

# PHYSICAL REVIEW B

## CONDENSED MATTER

THIRD SERIES, VOLUME 41, NUMBER 3

15 JANUARY 1990-II

### Low-frequency hydrogen-configuration fluctuations in niobium

B. D. Nevins and M. B. Weissman

*Department of Physics, University of Illinois at Urbana-Champaign, 1110 West Green Street, Urbana, Illinois 61801*

(Received 19 June 1989; revised manuscript received 8 September 1989)

Low-frequency resistance fluctuations in niobium films were found to have not only noise from long-range hydrogen diffusion, but also  $1/f$  noise associated with hydrogen. The noise statistics of this component often were not consistent with fluctuations of scattering cross sections from single hydrogen atoms or from small groups of hydrogen atoms. Some inhomogeneities of hydrogen concentration on a scale of roughly 10 nm seem to be required.

Hydrogen diffusion provides one of the better-understood mechanisms of low-frequency resistance fluctuations in metals. Scofield and Webb<sup>1</sup> first showed that in Nb films simple diffusion of H in and out of the sample causes fluctuations with geometry-dependent kinetics. The diffusing atoms are confined to the Nb, since an impenetrable surface oxide forms. Zimmerman and Webb<sup>2</sup> showed that in Pd, well below room temperature, H hopping between nearby lattice sites gave noise with a roughly  $1/f$  spectrum. The only complication in the interpretation of this noise was that the H sites were believed to have the full cubic lattice symmetry, so that noise quadratic in H concentration or bilinear in the concentration of H and other scattering sites would have been expected, although not found. Recently, H hopping noise has been observed in the amorphous materials Ni-Zr (Ref. 3) and Si-Pd (Ref. 4). The noise in these amorphous materials seems to fit a simple local-hopping model, except at high temperatures, for which the long-range diffusion contribution can be seen in sufficiently small samples.

In this paper we report on properties of the  $1/f$  noise in Nb samples, measured mainly at frequencies above those for which the long-range diffusion noise is important. We find that H is involved in the  $1/f$  noise, but that statistical properties of the noise are not consistent with any local-hopping picture. Rather, collective motions of large groups of solute H seem to be required—a mechanism unlike those previously shown to give  $1/f$  noise in other systems.<sup>5</sup>

### BACKGROUND

We were led to suspect anomalous properties of  $1/f$  noise in Nb by statistical measurements on noise measured with dc currents.<sup>6</sup> Slight non-Gaussian effects (e.g., variances in the noise power 5% larger than expected for Gaussian noise) were found in samples with volumes as large as  $10^{-11}$  cm<sup>3</sup>, unlike in any other material for which local defect motions are the noise source.<sup>5</sup> When measured with dc, the fluctuations in noise power in different octaves were not well correlated, which shows that the excess variance was not produced by a simple change in the some property of the whole sample. However, the possibility of drifts in H concentration due to initial spatial nonuniformities and to polarization produced over the course of the experiments made systematic study with dc measurement techniques difficult.<sup>7</sup> Also, since anomalously large variances and other non-Gaussian effects require that the noise come from a relatively small number of objects (which must therefore each be relatively large),<sup>5</sup> there was some question as to whether the large fluctuations were being produced by the effect of the dc current on the H, or whether they were present in the absence of current. Indeed, measurements of the imaginary cross spectrum between adjacent regions with a dc current flowing showed noise produced by positively charged mobile objects, but with magnitudes that were extremely sensitive to the direction of current flow. Hence we undertook the present study of the  $1/f$  noise in small Nb samples, probed by ac currents, with H concen-

trations partially controllable with dc voltages.

