1/*f* Resistance Noise Complements Anelasticity Measurements of Hydrogen Motion in Amorphous $Pd_{80}Si_{20}$

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The time-dependent resistance fluctuations due to motion of H in amorphous PdSi metal films exhibit 1/*f* noise with two thermally activated peaks, one at 80 K and one shifting with H concentration between 160 and 130 K. The higher peak closely matches an internal-friction peak, showing that the same H hops can relax elastic strain and modulate resistance, while the lower peak reflects hops that do not relax strain. Thus resistance fluctuations and mechanical dissipation provide complementary probes of defect motion.

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Time-dependent resistance fluctuations (1/*f* noise) have been observed in metals for the last two decades.[1,2] The developing consensus about the microscopic mechanism raises two basic questions: What physical entities cause the time-dependent fluctuations, and how do they modulate resistance? The physical entities seem to be some sort of mobile defect which elastically scatter conduction electrons, and the resistance modulation is attributed to the dependence on scatterer positions through quantum interference of the conduction-electron wave function.[3-5] Previous experiments on microcrystalline metal films show temperature dependence implying thermally activated atomic motion,[1] and rough scaling of noise intensity with the concentration of elastic electron scatterers[2] and with radiation damage,[2] which all suggest that atomic-scale scatterers undergoing thermally activated motion modulate the resistance.

We have established the specific mechanism for a particular, well-defined system, where the 1/*f* noise is produced by the motion of H introduced into polycrystalline Pd films.[6] We found that (1) resistance fluctuations were produced by thermally activated atomic-scale hops of the protons with an activation energy and prefactor in agreement with measurements from long-range proton diffusion, (2) that quantum interference concepts in the clean limit[3,4] account for the resistance modulation, and (3) that the H interacts with extended defects rather than with itself to provide the necessary site asymmetry.[6]

Recent experiments on highly disordered films[7,8] appear to confirm the applicability of quantum interference in the dirty limit.[5] However, the identities of the mobile physical entities implicated in 1/*f* noise generation remain generally unknown except for extrinsic H in metals.[6,9]

Because mobile atomic-scale defects are also implicated in mechanical anelasticity or internal friction,[10] many suggestions of a correspondence have appeared.[2,9,11] Resemblance of measurements of 1/*f* noise in amorphous Ni-Zr alloys (presumed to contain hydrogen) to internal friction data has been noticed but not quantitatively compared.[9] The existence of a well-defined internal friction peak due to proton hopping in amorphous *a*-$Pd_{80}Si_{20}$ metallic alloys,[12] and our success in characterizing the 1/*f* noise due to proton hopping in microcrystalline Pd films,[6] suggested the opportunity for a definitive comparison of 1/*f* noise and internal friction. (Internal friction is not generated by H hopping in crystalline Pd due to the octahedral interstitial site symmetry.) Because *a*-$Pd_{80}Si_{20}$ is one of the best characterized amorphous metallic alloys, we also studied the 1/*f* noise in the H-free, controlled amorphous metal (to be reported elsewhere).

To perform the quantitative comparison, we have now measured the 1/*f* noise due to motion of controlled H concentrations in films of well-defined, single-phase amorphous *a*-$Pd_{80}Si_{20}$ metallic alloy with well-established H solution properties.[12] We have found and report here a remarkable correspondence and contrast between our 1/*f* resistance noise and previously published internal friction (IF) measurements which provide a basis for characterization of features of the atomic motion responsible for 1/*f* noise in amorphous metals.

