Hall Voltage Induced by Hydrogen Diffusion in Palladium

A. H. Verbruggen, R. Griessen, and J. H. Rector

Natuurkundig Laboratorium, Vrije Uniersiteit, Amsterdam, The Netherlands

A Hall-type voltage induced by the fast diffusion of hydrogen in a metal (palladium) in a strong magnetic field has been detected. The sign and the magnitude of this voltage imply that hydrogen in palladium acts as a particle of charge $Z_H = 1$. The presence of this effect is strong experimental evidence for the existence of the controversial direct-force term (i.e., the action of an electric field on the unscreened charge of an ion in a metal) in the theory of electromigration.

In this Letter we report the first observation of a Hall-type voltage induced by the fast diffusion of hydrogen in a metallic sample placed in a strong magnetic field. There is no *external* electronic current involved in this experiment. Inside the sample, charge transport is only due to a gradient in the chemical potential of the hydrogen. As will be shown, this effect (which in the following will simply be called the proton-Hall effect) can be used to determine the state of ionization of hydrogen in a metal. Moreover, the magnitude and the sign of the proton-Hall effect provide evidence in favor of the existence of the controversial direct-force term in the theory of electrotransport of an interstitial impurity.[1-12] The presence of this force was still questionable since an unambiguous interpretation of electrotransport experiments has not been given yet.[12]

The basic configuration required for the detection of the proton-Hall effect is schematically shown in Fig. 1. A gradient in the concentration of hydrogen in a sample is set up by a difference in hydrogen gas pressure on the two faces perpendicular to the x axis. The remaining four faces are assumed to be impermeable for hydrogen. The magnetic field is in the z direction and the Hall voltage induced by the diffusing proton is measured in the y direction. For hydrogen in palladium a rough estimate of the proton-Hall voltage yields ≈ 1 nV for a $l = 1$-cm sample in a 10-T magnetic field. As the detection of such small voltages at several hundred degrees Celsius in a hydrogen atmosphere would be quite difficult the setup chosen for the actual measurements is somewhat different, though the basic idea is similar to that shown in Fig. 1.

In order to increase the proton-Hall voltage the sample has a length of typically 6 m and is wound in the form of two interpenetrating coils as shown in Fig. 2. The ribbonlike palladium sample has a thickness of 25 μm and is gold plated on one side to have hydrogen diffusing through one face of the

ribbon only. It is easily seen that in this configuration the proton-Hall voltages induced in the two coils add up while eventual instabilities in the external magnetic field are compensated.

One of the main difficulties of the present experiment was that the coils increase in size during hydrogen uptake. For hydrogen in palladium the relative length increase produced by 1 at.% of hydrogen is $d\ln l / dn_H = 6 \times 10^{-4}$ where $n_H = [H]/[Pd]$. In an uncompensated coil setup this dilatation of the host metal lattice would induce voltages which are more than one order of magnitude larger than that of the proton-Hall effect. Even for the compensated coil arrangement shown in Fig. 2 the deformation of the ribbon produces a signal which is comparable to the proton-Hall voltage itself. This is the reason why the exact deformation of the coils is measured by
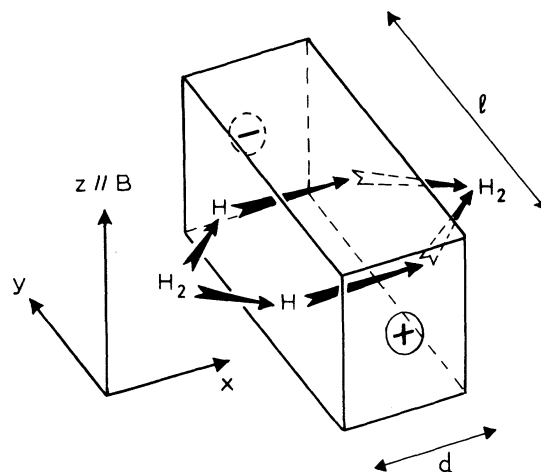