H in bulk crystalline Nb is known to have a very rich phase structure.<sup>8</sup> In films, however, distinct phase transitions are not observed at H concentrations which would give hydride precipitation in the bulk.<sup>1,9</sup> The bulk hydride phase results from attractive forces between nearby atoms in solution. In films, these attractive forces may still be present, but the constraints on expansion created by the substrate, inhomogeneous strains, and the presence of large numbers of extended defects, disrupt the formation of macroscopically distinct phases.<sup>10</sup> On the basis of x-ray-diffraction results, it has been proposed that no phase separation occurs in films of 40 nm thickness up to concentrations of more than one H per Nb.<sup>9</sup> While such evidence makes the existence of sharply demarcated hydride phases quite unlikely, it does not convincingly prove that the H concentration in the film is uniform. In free-standing films, the H spontaneously segregates toward one side of the film, producing a macroscopic curling, indicating that the attractive forces are still present when the substrate clamping is removed.<sup>11</sup>

The picture of how H is distributed in thin Nb films is thus far from clear. There are prior grounds for suspecting that there might be some sort of H clustering in Nb films, but neither the typical cluster size nor its dynamics in equilibrium or steady state can be inferred from such general considerations. We shall see that electrical noise provides information on both of these questions.

#### SAMPLE FABRICATION AND TECHNIQUES

Nb films were sputtered in an atmosphere of 5 m Torr argon. The chamber usually reached a pressure of less than  $8 \times 10^{-7}$  Torr before argon was admitted for sputtering. The 40-nm Nb films were sputtered at approximately 1 nm/s on glass or sapphire substrates. The films typically had resistivity  $\rho = 70 \mu\Omega \text{ cm}$ . The resistance of such a film decreases about 15% when the temperature is reduced from 300 to 77 K.

Complete four-arm bridges were patterned by photolithography. Such bridges have the advantages of being relatively immune to temperature fluctuations, temperature gradients, and contact noise while not requiring large current-limiting resistors and, hence, high-power current sources. Each arm of the bridge has dimensions  $2 \mu\text{m} \times 10 \mu\text{m} \times 40 \text{ nm}$ , with a resistance of about  $90 \Omega$  across two opposite corners. Samples were fabricated using either lift off or by using a  $\text{CF}_4$  plasma etch masked by 1350J-SF photoresist from AZ products. Additional arms were included for use in controlling H concentration, as shown in Fig. 1.

Wire leads were attached to the sample at silver contact areas. Leads were attached by soldering tinned copper wires to the silver films. These soldered leads had no measurable noise. Leads were also connected by pressing the tinned copper wire onto the silver with indium pads.

Noise measurements were made using ac probe currents in the range of 2–5 kHz. Both commercial and home-built lock-in amplifiers were used for demodulating

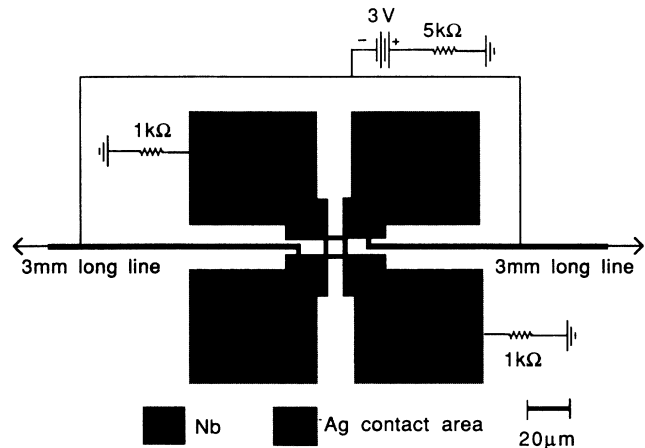


FIG. 1. Bridge sample geometry, including extra arms for introducing dc bias. Typical choices for removing hydrogen were 3 V in series with a  $5\text{-k}\Omega$  resistor. This caused a voltage drop of approximately 1 V across the long line of niobium.

the signal. Signal analysis was performed by a LSI-11 computer equipped with 12-bit (binary digit) analog-to-digital converters and a SKYMNK array processor to perform fast Fourier transforms (FFT's) and other vector operations.