The PdSi films were rf sputtered from a composite target[13] (perforated Pd foil over an Si target) to form a nominal $Pd_{80}Si_{20}$ composition on a polished sapphire substrate. Thermodynamic and diffusion properties of H in *a*-$Pd_{80}Si_{20}$ are qualitatively similar for sputtered films and splat-cooled bulk samples.[14] The absolute composition was confirmed to within the uncertainty of about 2 at.% using Rutherford backscattering (RBS) and energy dispersive spectroscopy (EDS) in a scanning electron microscope (SEM). Lateral and depth uniformity were confirmed using EDS and RBS, respectively. The lack of crystallinity was confirmed by x-ray analysis. At all H concentrations, the resistivity was linear in T, with a residual resistivity of about 70 $\mu\Omega$ cm, corresponding to a mean free path of order a few interatomic spacings. The film was patterned using standard photolithography and ion etching to form four five-probe (standard four-probe plus a center tap) noise samples.[15]

Samples were charged with hydrogen by exposure to H_2 gas at room temperature at pressures $4 < P < 650$ Torr; see Ref. 6 for details. Resistivity versus pressure P agreed well with the literature; X_H was about 2 at.% for $P \approx 1$ atm.[16]

A total of 400 measurements of the voltage fluctuations $S_V(f,T;I)$ were recorded using an ac current I (700 Hz) in a symmetric Wheatstone bridge configuration.[15] We confirmed that $S_V \propto I^2/A$ (A is the sample area) at various T and X_{H}, and that contact noise was absent.[15] Thus the measured voltage noise was produced by resistance fluctuations distributed throughout the conductor volume between the voltage contacts. We define $S_R(f,T) = [S_V(f,T;I) - S_V(f,T;0)]/I^2$. Typically, $I \approx 2$ mA, corresponding to a current density of 10^6 A/cm^2. Noise measurements spanned three (0.01-10 Hz) to five (0.001-100 Hz) decades of frequency f.

Figure 1 shows the temperature dependence of the absolute intensity of $S_R(f,T)$ (points connected by light dotted lines) measured for four concentrations obtained by the denoted charging pressures, and for the uncharged film for comparison. For all noise spectra, $S_R(f,T) \propto f^{-\alpha}$ with $0.6 < \alpha < 1.2$. Similar to H in polycrystalline Pd,[6] the H-induced $1/f$ noise dominates the uncharged amorphous PdSi film noise in the temperature range shown, even though resistance noise in the uncharged amorphous film (to be reported elsewhere) is about 100 times larger than in the uncharged pure Pd films. All noise data in this paper correspond to a sample of thickness 135 nm, width 2 μm, and half-length 41 μm (about 8×10^{11} atoms). Duplicate (shaded) points show reproducibility during the temperature scan. The three solid points represent the noise for a separate charging and scan, *showing the excellent absolute reproducibility achievable in this system.* The noise intensity shows two peaks as a function of T, and flattens below about 40 K (not shown). We denote the peaks as 1 (at about 80 K) and 2 (between 130 and 160 K). $S_R(f,T)$ increases slowly with charging pressure as shown. The shape of peak 1 is unchanged with H concentration; peak 2 shifts to lower T at higher X_{H}.

