

Microscopic Scatterer Displacements Generate the $1/f$ Resistance Noise of H in Pd

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(Received 22 February 1988)

The resistance changes generated by individual microscopic displacements due to dissolved hydrogen ions hopping between neighboring sites within palladium films create intense $1/f$ noise at low temperature. Crossover to one-dimensional diffusion-mediated number-fluctuation noise occurs for $T \gtrsim 150$ K. The measured resistance change per proton displacement is comparable to the resistance per proton as predicted by applicable quantum-interference theories.

PACS numbers: 72.70.+m, 66.30.Jt, 72.10.Fk

Low-frequency resistance fluctuations in microscopic metal conductors have attracted extensive study, but the mechanism of their ubiquitous $1/f$ noise has evaded identification.¹ It poses two linked questions: What mechanism generates the temporal fluctuations? How does it modulate resistance? Experiments have correlated the noise intensity with the number of elastic scatterers contributing to the resistivity.² Temporal fluctuations of the resistance are commonly ascribed to some thermally activated scatterer motion. At $1/f$ spectrum (power spectral density $S_R \propto 1/f^\alpha$ with $\alpha \sim 1 \pm 0.2$ over many decades of frequency f) implies a wide range of relaxation times $\tau_i = \tau_{0i} \exp(E_i/kT)$ that can be provided by a distribution of activation energies $P(E_i)$ spanning a few kT . Now some fresh theoretical ideas about the magnitude of the resistance modulation per scatterer have motivated our experiments.

In calculation of the resistance due to elastic scattering, the retention of quantum phase coherence³ of the conduction-electron wave function shows that spatial rearrangement of scatterers, without changing the total number, can generate universal conductance fluctuations of magnitude e^2/h .⁴ Feng, Lee, and Stone⁵ have calculated the resistance change δr caused by a microscopic displacement of a point scatterer (for example, an impurity moving between neighboring interstitial lattice sites) in the presence of many other elastic scatterers. Pelz and Clarke⁶ and Hershfield⁷ have calculated δr for a clean limit where the pertinent relative displacement is of one scatterer in the neighborhood of one other point defect. Thus model calculations are available for the more⁵ and less^{6,7} disordered limits. In the latter case a change in the relative resistance $\delta r/r \sim 0.1$ is found for an atomic-scale motion of a point scatterer within the conductor. To test implications of quantum interference models for $1/f$ noise, experiments should aim to measure the total magnitude of resistance fluctuations generated by known numbers of moving scatterers. This paper reports such an experimental test.

We have measured the resistance fluctuations due to hydrogen ions moving in thin palladium films, where H^+

is highly soluble, enters controllably from the gas phase, scatters conduction electrons, and diffuses rapidly. Above 200 K we observe resistance fluctuations due to fluctuations of the number of protons mediated by one-dimensional H^+ diffusion through the permeable sample ends.⁸ At lower temperatures the H^+ number fluctuations shift to lower frequencies as diffusion slows, revealing hydrogen-produced $1/f$ noise with frequency and temperature dependences which implicate thermally activated H^+ motion on an atomic scale. With the number of moving scatterers determined by the variance of high-temperature number-fluctuation noise, we have determined $\delta r/r$ for microscopic H^+ motion in Pd at lower temperatures, and have compared it with theoretical predictions.

Two Pd films were studied: Film *A* (500 Å thick) had a residual resistivity ratio $RRR = \rho(295 \text{ K})/\rho(4.2 \text{ K})$ of 2.5, where ρ is the resistivity; film *B* (1000 Å thick) was deposited at 700°C with an RRR of 7.5. Sapphire substrates were presputter etched for 10 sec to increase film adhesion. Pd was sputtered in 10^{-2} Torr of argon (base pressure of 2×10^{-7} Torr), at about 15 Å/sec. The films were patterned with use of photolithography and ion-mill (dry) etching. Seven resistance-noise samples consisting of straight lines from 0.6 to 8 μm wide, with nominal length-to-width ratios of 20, were formed with five probe branches.⁹