The key techniques used in these studies are measurements of the statistical properties of the noise. These techniques have been described elsewhere.<sup>5</sup> Briefly, the variances and covariances of the noise power in a set of octaves (the highest band used is a half-octave, for reasons connected with aliasing) were determined from a series of discrete 1024-point Fourier-transform noise-power measurements. These quantities can be compared with the prediction for Gaussian noise, which is found whenever the noise results from a large number of independent objects. Deviations, usually in the form of excess variances and nonzero covariances, indicate that a significant fraction of the noise comes from a small number of objects.

We also analyze the time history of the fluctuations in noise power which causes the excess variance. This time history can be characterized by a second spectrum which shows the frequency dependence of the noise-power fluctuations. To find the second spectrum, the excess noise power in a particular octave was measured repeatedly. These noise powers are now treated as a new time series, whose power spectrum can be computed as a normal FFT. Thus one input point for the second spectrum is obtained from a FFT performed on 1024 first-spectrum voltage measurements. This shows the principal difficulty of the technique—the long times required to accumulate good statistics.

For Gaussian noise the second spectrum is uniquely determined by the first spectrum, and is white for broadband first spectra. Thus, the Gaussian prediction provides a natural normalization for the second spectra.

The dc field used to control H concentration was provided by batteries, as shown in Fig. 1. When the bridge

area was at about +1 V relative to the end of the long lead, the H would leave the bridge area in about 2 h, as judged by the change in resistance. While the dc voltage is on, an electron current continues to flow. But since the H cannot leave the Nb, there will be no steady-state current of H atoms. The spatial distribution of H should reach a static equilibrium.

The effects of a dc field on the equilibrium H concentration can be predicted by a simple Boltzmann distribution, to the extent that the H forms an ideal solution. Deviations will occur at high concentrations, for which interactions and large-scale strains are important, and also at low concentrations for which any special trapping sites are important. Nevertheless, we shall use this simple picture to give a qualitative idea of the effects of the applied fields.

When draining out the H, the voltage between the bridge area and the long leads was much greater than  $kT$ , so that after equilibration there were virtually no freely diffusing H atoms in the bridge area, although some H tightly trapped at defects could remain. The typical reduction in resistance was 1–2%. Assuming that the usual values for the resistivity change due to free H apply at low concentrations,<sup>12</sup> the typical initial free-H concentration was then about 1–2%, comparable to the values in previous studies of lithographically patterned films.<sup>1</sup>

For negative bridge voltages the H concentration increases. Quantitative calculations are more complicated, even assuming that the H forms an ideal solution. Under this assumption, the hydrogen concentration at a position  $x$  is given by  $\rho(x) = \rho_m e^{-ezV(x)/kT}$ .  $V(x)$  is the dc voltage at  $x$ ,  $e$  is the unit electronic charge,  $z$  is the effective charge number on the H [close to 1 (Ref. 13)], and  $\rho_m$  is the H concentration where  $V=0$ .

For a uniform strip of length  $L$  with one end grounded and the other at positive potential  $V$ , the concentration at the grounded end is given approximately by  $\rho = \rho_0(1 + zeV/2kT)$  for  $eV < kT$  and by  $\rho = \rho_0 zeV/kT$  for  $eV > kT$ .  $\rho_0$  is the initial uniform concentration with no dc field.

The geometry of our samples complicates this picture because the area of the bridge and Nb contacts is much wider than the long leads. The entire bridge area is nearly at equal potential ( $e\Delta V < kT$ ), and the area of Nb at this potential is about  $2000 \mu\text{m}^2$ . The area of each long lead is about  $4000 \mu\text{m}$  long by  $7 \mu\text{m}$  wide =  $28\,000 \mu\text{m}^2$ . The sample geometry can be analyzed as along strip with a wide section near one end, corresponding to the bridge area. For low voltages these complications have little effect. However, when a significant fraction of the total H is in the bridge, the concentration begins to saturate. The maximum possible concentration depends on the ratio between the bridge area and the total sample area.  $\rho_{\text{max}} = \rho_0 \times [(\text{total area})/(\text{bridge area})] = 28\rho_0$  for our sample geometry. Thus voltages much in excess of 1 V could not increase the H concentration in the bridge much.