FIG. 1. Schematic configuration for the observation of the proton-Hall effect. The diffusion of hydrogen in the metallic sample (thickness d and length l) is due to a difference in the H_2-gas pressure on the left- and right-hand sides of the sample. The diffusion-induced voltage is measured perpendicularly to the magnetic field and the diffusion directions.
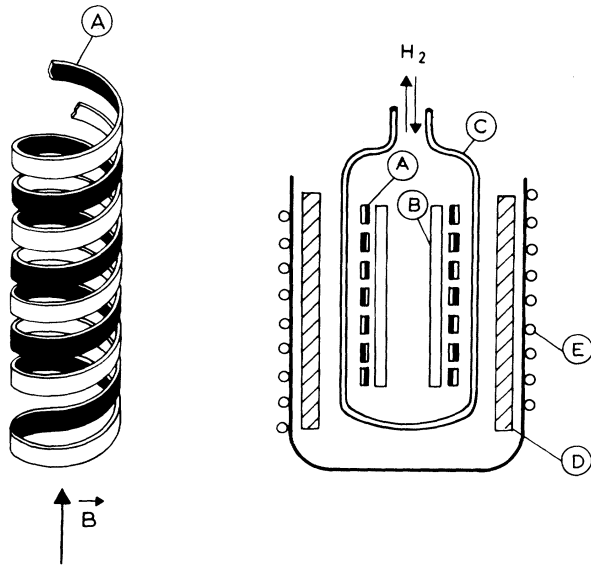
FIG. 2. The interpenetrating coil configuration used for the actual measurements of the proton-Hall effect. A: palladium ribbon of 25 μm thickness plated with $\sim$2 μm gold on one side (black side in the figure); B: Pyrex support; C: sample chamber connected to hydrogen gas handling system; D: oven; E: modulation coil for measurements of the coil expansion during hydrogen absorption or desorption. The whole setup is contained in the room-temperature bore of a 12-T superconducting magnet.
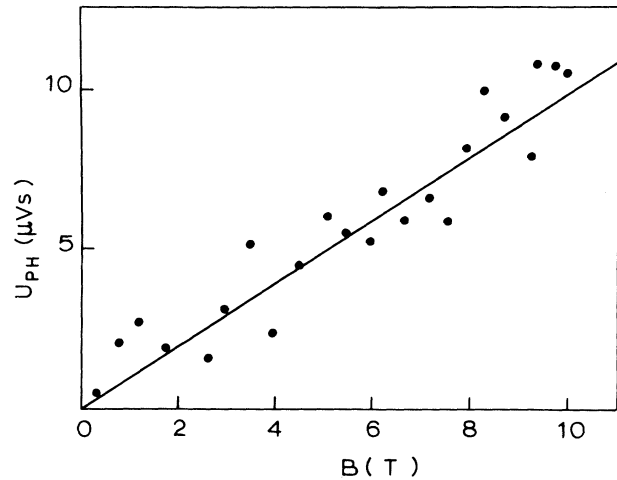

FIG. 3. Integrated proton-Hall signal [see Eq. (1)] as a function of magnetic field. The temperature is 583 K. The measurements correspond to absorption of hydrogen, when the hydrogen pressure in the sample chamber C (see Fig. 2) is increased from 100 to 600 Torr. The amount of hydrogen absorbed in such a cycle is 0.75 at.%. The slope of the fitted straight line is 1 μV$\cdot$sec/T and agrees within experimental errors with the slope determined from desorption experiments.

means of a modulation technique simultaneously with the voltage V_y in the y direction. This makes it possible to correct V_y for the voltage induced by the geometrical changes of the coil during hydrogen absorption or desorption.

The gold-plated Pd ribbon is wound in a Pyrex frame and maintained in place by means of high-temperature Thermokitt Roth cement. The sample space, which can be evacuated or filled with hydrogen, is located inside a water-cooled oven contained in the room-temperature bore of a 12-T superconducting magnet. In the water-cooled space of the oven there is a modulation coil which superimposes a small ac component on the steady magnetic field for the determination of changes in the coil dimensions during hydrogen absorption.

In a typical run the temperature is maintained constant within $\sim$0.01 K while hydrogen is added to or removed from the sample space. The variations of pressure are carried out with a time constant τ which is significantly larger than the typical diffusion time constant $\tau_D = d^2/D(T)$ where d is the thickness of the ribbon and $D(T)$ is the diffusion coefficient at temperature T. In this way

eventual variations in the kinetics of absorption (or desorption) have only negligible effects on the time dependence of the effect.

Since the time dependence of the proton-Hall voltage V_{pH} is not of direct interest in the context of the present work we consider the integrated proton-Hall voltage U_{pH} defined as

$$U_{pH} = \int_0^\infty V_{pH}(t)\,dt. \tag{1}$$

Experimentally the quantity $U_y = \int_0^\infty V_y\,dt$ is determined by integrating graphically the V_y vs t curve. The quantity $U_{ind} = \int_0^\infty V_{ind}\,dt$ is calculated from the modulation measurements and the actual (dc) magnetic field. Subtracting U_{ind} from U_y yields U_{pH}.

As shown in Fig. 3, U_{pH} varies linearly with the magnetic induction B. At $B = 10$ T, $U_{pH} = 10 \times 10^{-6}$ V$\cdot$sec. Since the absorption of hydrogen lasts for $\sim$20 sec this means that, on the average, the proton-Hall voltage is $V_{pH} \sim 0.5$ μV. The sign of the effect is given in accordance to the convention indicated in Figs. 1 and 2. The large scatter in the experimental points in Fig. 3 is due to the fact that V_{pH} represents only 20% of the measured voltage V_y. From measurements of the proton-Hall effect for samples of various lengths l at temperatures between 470 and 580 K at hydrogen pressures

between 100 and 700 Torr we find that

$$\frac{U_{pH}}{lBn_H} = (1.7 \pm 0.8) \times 10^{-7} \frac{V \cdot sec}{T \cdot m \cdot at.\%H}. \qquad (2)$$

Both the sign and the magnitude of the integrated proton-Hall effect can be understood as follows. As a consequence of charge neutrality the total *electric* current vanishes in the main hydrogen diffusion direction (the x axis in Fig. 1). Thus

$$n_e \vec{v}_e = Z_H n_H \vec{v}_H, \qquad (3)$$

where n_e (n_H) is the density of conduction electrons (hydrogen), v_e (v_H) is the drift velocity of electrons (hydrogen), and Z_H is the charge of hydrogen in a metal. For a bare proton $Z_H = 1$, for a neutral atom $Z_H = 0$, and for "anionic" hydrogen $Z_H = -1$.