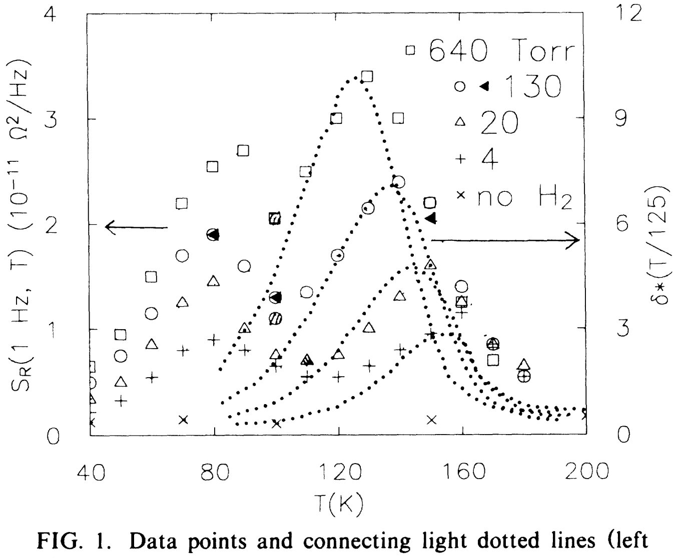

FIG. 1. Data points and connecting light dotted lines (left axis) present the temperature dependence of the absolute power spectral density of resistance fluctuations $S_R(f,T)$ for the four indicated H_2 charging pressures, and for the uncharged film. Some duplicate (shaded) points illustrate the reproducibility during a scan of T and the solid points illustrate the absolute reproducibility of a separate H charge and T scan. The heavy dotted lines (right axis) are measurements (Ref. 12) of internal friction (IF) in $Pd_{82}Si_{18}$ at charging pressures 700, 100, 20, and 3.3 Torr, scaled with no free parameters to correspond to the $1/f$ noise curves, as described in the text.

The behavior of peak 2 with X_{H} closely resembles internal friction data associated with H in PdSi. IF measures the mechanical dissipation of energy as a defect moves in a lattice in response to an applied strain. The measured quantity is the logarithmic decrement δ, the logarithmic decrease per vibration period of the amplitude $A_n \propto \exp(-n\delta)$. For an anelastic process involving a distribution of relaxation times τ_i, δ can be written as[12]

$$\frac{\delta(f,T)}{\pi} = \sum_i \Delta_i \frac{\omega\tau_i}{1+\omega^2\tau_i^2}\,; \tag{1}$$

similarly, the resistance noise[1]

$$\omega S_R(f,T) = \sum_i (\delta r_i)^2 \frac{\omega\tau_i}{1+\omega^2\tau_i^2}\,. \tag{2}$$

Here, $f = \omega/2\pi$, τ_i is the relaxation time of proton i, $\Delta_i \propto 1/T$ is the relaxation strength,[12] and δr_i is the magnitude of the resistance fluctuation per proton. The correspondence of both the physical origins and the formulations of $1/f$ noise and IF compel their quantitative comparison. The heavy dotted lines in Fig. 1 are IF measurements of logarithmic decrement δ at similar charging pressures for a $Pd_{82}Si_{18}$ splat-cooled ribbon.[12] δ is multiplied by T to normalize the $1/T$ dependence of the relaxation strength,[12] by assuming that $\delta r(T) \equiv \delta r_i$ is constant with T; we will return to this point later. δ was measured at $f_b = 126$ Hz; to compare the temperature dependence to $S_R(f,T)$ at the convenient frequency of $f_a = 1$ Hz, we have shifted the IF data measured at T_b along the temperature axis to T_a to represent the thermally activated shift in frequencies:

$$\ln(f_a/f_b) = E/kT_a - E/kT_b\,. \tag{3}$$

This shift, strictly valid only in the limit of a single activation energy E, introduces a distortion in $\delta(T)$ of at most 4%, given the width of the distribution of activation energies $\Delta E \approx 0.15$ eV and E, both deduced from IF measurements.[17] *We emphasize that there are no free parameters in Fig. 1 other than selection of appropriate vertical scales so that $S_R(f,T)$ and δ lie on the same graph, in order to quantitatively compare temperature dependences of thermally activated processes.* There is obvious agreement between the noise peak 2 and the IF data in absolute peak positions in T, relative peak heights, and peak shift with X_{H}. For comparison, $1/f$ noise[1] and IF[10] measurements in metals without H usually peak at or above room temperature; the difference is due to the lower E for H motion compared to other mobile defects.

To examine whether both resistance noise peaks are due to thermally activated processes, we consider the dependence of $S_R(f,T)$ on frequency. In Fig. 2(a), we have plotted $S_R(f,T)$ measured at three different frequencies, and computer-generated spline fits. The movement of all features above 40 K with frequency is obvious: higher frequency corresponds to a higher T. This is a strong qualitative signature of the thermal activation relation $\tau=\tau_0 e^{E/kT}$. There are (at least) two ways of quantitatively analyzing for this.