By pumping in H, we could increase the resistance of the films by up to 90% (depending on the stability of individual films). Removing the H would then decrease the resistance to within 7% of the original resistance. This behavior is very much different from that of bulk Nb, in

which hydride phases form with resistances close to that of pure Nb. The maximum, nearly reversible resistivity change was, however, close to that observed in other work on films without distinct hydride precipitates.<sup>9</sup> The slight irreversibility is presumably due to the formation of defects in response to the strain induced by the H.

## NOISE RESULTS

With no dc field most samples showed a long-range diffusion noise regime between 0.35 and 7 Hz. The diffusion noise can be identified by the characteristic spectral shape close to  $f^{-3/2}$ . Between 0.1 and 0.35 Hz, the spectral form was between  $f^{-1}$  and  $f^0$ , and close to  $1/f$  below 0.1 Hz. In most samples the spectrum was close to  $f^{-1}$  above about 10 Hz. Within the accuracy of the extrapolation, the magnitude of the  $1/f$  component was typically 3 times as large below the diffusion regime as above it. The low-frequency rolloff point of the  $f^{-3/2}$  regime corresponded to a diffusion constant of  $3.5 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ . Nb films with lower resistivity have been previously reported<sup>1</sup> to have twice this H-diffusion rate. Bulk samples have diffusion coefficients larger yet by an order of magnitude.<sup>14</sup> The diffusion noise was consistently Gaussian, as expected since the number of more or less independent H atoms involved is very large.

The Hooge parameter  $\alpha$  is a dimensionless measure of noise power.  $\alpha \equiv NfS_v(f)/V^2$ , where  $N$  is the number of atoms in the sample,  $S_v$  is the spectral density of the noise power at frequency  $f$ , and  $V$  is the rms voltage across the sample. Before applying a dc voltage, the samples showed  $\alpha$ 's ranging from  $4.4 \times 10^{-5}$  to  $1.2 \times 10^{-3}$  at frequencies above the diffusion-noise regime.

Removing mobile H with a dc field reduced the diffusion noise to negligible levels above a  $1/f$  background, as expected and as illustrated in Fig. 2.

Figure 3 shows that removing mobile H also reduced the amount of  $1/f$  noise at frequencies above the diffusion regime. When the H was removed, the resis-

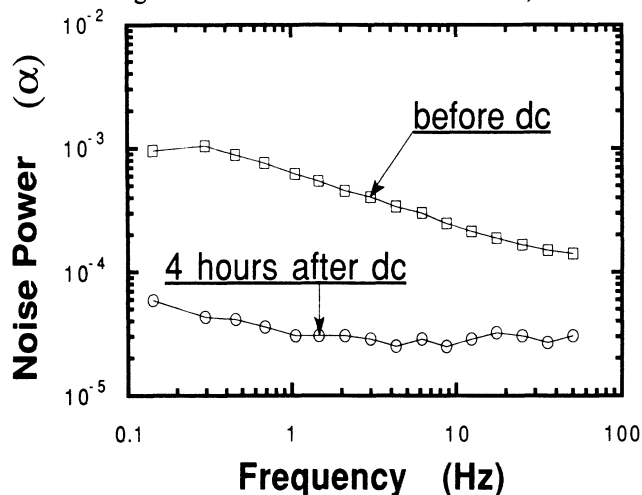


FIG. 2. The diffusion noise in sample C was reduced when the bridge was at positive potential. The voltage along the long lead was approximately 1 V.  $1/f$  noise appears horizontal in such a plot.