Noise and resistance measurements were made at various hydrogen concentrations and temperatures $20 \text{ K} < T < 300 \text{ K}$. We charged the Pd films by exposing them at room temperature to hydrogen gas (99.9% purity) at the pressure required to obtain the desired hydrogen concentration. Four-point sample resistances were monitored during each pressure change. Charging behavior, pressure dependence, equilibration time, and hysteresis in the resistance were consistent with the literature.¹⁰ A preliminary charge-discharge cycle eliminated the hysteresis. After hydrogen charging the Pd film surfaces conveniently poison, eventually preventing proton exchange except past the sample ends. Proton exchange through the surface can be restored by a low-pressure low-energy

O₂ plasma etch. The range of H⁺ concentrations was chosen to avoid film damage by precipitation of the β hydride phase and to at least double the 1/f noise relative to the uncharged Pd film.

A total of 930 measurements of the power spectra of voltage fluctuations $S_V(f, T; I)$ on five-probe samples were recorded with use of an ac current I (700 Hz) in a symmetric Wheatstone bridge configuration.⁹ Noise measurements were reproducible within about 30% over a time scale of weeks, with $S_V \propto I^2/\Omega$ (Ω is the film sample volume) at various temperatures and concentrations. Checks for contact noise⁹ were always negative. Thus the measured voltage noise was produced by resistance fluctuations distributed throughout the conductor volume between the voltage contacts. The resistance-fluctuation power-spectra density is defined as

$$S_R(f, T) = [S_V(f, T; I) - S_V(f, T; 0)]/I^2.$$

Typically $I \approx 10$ mA, corresponding to a current density of 2×10^6 A/cm². Noise measurements spanned three (0.01 to 10 Hz) to five (0.001 to 100 Hz) decades of frequency.

Extensive studies of the diffusion of hydrogen in metals characterize this experimental system.¹¹ In bulk Pd the diffusion constant is $D = 10^{-7}$ cm²/sec at 300 K and obeys $D(T) = D_0 \exp(-E/k_B T)$ down to $T = 50$ K (Ref. 12) with activation energy $E \approx 0.2$ eV.¹¹ In the disordered glass Pd₈₀Si₂₀ the activation-energy distribution $P(E)$ for proton anelasticity is spread over about 0.15 eV.¹³

We are interested in proton motion on the time scale of our measurements (0.001–100 Hz). There are two regimes of interest: Above about 150 K macroscopic diffusion over the sample length L allows for fluctuations of the number of protons. At lower temperatures, the relevant proton motion is hopping between neighboring interstitial sites. The noise measurements clearly exhibit these two regimes of proton movement.

Above 150 K, $S_R(f, T)$ has the distinctive spectral shape expected of one-dimensional diffusion-mediated number fluctuations in our sample geometry⁸: flat below a knee frequency f_c and $f^{-3/2}$ above it, as illustrated by the spectrum at 280 K in Fig. 1. Like previous noise measurements on niobium with hydrogen near room temperature,⁸ the resistance fluctuations are produced by changes of the number of protons in the sample volume as they diffuse through the permeable sample ends. The knee frequencies $f_c = D/\pi L^2$ scale with sample length L and yield $D \approx 8 \times 10^{-7}$ cm²/sec at room temperature. At lower temperatures f_c drops below the accessible limit $f_c \approx 0.01$ Hz so that D was determined from the noise intensity at fixed frequency $f \gg f_c$. Plotting $\ln[S_R(1 \text{ Hz}, T)]^2$ vs T^{-1} yielded activation energies $E \approx 0.25 \pm 0.05$ eV for film *B* and $E \approx 0.15 \pm 0.05$ eV for film *A* for $180 \leq T \leq 300$ K. $S_R(f, T)$ has the same frequency and temperature dependence for all H⁺ concentrations:

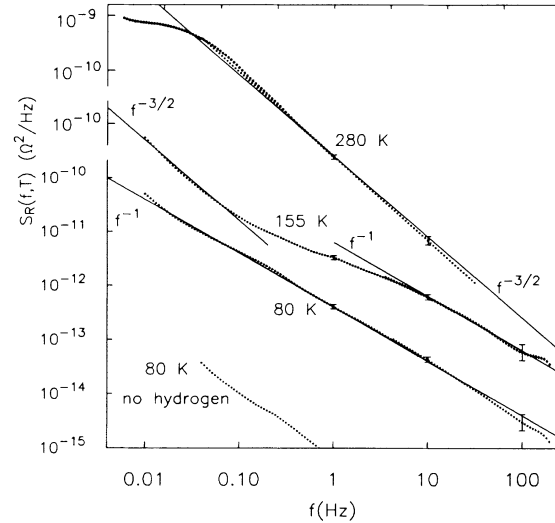


FIG. 1. Power spectral densities of resistance fluctuations in film *B* (RRR of 7.5). Upper three curves ($X_H = 5$ at. %): $T = 280$ K, showing diffusion spectrum proportional to $f^{-3/2}$ above the knee frequency of 0.01 Hz; $T = 155$ K, showing the crossover from $f^{-3/2}$ to $1/f$; $T = 80$ K, $1/f$ noise. Curves at 155 and 280 K have been vertically offset. Solid lines display indicated power laws. Error bars reflect statistical uncertainty, and background noise subtraction. Bottom curve: $1/f$ noise of the uncharged film at 80 K for comparison.

$S_R(f, T) \propto R_H$, which is the resistance change observed upon hydrogen charging. The concentrations X_H of mobile protons which contribute to the resistance were determined from the variances $\langle(\Delta R)^2\rangle$ of the number-fluctuation noise as $X_H^{-1} = 2N_a \langle(\Delta R_H)^2\rangle/R_H^2$, where N_a is the number of atoms in the sample length L , and it is implicitly assumed that R_H is attributable entirely to the mobile concentration X_H .

Our measured specific proton resistivity $d\rho/dX_H \approx \rho/X_H \approx 0.1 \mu\Omega \text{ cm/at. \%}$ is consistent with previous results in Pd films.¹⁰ However, comparison with data on pure bulk Pd (Ref. 14), where $d\rho/dX_H \approx 0.3 \mu\Omega \text{ cm/at. \%}$, suggests that much of the H⁺ in Pd films is segregated¹⁴ to the neighborhood of extended defects such as grain boundaries or dislocations where scattering by H⁺ may be significantly diminished.

At lower temperatures where D is small, the number-fluctuation noise shifts to lower frequencies where it is no longer observable in our experiments. Instead, a new phenomenon is revealed: The presence of hydrogen produces $1/f$ noise, $S_R(f, T) \propto 1/f^\alpha$ where $0.9 < \alpha < 1.2$, as illustrated by the $1/f$ spectrum at 80 K in Fig. 1. The spectrum at $T = 155$ K in Fig. 1 shows the crossover from the $f^{-3/2}$ number-fluctuation noise still detectable below 0.1 Hz to $1/f$ noise which dominates above 10 Hz. The shape of the spectrum at 80 K is typical of the entire range $20 \text{ K} < T < 120 \text{ K}$. The temperature dependence of the intensity of the low- T noise represented by $S_R(1$

$S_R(T)$ has a local minimum at 170 K, peaks near 120 K, and then falls off monotonically with T as shown in Fig. 2. The plots of $S_R(1 \text{ Hz}, T)$ for each of four values of X_H have been normalized to their intensity at 110 K, $S_R(1 \text{ Hz}, 110 \text{ K})$, to show their common T dependence. The inset shows that their absolute intensities $S_R(1 \text{ Hz}, 110 \text{ K}) \propto X_H$, as expected for noise due to independently moving protons.