A standard analysis for internal friction measurements (among others) examines the shift in temperature-dependent features with measurement frequency. For thermal activation with a single E, an Arrhenius plot of $\ln f$ vs $1/T_p$, where T_p is the noise peak position from Fig. 2(a), should be a straight line with a negative slope and y intercept determined by E and τ_0; for a narrow distribution of activation energies $D(E)$, this will yield a reliable estimate for the average E.[10] Best straight-line fits for all X_H (not shown) yield reasonable microscopic attempt times τ_0 ranging between 10^{-10} and 10^{-16} s; this spread is due to the narrow range of $1/T$, uncertainty in T_p from the coarseness of the T scan, and the long extrapolation to $1/T=0$. For peak 1, E ranges between about 0.15 and 0.20 eV; for peak 2, between 0.33 and 0.45 eV. We note that the corresponding values for the single IF peak are[18] $\tau_0 \approx 10^{-15}$ s, and E between 0.32 and 0.45 eV, close to the values for peak 2.

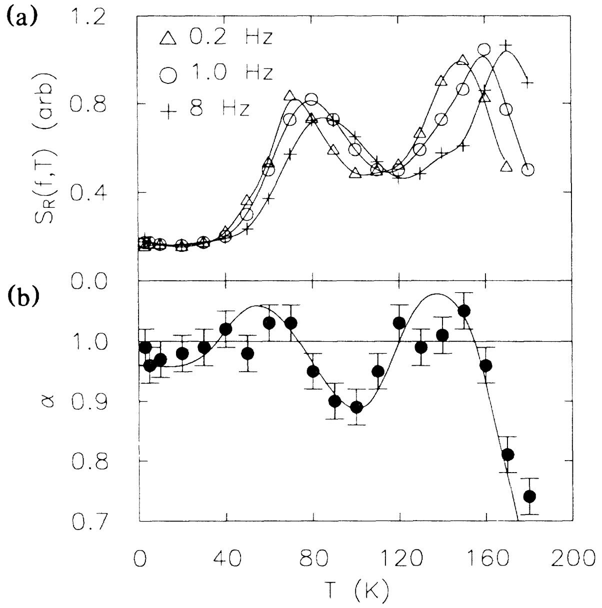

FIG. 2. (a) Data points are the noise $S_R(f,T)$ (4 Torr) measured at three frequencies f. The curves have been normalized to fit on the same graph. Lines are computer-generated spline fits. The shifts with f of all features including peak position suggest that both peaks are thermally activated. (b) Standard noise test for thermal activation. Data points are the measured spectral exponent $\alpha(T)=-\partial\ln S_R/\partial\ln f$ at 1 Hz. The solid lines are predictions for $\alpha(T)$ from the temperature dependence of $S_R(f,T)$ (see text). The dips in $\alpha(T)$ at the temperatures of both peaks in $S_R(f,T)$ confirm thermal activation of the noise. The horizontal line at $\alpha=1$ corresponds to $\partial\ln S/\partial\ln T=1$.

The second method of analyzing for thermal activation, standard for resistance noise measurements with a broad $D(E)$, considers the spectral exponent $\alpha(T) = -\partial\ln S_R(f,T)/\partial\ln f$. For a single characteristic time, $S_R(f,T)$ is a Lorentzian, so that α is 2 for T well below the peak, and 0 well above. For $1/f$ noise with a smooth distribution of activation energies, we expect a more gentle trend, with α decreasing as T passes from below to above the peak. One obtains[1] a scaling relation between the frequency and temperature dependence of $S_R(f,T)$: $\alpha(T)=1-[\partial\ln S_R(f,T)/\partial\ln T-1]/\ln(\omega\tau_0)$, assuming $\delta r(T)$ is constant. Values of α measured at 1 Hz for the 4-Torr charging pressure, where the two noise peaks are well separated, is plotted in Fig. 2(b). Also plotted is the curve for $\alpha(T)$ calculated from the above equation, using the spline fit to $S_R(f,T)$ in Fig. 2(a) and an average $\tau_0=10^{-13}$ s. The excellent agreement is strong evidence that both peaks are thermally activated. All H concentrations show similar trends, qualitatively and quantitatively. We note that this test for the scaling of α vs T shows much stronger features than have been previously observed,[1] because $S_R(f,T)$ for H motion has strong, discrete peaks in T.[9]