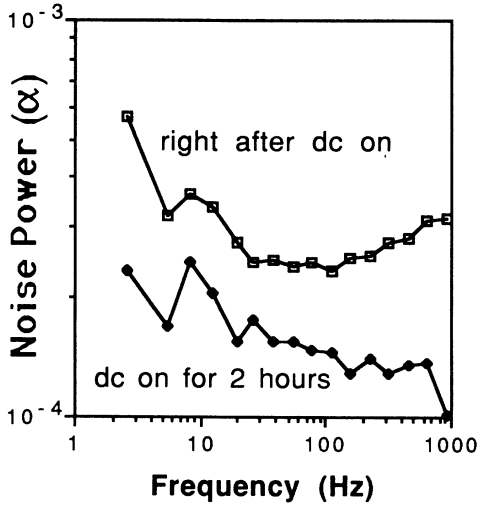


FIG. 3.  $\alpha$  was reduced in sample *I* when the bridge was at +0.5 V relative to the end of the long lead.

tance would usually decrease by about 1%, and the  $1/f$  noise was usually reduced by about 50%. However, the amount of  $(1/f)$ -noise reduction did show sample-to-sample variation. In two samples, the  $1/f$  component was reduced by only 20%, but in one sample it was reduced tenfold.

Although the dc field removed H responsible for diffusion noise, we believe that there may also be a significant amount of H stuck at defects, especially grain boundaries. Such H would not be removed by the dc field, but might still participate in noise-making fluctuations.

Making the bridge area negative relative to the line reservoir increased the H concentration and increased the resistance and noise power. Figure 4 illustrates the increase in  $(1/f)$ -noise power as the bridge is made more negative. There was no simple relationship between resistance increase  $\Delta R$  and noise-power increase. In one sam-

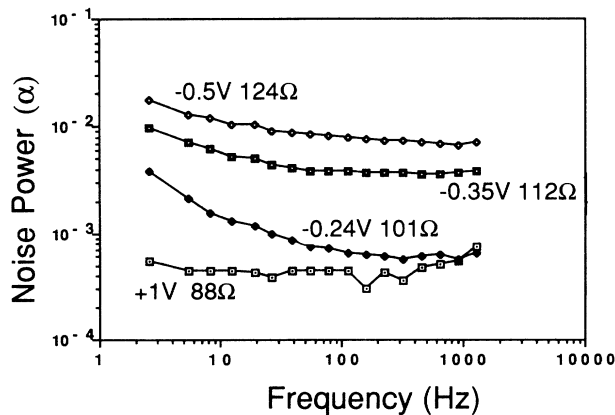


FIG. 4. Increasing the H concentration increased the noise in sample *F*. Written by each noise curve is the dc voltage and bridge resistance during the time the corresponding noise was measured.

ple the diffusion-noise power increased faster than either  $(\Delta R)^1$  or the  $1/f$  background. In other samples, the diffusion noise increased more slowly and was obscured by the increasing  $1/f$  noise. A resistance increase of 30% typically produced a  $(1/f)$ -noise power increase of 20-fold. At higher resistances, the samples often disintegrated.

One sample showed no clear diffusion-noise regime, although its power spectrum was steeper than  $1/f$  below 5 Hz. This sample had the highest resistivity,  $\rho = 205 \mu\Omega \text{ cm}$ , and the highest  $\alpha$ ,  $\alpha = 1.2 \times 10^{-3}$ , of the samples studied.

NON-GAUSSIAN NOISE

Of eight samples studied, three showed non-Gaussian noise. Sample *A* had apparently Gaussian  $1/f$  noise when the mobile H was removed. But when the resistance had been increased 80% by readdition of H, the noise became non-Gaussian. When the H was allowed to diffuse out, the excess variance below 4 Hz was reduced by a factor of 2, but significant non-Gaussianity remained.

Sample *C* originally showed Gaussian diffusion noise, but when the H was removed the residual  $1/f$  noise had excess variances of about 0.6 at 1 Hz in an octave consisting of four discrete Fourier bins. Above 1 Hz any excess variance was obscured by white noise.

Sample *I* originally had Gaussian  $1/f$  noise, but after the mobile H was removed and allowed to diffuse back, it had significant excess variance. The most extensive data were taken on this sample, which showed very stable non-Gaussian effects in the absence of any dc field. Figure 5 shows the excess variance of sample *I* as a function of frequency.