The broad $1/f$ spectrum of $S_R(f, T)$ combined with the pronounced intensity maximum in T suggests a discrete thermally activated process with a limited range of activation energies and prefactors.¹ We hypothesize that individual, temperature-independent resistance fluctuations of average magnitude δr are produced by proton "hopping" between nearest-neighbor interstitial sites spaced $l = 2.8 \text{ \AA}$ apart. Thus, the noise peak at hopping frequency $f_h = 1 \text{ Hz}$ corresponds to an effective diffusion constant $D = f_h l^2 / 6 \approx 10^{-16} \text{ cm}^2/\text{sec}$. For comparison, the extrapolation of our data on $D(T)$ from the number-fluctuation noise regime places a 1-Hz hopping frequency at 90 K. Published measurements¹² of anelastic relaxation of the bulk Pd hydride phase yield a nearest-neighbor hopping frequency of 1 Hz at 80 K. We think that both these temperatures are consistent with the $1/f$ noise peak temperature of about 120 K within the accumulated uncertainties.

It remains to determine the magnitude of the resistance fluctuation per proton hop implied by the observed $1/f$ noise intensity. Attributing a $1/f$ noise variance

$$\langle [\Delta R(T)]^2 \rangle = \sum_i [\delta r_i(T)]^2 = N_H [\delta r(T)]^2$$

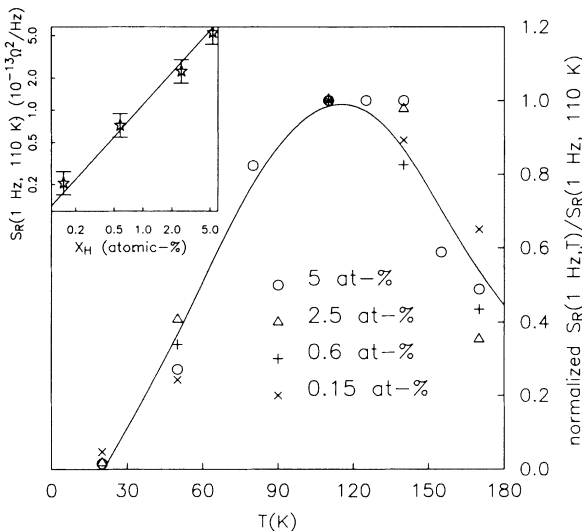


FIG. 2. Temperature dependence of the noise intensity $S_R(1 \text{ Hz}, T)$ for the four hydrogen concentrations in film *B* (RRR of 7.5) normalized to $S_R(1 \text{ Hz}, 110 \text{ K})$ for each X_H . The solid curve is a guide to the eye for the common temperature dependence. Inset: Log-log plot of the X_H dependence of the absolute noise intensity $S_R(1 \text{ Hz}, 110 \text{ K})$; the solid line represents $S_R(1 \text{ Hz}, 100 \text{ K})$ linear in X_H . Error bars show reproducibility of 30%.

to a sum over $N_H = X_H N_a$ independent hopping protons suggests a normalized measure $\delta r/r \equiv \{N_H \langle [\Delta R(T)]^2 \rangle / R_H^2\}^{1/2}$ of the resistance noise per proton, where $r = R_H / N_H$. But the variance does not exist for $S_R \propto 1/f$ since $\langle [\Delta R(T)]^2 \rangle = \int_{-\infty}^{\infty} S_R(f, T) df$. However, the divergence is suppressed by spectral limits due to thermal activation with a finite range ΔE of the distribution of activation energies $P(E)$. With use of the Dutta-Dimon-Horn approximation¹ with a single attempt frequency $\tau_0^{-1} = 6D_0/l^2 = 2 \times 10^{13} \text{ Hz}$, the temperature dependence of $S_R(f, T)$ implies that $P(E)$ has an asymmetric maximum around 0.2 eV, and a full width $\Delta E \approx 0.2 \text{ eV}$. With neglect of the temperature dependence of $\delta r(T)$,¹⁵ this approximation also yields $\langle [\Delta R(T)]^2 \rangle$ from $S_R(f, T)$ as

$$\langle (\Delta R)^2 \rangle \approx -f \ln(2\pi f \tau_0) \int_0^{\infty} dT' S_R(f, T') / T'$$