Thus, both peaks in $S_R(f,T)$ are thermally activated, with reasonable activation energies and attempt times. Peak 2 has an obvious interpretation: The noise is produced by the same microscopic hops that produce the IF. Note that, in contrast to polycrystalline materials, both liquid- and vapor-quenched (sputtered) amorphous $Pd_{80}Si_{20}$ samples have the same measured diffusion activation energies,[14] within our uncertainties. The agreement in Fig. 1 demonstrates the connection between $1/f$ noise and IF, which had been hypothesized,[2,11] but had not been demonstrated experimentally. By comparison with the results of Gorsky anelastic creep measurements,[18] we infer that peak 2 may probe the microscopic movements which provide long-range diffusion.

We now consider the noise peak 1: There is no indication that an analogous peak exists in the IF logarithmic decrement (δ) data. Thus we surmise that anelasticity is insensitive to H jumps between the sites corresponding to noise peak 1. In particular, we hypothesize that there exist (at least) two classes of intersite jumps available to the protons. The sites corresponding to noise peak 1 must be elastically equivalent, so that the motion produces no IF; the resistance fluctuations can be produced by a geometry which still satisfies the asymmetry requirements of quantum interference with a longer range.[3,4] The amorphous structure provides a dense concentration of such asymmetries. These data show that this peak corresponds to lower activation energy barriers than the IF-producing sites. This concept of a bimodel $D(E)$ is supported by quasielastic neutron-scattering measurements of $Pd_{85}Si_{15}H_{7.5}$,[19] which have directly revealed two well-separated regimes of jump rates at temperatures near room temperature. At 80 °C, the two rates differed by a factor of 50;[19] if the difference in rates is purely due to a difference in E, then that difference is 0.13 eV, similar to the difference between peaks 1 and 2 at the highest concentration.

We propose a simple nearest-neighbor model for the two qualitatively different interstitial sites that accounts for the two peaks in $D(E)$, by reasoning in analogy with a model for transition-metal binary alloys.[20] Octahedral interstitial sites, as pure Pd, are assumed for octahedra with six Pd nearest neighbors and are denoted Pd_6; similarly sites surrounded by five Pd and one Si are denoted Pd_5Si_1, etc. The dynamics differ as follows: A jump between neighboring Pd_6 sites or between Pd_6 and Pd_5Si_1 sites goes through a Pd_2 edge; between Pd_5Si sites goes through a PdSi edge. The nearest-neighbor symmetry in adjacent Pd_6 sites sharing Pd_2 edges and possibly Pd_4Si_2 sites sharing Si_2 edges appears to be sufficient so that the site energies are not sufficiently split by an anisotropic strain to generate a detectable internal friction signal even in the amorphous matrix. We suppose that hops between such sites correspond with the lower-temperature $1/f$ noise peak. The site energies of lower symmetry sites that include a silicon atom should generally be split by an applied anisotropic strain leading to IF and thus to the observed IF peak. The activation energies E for H motion through the three edges Pd_2, Si_2, and PdSi should differ since a silicon atom is smaller than a palladium atom. Why there are two peaks in the quasielastic neutron scattering and in the $1/f$ conduction noise and only one in the IF which corresponds to the higher-temperature $1/f$ noise peak is not clear. We note that the activation energy for H diffusion in pure Pd, corresponding to Pd_6-Pd_6 jumps, is about 0.2 eV as is the observed lower temperature $1/f$ noise peak (without a matching IF peak as expected).