Table I shows the covariance matrix for this sample. The off-diagonal terms fall off for widely separated frequencies, indicating that whatever affects the noisiness of the sample is not a single parameter affecting all frequency ranges simultaneously. Figure 6 shows the correlation

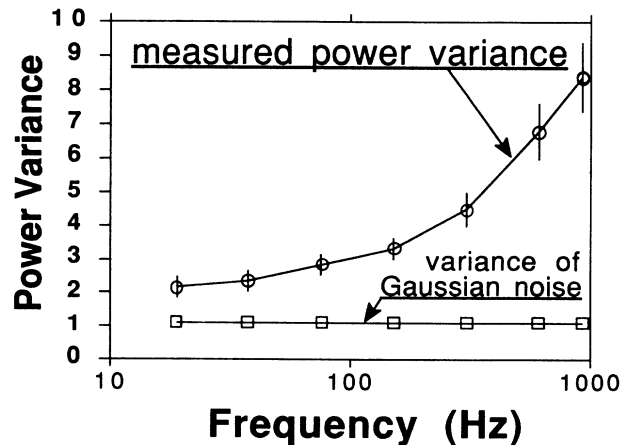


FIG. 5. Power variance vs frequency in sample *I*.  $12 \times 1024$  sweeps, each from 1024 data points, were used. The variances were corrected to eliminate the effect of the Gaussian Johnson noise superimposed on the  $(1/f)$ -noise signal.

TABLE I. Covariance matrix for sample *I*, taken from 400 1024-point data samples. The diagonal elements represent the variance of noise power in each frequency octave, normalized so that Gaussian noise would give 1. The off-diagonal elements are the correlation coefficients between power fluctuations in the different octaves. The correlation coefficients were corrected to eliminate the effect of the Gaussian component of the  $(1/f)$ -noise signal. Octave 6 is centered at 72 Hz. Higher octave numbers have higher frequencies. "Octave" 6.5 is a half-octave.

Octave	1	2	3	4	5	6	6.5
1	1.21						
2	0.94	1.21					
3	0.63	1.02	1.88				
4	0.58	0.90	0.89	2.65			
5	0.68	0.70	0.95	0.89	3.5		
6	0.54	0.65	0.81	0.80	1.0	4.72	
6.5	0.50	0.43	0.67	0.71	0.90	0.98	4.19

of the excess variance between octaves as a function of their frequency ratio, whose significance is discussed later.

Figure 7 shows a second spectrum of noise power from sample *I*. Several properties should be noted. First, the second spectrum is nowhere near white, which means that the noise cannot come from a simple superposition of two-state systems, no matter how large. Second, the second spectrum is far from  $1/f^2$ , which means that it is not due to steady drifts in the noisiness of the sample. (These features had also been noted in previous measurements made with dc currents.) In the data shown here there were no discernible long-term drifts in the sample noisiness, nor were there discernible drifts in the sample resistance.

The combination of the second spectral shape (Fig. 7)

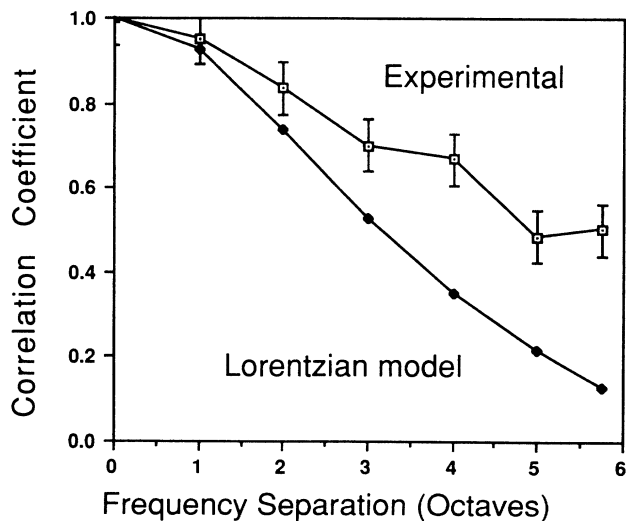


FIG. 6. The correlation coefficient of power fluctuations between different octaves in sample *I*. The correlation includes only the non-Gaussian component of noise. The experimental correlation (open squares) come from taking the average of off-diagonal terms in Table I. The Lorentzian prediction (solid diamonds) assumes noise from Lorentzian sources with a  $1/f$  distribution of characteristic rates, with each Lorentzian source having an independently modulated noise-power amplitude.