In the direction where V_{pH} is measured (the y axis in Fig. 1) the total electric current is also zero. Moreover, in our experiment we expect the hydrogen current in the y direction j_H^y to be negligible. This assumption is in principle difficult to justify since the diffusion process of hydrogen in a metal is not known in great detail. However, two qualitative remarks can be made. First, by using classical arguments it is easy to show that the electrostatic forces arising from the surrounding atoms and electrons on the proton are at least six orders of magnitude larger than the Lorentz force in a magnetic field of 10 T, when the velocity of the hydrogen is derived from its vibration frequency. Secondly, describing the diffusion of hydrogen in a magnetic field within the small-polaron hopping theory of Emin and Holstein[13] a three-site coincidence is needed for a preferential diffusion step. Three-site coincidences are much less probable than the normal two-site coincidences, needed in the normal diffusion process.

Charge neutrality together with the vanishing of the hydrogen current in the y direction ($j_H^y = 0$) leads to the condition

$$\int_0^d j_e^y(x) dx = 0. \qquad (4)$$

In the classical Hall configuration the Lorentz force on the electrons is homogeneous (i.e., the electron current does not depend on x). In the steady state this force is compensated by a uniform electrostatic field E_s and no Hall currents are flowing. However, in our case the velocity of the diffusing hydrogens in the x direction is not constant and consequently the magnitude of the induced conduction-electron current varies with x. This means that the Hall field is not constant and the cir-

culating electronic currents are present. For the special geometry used in this work the length-to-thickness ratio is so large ($l/d \cong 3 \times 10^5$) that the compensating electrostatic field can be considered as being homogeneous in the x direction. Equations (3) and (4) lead then to the following expression for the time-integrated hydrogen-induced Hall voltage:

$$U_{pH} = (Z_H eldR_H n_\infty / 2\Omega)B, \qquad (5)$$

where e is the electron charge, R_H the Hall coefficient of the host metal, n_∞ the final hydrogen concentration in the sample, B the magnetic field, and Ω the atomic volume of the metal. As can be seen in Eq. (5) U_{pH} does not depend on the details of the diffusion process. U_{pH} depends weakly on temperature through the temperature dependence of the Hall coefficient and the thermal expansion of the host metal lattice. The most important feature of Eq. (5) is that U_{pH} does not depend on the *effective* charge Z_H^* (as is the case for electromigration experiments) but only on the bare charge of hydrogen (which corresponds to the so-called direct-force charge in the theory of electromigration[1-12]). Measurements of the proton-Hall effect are thus well suited to decide whether hydrogen in palladium is protonic, neutral, or anionic in nature.[14] From the sign and the nonvanishing of the observed proton-Hall effect, it follows directly that hydrogen does not enter palladium in the form of an anion (as is conceivably the case for hydrogen in early transition metals) or a neutral atom.

Using the values of Frank[15] for the Hall coefficient of palladium $R_H = 9 \times 10^{-11}$ m^3/A·sec, $\Omega_{Pd} = 1.4729 \times 10^{-29}$ m^3, and $Z_H = 1$, we find from Eq. (5)

$$\frac{U_{PH}}{lBn_H} = 1.2 \times 10^{-7} \frac{V \cdot sec}{T \cdot m \cdot at.\%H} \qquad (6)$$

in remarkable agreement with the experimental value given in Eq. (2). This agreement indicates unambiguously that hydrogen dissolved in palladium has a bare charge of approximately +1.

This conclusion is relevant to the controversy about the existence of the direct-force term in the theory of electromigration. According to Sham,[9] Das and Peierls,[7] Sorbello,[5,6] and Schaich[10] the force acting on an ion in a metal in the presence of an electric field $\vec{E}$ is given by

$$\vec{F} = \vec{F}_d + \vec{F}_w = Z_d e\vec{E} + \vec{F}_w, \qquad (7)$$

where $\vec{F}_d = Z_d e\vec{E}$ is the direct force due to the action of the electric field on the charge of the bare

(unscreened) ion and $\vec{F}_w$ is the wind force due to the interaction of conduction electrons with the migrating ion. In contrast to this Bosvieux and Friedel[1] and Turban, Nozières, and Gerl[2] defend the view that in the case of an interstitial such as hydrogen in a metal $Z_d = 0$ because of the complete screening of the ion. In electromigration experiments it is usually found that $F_w \gg F_d$ so that a clear-cut answer to the question of the existence of the direct force has not been given yet. The experimental results reported in this Letter on the proton-Hall effect are strong evidence in favor of the existence of the direct force. A detailed discussion of this point will be given elsewhere.

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