In conclusion, our measurements of the $1/f$ noise induced by hydrogen in the amorphous metal $Pd_{80}Si_{20}$ reveal two thermally activated resistance noise peaks with activation energies and attempt times that correspond to the two hopping rates previously observed in quasielastic neutron-scattering measurements.[19] Our higher-temperature peak (peaking between 130 and 160 K) accurately matches internal friction data for amorphous PdSi in all essential aspects. This agreement confirms the notion[2,11] that both resistance fluctuations and internal friction can reflect the same microscopic motion of mobile defects. However, our lower-temperature noise peak does not correspond to any feature in the internal friction, contrary to this notion. This conflict is accounted for by the existence of two classes of proton hops in the alloy: those that relax strain by hops between asymmetric sites (such as Pd_5Si-Pd_5Si) and those nonrelaxing hops between centrosymmetric sites (Pd_6-Pd_6).

We see that $1/f$ resistance noise (defect-electron interface) and internal friction (defect-matrix strain interaction) in metals do provide complementary, nonredundant, probes of defect movement. It may be fruitful to examine the internal friction of H in polycrystalline Pd thin films, which correspond to our previous $1/f$ noise measurements,[6] in an attempt to identify relevant differences between the defect structure of Pd thin films and macroscopic Pd crystals.

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[1] P. Dutta and P. H. Horn, Rev. Mod. Phys. **53**, 497 (1981), and references therein.

[2] M. B. Weissman, Rev. Mod. Phys. **60**, 537 (1988), and references therein.

[3] Jonathan Pelz and John Clarke, Phys. Rev. B **36**, 4479 (1987); see also Refs. 14 and 15 therein.

[4] Selman Hershfield, Phys. Rev. B **37**, 8557 (1988).

[5] Shechao Feng *et al.*, Phys. Rev. Lett. **56**, 1960 (1986).

[6] Neil M. Zimmerman and Watt W. Webb, Phys. Rev. Lett. **61**, 889 (1988).

[7] Norman O. Birge *et al.*, Phys. Rev. Lett. **62**, 195 (1989).

[8] G. A. Garfunkel *et al.*, Phys. Rev. Lett. **60**, 2773 (1988).

[9] See also G. B. Alers *et al.*, Phys. Rev. B **40**, 900 (1989).

[10] A. S. Nowick and B. S. Berry, *Anelastic Relaxation in Crystalline Solids* (Academic, New York, 1972).

[11] S. Kogan and K. Nagaev, Fiz. Tverd. Tela (Leningrad) **24**, 3381 (1982) [Sov. Phys. Solid State **24**, 1921 (1982)].

[12] B. S. Berry and W. C. Pritchet, in *Hydrogen in Disordered and Amorphous Solids,* edited by G. Bambikidis and R. Bowman, Jr. (Plenum, New York, 1986); see other articles for general information on H in amorphous metals. Berry and Pritchet [Z. Phys. Chem. **163**, 381–390 (1989)] have recently found Δ_i in $Pd_{86}Si_{14}$ is approximately independent of T; the difference from the usual $1/T$ dependence is not significant in our analysis of Fig. 1.

[13] T. S. Tighe *et al.*, Bull. Am. Phys. Soc. **34**, 610 (1989).

[14] U. Stolz *et al.*, J. Less-Common Met. **103**, 81 (1984).

[15] John H. Scofield, Rev. Sci. Instrum. **58**, 985 (1987).

[16] R. Feenstra *et al.*, J. Phys. F **16**, 1965 (1986).

[17] B. S. Berry and W. C. Pritchet, Phys. Rev. B **24**, 2299 (1981).

[18] B. S. Berry and W. C. Pritchet, in *Nontraditional Methods in Diffusion,* edited by G. E. Murch, H. K. Birnbaum, and J. R. Cost (The Metallurgical Society of the American Institute of Mining, Metallurgical and Petroleum Engineers, Philadelphia, 1983), p. 83.

[19] D. Richter *et al.*, Phys. Rev. Lett. **57**, 731 (1986).

[20] J. H. Harris, W. A. Curtin, and M. A. Tenhover, Phys. Rev. B **36**, 5784 (1987).