with the falloff in the off-diagonal covariance terms (Fig. 6), and the lack of discernible drifts in sample resistance, makes it extremely implausible that the non-Gaussian behavior of the noise is due to long-term drift in H concentration. Since these measurements were done with ac currents, there is no obvious reason for drifts to occur anyway.

## DISCUSSION

Our observations of noise-power dependence on H concentration were inconsistent with each H atom behaving as an independent scattering site. If the fluctuations in the scattering from each atom were independent, both diffusion noise and  $(1/f)$ -noise power (above some background unrelated to H) would scale simply as  $(\Delta R)^1$ .

The presence of  $1/f$  noise whose magnitude is strongly associated with the H concentration is itself somewhat surprising. The frequency range of this noise is six to ten decades below the characteristic hopping time of individual H atoms, inferred from the diffusion constant. The noise from such hops would then be expected to have a

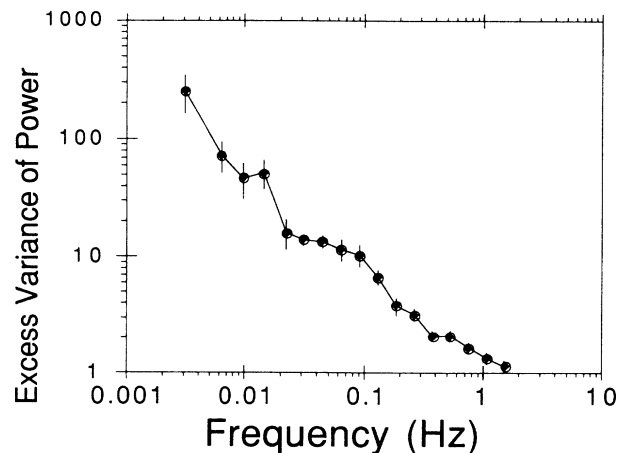


FIG. 7. Second spectrum of noise power in the octave around 500 Hz from sample *I*. The data used are the same as those in the next-to-last point of Fig. 5. The Gaussian second spectrum, defined as unity, was subtracted from the curve.

spectrum much flatter than  $1/f$  in our observation range. In fact, a relatively white component of the noise was detectable in some samples above 100 Hz and might well be due to the individual hopping steps, as found in other systems.<sup>2-4</sup> The  $1/f$  noise from H in Nb must then be due to either a fraction of the H atoms which hop at much slower rates than the rest, or to some other process involving the H atoms. The magnitude of the  $1/f$  noise was not so large that we could use it alone to rule out the possibility that a fraction of the H hopped slowly enough to give this noise.

The non-Gaussian effects provide limits on the size of independent fluctuators. The noise in any octave comes primarily from events whose duration is approximately the inverse of the characteristic frequency of the octave. The variance in the noise in an octave, other than that due to simple sampling of Gaussian fluctuations, arises from the variance in the number of these events. If, for example, the events occur with a Poisson distribution, the fractional variance is the inverse of the number of events. The absolute noise magnitude in the octave, however, gives the total variance in the resistance which comes from that same number of events. Thus by putting together the noise magnitude and its non-Gaussian variation, we can estimate the size of the resistance change per event. This, in turn, can be converted to the more physically meaningful scattering-cross-section fluctuation size, assuming that it is the scattering rates which fluctuate, since we know the approximate mean free path. From analytical calculations and simulations of various models,<sup>7</sup> we know that a given variance in the spectral density sets a lower limit on the size of the largest fluctuating cross sections involved in the noise, regardless of the details of the model.