Since the variance of the number fluctuations at high temperature determines N_H we have

$$\delta r/r = (\langle [\Delta R(\text{low } T)]^2 \rangle / \langle [\Delta R(\text{high } T)]^2 \rangle)^{1/2}$$

Thus measurement of the ratio of the variances both in the high- T number-fluctuation regime and in the low- T $1/f$ noise regime yields the resistance change δr per independent proton hop relative to the static resistance change per proton present in solution as $\delta r/r \approx 0.2$ (film *A*) and $\delta r/r \approx 0.4$ (film *B*). These results are subject to a factor of 2 accumulated experimental uncertainty and the assumption that X_H is temperature independent.

We aim to compare $\delta r/r$ for our $1/f$ noise with the predictions of all quantum-interference scattering theories. Unfortunately that of Feng, Lee, and Stone⁵ is applicable only in the very dirty limit, not yet attained. However, the calculations of Pelz and Clarke⁶ and Hershfield⁷ do apply in our scattering regime and their δr is temperature independent. Pelz and Clarke⁶ considered the scattering fluctuations due to reorientation of pairs of various identical point defects, including vacancy and interstitial pairs; they obtained $\delta r/r \leq 0.25$. Hershfield considered the effects of quantum interference on the resistance fluctuations produced by pairs of generic point defects as a function of the pair spacing. Application of his theory predicts $\delta r/r \approx 0.3$ for an H-vacancy pair in Pd. Both theories yield magnitudes for $\delta r/r$ in agreement with our data within the uncertainty.

Nevertheless, both theories consider close pairs of isotropic point defects. For pairs of protons in Pd, which are individually isotropic defects, $S_R(f, T) \propto X_H^2$, but we found $S_R(f, T) \propto X_H$ as shown in the inset of Fig. 2. Thus, most of the protons must be "paired" with some other lattice disorder, such as a point defect, dislocation, or grain boundary. The RRR values establish the presence of sufficient disorder. The low values of dp/dX_H and the relatively large ΔE both suggest the proximity of protons to extended lattice defects.

We have identified one source of $1/f$ resistance noise

in a metal conductor as thermally activated atomic-scale hopping of a mobile solute. Use of H^+ in Pd to study $1/f$ noise provides control of the identity and number N_H of noise-producing defects. The attribution of the $1/f$ noise to H^+ motion is confirmed by the distinctive temperature dependence. Quantum-interference theories^{6,7} of scattering do predict a magnitude of the resistance fluctuations for microscopic scatterer motion in agreement with our experimental results. These theories are applicable to pairs of point defects. We suggest theoretical calculation to determine whether a point scatterer moving near an extended defect may produce similar resistance fluctuations. We note that, if extended defects in Pd films do attract and sequester protons so as to significantly diminish their effective scattering power, microscopic proton motion may account for the observed magnitude of $\delta r/r$, without explicit dependence on quantum interference. Finally, this work suggests that microscopic motion of significant, possibly nonequilibrium concentrations of scatterers might account for the ubiquitous room-temperature $1/f$ noise in metal films.¹⁶

We gratefully acknowledge helpful discussions with Selman Hershfield, Joseph Mantese, and Jonathan Pelz and the support of the National Science Foundation through Cornell's Materials Science Center (Grant No. DMR-85-16616) and National Science Foundation Grant No. DMR 84-14796.

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¹⁵Retention of a weak temperature dependence, say $\delta r(T) \propto 1/T$, skews $P(E)$ further toward lower E but does not change $\delta r/r$ within the experimental uncertainty.

¹⁶Compare $dp/dX \sim 1 \mu\Omega \text{ cm/at.}\%$ for typical metallic impurities and vacancies in metals with H^+ at $dp/dX_H \sim 0.1 \mu\Omega \text{ cm/at.}\%$.