.

At $t \rightarrow \infty$ a steady state is reached and the induced gradient in the chemical potential μ of the hydrogen is equal to the driving force $\mathbf{F} = Z^*e\mathbf{E}$. If c_0 is the initial homogeneous concentration and L the sample length, it is readily shown that in the steady state the hydrogen-concentration profile is given by

$$\frac{c(x)}{c_o} = \frac{p}{e^p - 1} \exp(px/L) , \qquad (4)$$

where $p = Z^*eEL/(fk_BT)$, f is the thermodynamic factor $[f = (c\partial\mu/\partial c)/(k_BT)]$, k_B is Boltzmann's constant, and T is the absolute temperature. For Nb and Ta, f was obtained from an interpolation of the Gorsky-effect data of Bauer, Völkl, Tretkowski, and Alefeld.[15] For V, f was calculated by using a lattice-gas model for μ with a mean hydrogen-hydrogen interaction energy of 0.17 eV (Ref. 16). The advantage of the steady-state method is that transport quantities such as the diffusion constant or the mobility of hydrogen are not involved in the data evaluation. The effective valence Z^* is obtained from the slope of a $\ln[c(x)/c_0]$-vs-x plot, since

$$Z^* = \frac{fk_BT}{eE} \frac{d}{dx} \ln[c(x)/c_0] . \qquad (5)$$

Experiments have been performed on samples containing about 1 at. % hydrogen between 0 and 250 °C for V and Nb, and between 100 and 250 °C for Ta.

Hydrogen loading of the hollow cylinder was performed at 625 °C by exposing the samples to a hydrogen atmosphere of appropriate pressure. The actual hydrogen concentrations were determined by vacuum extraction at 725 °C after completion of the measurements. An example of a typical run for VH_x at $T = 102.2$ °C is shown in Fig. 2. The hydrogen concentrations measured locally at five different points on
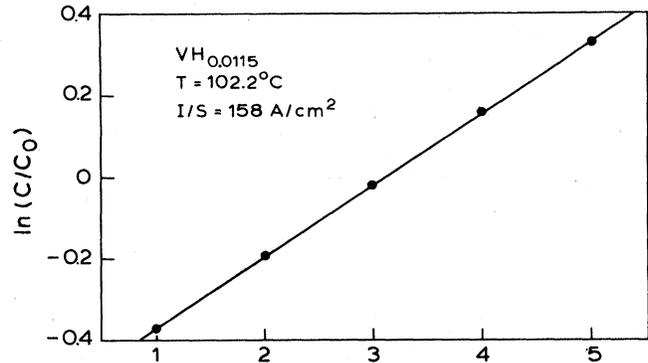
the sample fall almost perfectly on a straight line whose slope corresponds to $Z^* = 1.39$. Experimental results for Ta and Nb as well as additional data, especially on the time dependence of the hydrogen concentration profiles in all three metals, shall be given in Ref. 17.

In Fig. 3 the effective charge number Z^* for H in V, Nb, and Ta is plotted as a function of the reciprocal resistivity. The data are remarkably well described by the relation $Z^* = Z_d + K/\rho$. The parameters obtained from a least-square fit to the data are indicated in Table I. For H in all three metals, Z_d is clearly different from zero, in agreement with the theoretical views of Sorbello,[5,8,12] Sham,[4] Schaich,[7] and Landauer.[18] Especially interesting, however, is that the data in Table I suggest that although Z_d for H in V is very close to the value $Z_d = 1$ expected for a bare proton, sizable deviations are found in Nb and Ta.

In order to establish the significance of these deviations, it is necessary to discuss the accuracy of our experiments in some detail. First of all, we checked that thermomigration did not influence our measurements by carrying out experiments with a low-frequency alternating current instead of a direct current. Within experimental errors, no effect due to inhomogeneous Joule heating could be detected.

As can be seen in Fig. 3, all data points lie within $\Delta Z = 0.05$ from the fitted line. This may be considered as the probable error in our experiment. However, additional systematic errors might have been introduced during the data evaluation. The first one is related to the value of the lattice expansion per atomic percent hydrogen needed for the determination of the hydrogen concentration form the measured capacitance changes. According to Peisl,[13] these errors are 3% for Nb and Ta and 5% for V. In addition to this, we have to take into account an error of 1% resulting from the inaccuracy in the determination of the nominal hydrogen content. The second is concerned with the determination of the macroscopic electric field ($E = I\rho/S$, I is the current, ρ the resistivity, and S the cross-sectional area). In a separate experiment on the actual electromigration samples we measured ρ/S within an accuracy of $\sim 1\%$. With an estimated error of 2% in S, this leads to a 3% uncertainty in electrical resistivity. Another source of error might arise from an eventual temperature dependence of the lattice expansion on hydrogen content. However, especially for hy-
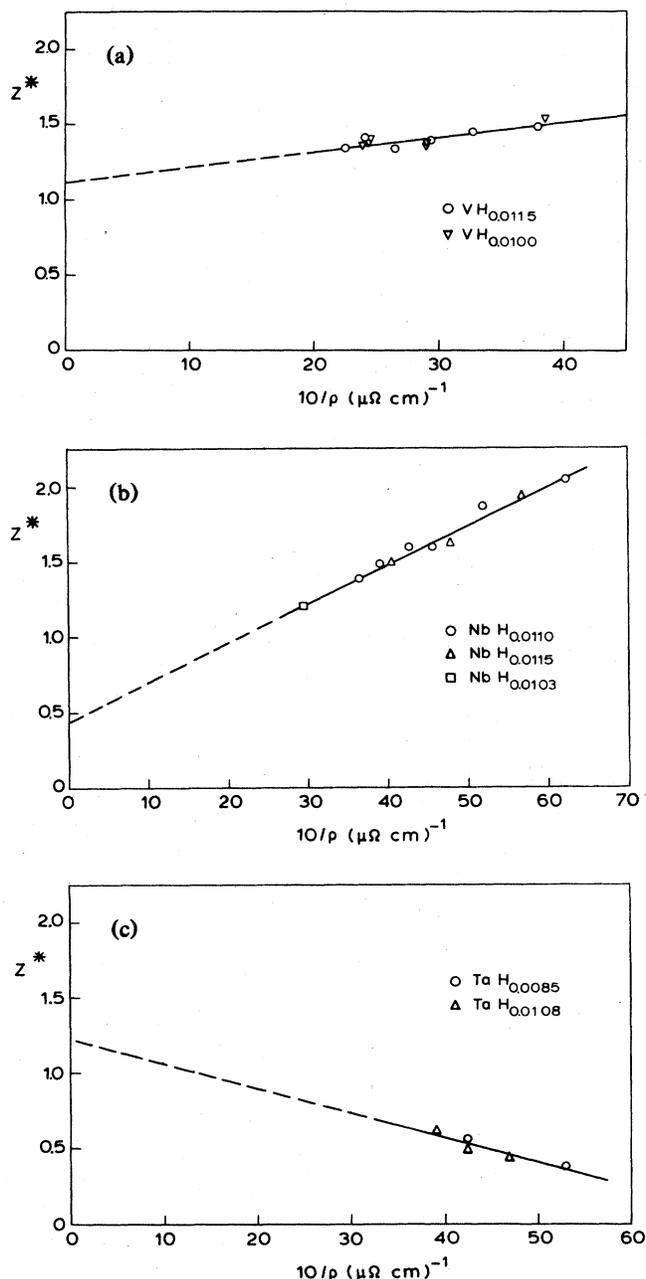
FIG. 3. Effective valence Z^* vs inverse resistivity for hydrogen in (a) V, (b) Nb, and (c) Ta. The lines are least-square fits to the expression $Z^* = Z_d + K/\rho$.

drogen in niobium, there is evidence that this quantity is temperature independent, as the experimental values obtained by Peisl[13] at room temperature are equal to those of Burkel[19] at $T = 200\,°C$. Finally, the error in the thermodynamic factor f is $\sim 1\%$.

All in all, this leads to a relative error in Z_d of approximately 10% for vanadium and tantalum and 20% for niobium. It is important to point out here that accuracy in Z_d cannot be improved by measuring Z^* over a larger temperature range by the steady-state method since (i) on the

TABLE I. Parameters obtained from fits of electromigration data for H in V, Nb, and Ta to the expression $Z^* = Z_d + K/\rho$.

	Z_d	K $(\mu\Omega\,\text{cm})$
V	1.11 ± 0.1	9.9 ± 1
Nb	0.44 ± 0.1	26 ± 2.5
Ta	1.23 ± 0.1	-16 ± 1.5

high-temperature side one is restricted to $\sim 300\,°C$ in order to prevent hydrogen from leaking out of the sample via an increasingly more permeable oxide surface layer, and (ii) on the low-temperature side the temperature must be above the coexistence line in the T-x-phase diagram in order to avoid segregation. Despite the relatively large errors, we conclude that the present experimental results show that Z_d is not necessarily equal to the bare valence of the impurity (in our case, $Z = 1$ for a proton).

From a theoretical point of view, deviations of the direct force from the force exerted by the macroscopic field $\mathbf{E}$ on the bare valence have been discussed by Landauer[11] and by Sorbello.[12] According to Landauer[11] the local spatial density of electrons in the vicinity of an attractive impurity potential is larger than its average value. Continuity of electron current then requires a reduction of the local electric field in the region of higher electron density. This leads to a reduction of the direct force as described by Eq. (2). Assuming the potential of hydrogen in the group-V transition metals to be attractive, one would then expect for all three metals a reduction of the direct force. This, however, is not borne out by the present experimental results.

Very recently Sorbello[12] succeeded in deriving a tractable expression for the direct force within the linear-response formalism. Model calculations for hydrogen interstitials in metals based on this expression indicate for the first time that Z_d is typically 10%–30% smaller than Z. For weak impurity potentials Z_d can be larger than Z. (See Table I of Ref. 12.) Although the calculations are restricted to isolated impurities described by a square-well potential in a free-electron gas, they show clearly that large variations in Z_d with the strength of the impurity potential occur when the potential is almost strong enough for the formation of a bound state.

On the basis of the results obtained by Gelatt, Ehrenreich, and Weiss,[20] from an application of the Slater-Koster[21] model to hydrogen in the 3d transition metals, as presented in their Fig. 8, hydrogen in V, Nb, and Ta is expected to have a "marginal-protonic" character; i.e., it has a certain tendency to form an H^- ion. This might explain the large difference in the values we found for Z_d (and K) in these three metals, which have very similar electronic structures. Further theoretical work which includes the effects of band structure and of atomic configuration is needed on this point.

In conclusion, we have shown that the total force $\mathbf{F} = Z^* e \mathbf{E}$ acting on a charged impurity is made up of a temperature-dependent term proportional to the reciprocal electric resistivity and a temperature-independent term $Z_d e \mathbf{E}$. By using VH_x, NbH_x, and TaH_x as model substances, we established for the first time that Z_d is *essentially* different from the bare valence of the impurity.

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