For comparison, we can analyze the excess variance due to fluctuations from a set of two-state scatterers. We will assume, in accordance with the observed  $1/f$  spectrum, that the scatters have characteristic times which are chosen randomly from a distribution with constant density on a logarithmic scale of characteristic time. We also assume that the fluctuations of each scatterer affect the resistance by the same amount. Under these conditions, the spectral density of the noise has a fractional variance equal to  $2/\pi^2 nU$ , where  $n$  is the average number of scatterers per logarithmic unit in characteristic frequency per volume, and  $U$  is the sample volume.<sup>7</sup> Ordinarily, for fixed sets of two-state switchers, non-Gaussian effects are very small. However, if parameters such as the characteristic switching rates are not constant, the variance in the spectral density that would appear across an ensemble of samples of fixed two-state switchers appears in any one sample as a function of time.<sup>5</sup> (Such a picture is, in fact, indicated by the observed second spectra.) Substantial non-Gaussian effects result when  $nU$  is not much bigger than 1.

This model of two-state systems with slowly fluctuating parameters produces as large non-Gaussian effects as any plausible model with a given individual fluctuation size, for two reasons. First, two-state systems contribute Lorentzian spectra, which are as narrow as any plausible component in  $1/f$  noise. For a given noise level, the nar-

rower the individual spectral components are, the fewer that contribute to the noise in any octave, giving the largest random variance. Second, if we assume that each two-state system is stable for the length of a single spectral sweep, but disappears or acquires a new characteristic frequency during the overall data-collection time, all of this random variance appears as excess temporal variation in the spectral density. The data for sample *I* then require  $nU < 20$ .

This model also relates the average noise amplitude to the fluctuating cross section of each scatterer.  $\alpha = S_R(f)fn_A U/R^2 < n_A n \sigma^2 \lambda^2/4$ , where  $n_A$  is the concentration of metal atoms,  $\sigma$  the fluctuating scattering cross section, and  $\lambda$  the electron mean free path. We then have  $\sigma > 2(\alpha/n_A n)^{1/2}/\lambda$ . Numerically, for  $\alpha = 10^{-3}$ ,  $U = 3 \times 10^{-12}$  cm<sup>3</sup>,  $n_A = 6 \times 10^{22}$  cm<sup>-3</sup>,  $\lambda = 10$  nm, and  $nU = 20$ , we find  $\sigma > 10^{-13}$  cm<sup>2</sup>. Fluctuating cross sections estimated from previous data,<sup>7</sup> some taken with dc driving fields, were in the range  $10^{-13}$ – $10^{-12}$  cm<sup>2</sup>. (Modification of the assumptions to allow a range of fluctuating cross-section sizes would allow a larger total  $n$ , but also require a larger maximum  $\sigma$ .)

Fluctuating scattering cross sections greater than  $10^{-13}$  cm<sup>2</sup> cannot come from any pointlike scatterer, for which the maximum cross section is about  $10^{-15}$  cm<sup>2</sup>. Since we are in the limit in which the cross section exceeds the squared Fermi wavelength, the cross section gives a lower estimate for the size of the scatterer. We can conclude that 3 nm is a lower bound for the size of the largest fluctuating scatterers, assuming that they are very strong scatterers. More plausible estimates from the data would be in excess of 10 nm, since a number of inequalities have to be near their limits to produce the lower estimate. This 10-nm plausible size scale is not far from the sample thickness.

The large sample-to-sample variations are reminiscent of the effects observed in strained samples of several metals.<sup>15</sup> Some strain is introduced by changing the H concentration, but we do not think that the unusual noise statistics are simply due to large strain-induced defects, for three reasons. First, non-Gaussian effects appear in samples to which no dc fields have been applied, in those for which removing and readding about 1% H could introduce a small strain of about  $10^{-3}$ , and in those for which adding H could introduce larger strains. Second, the  $1/f$  noise depends monotonically on H concentration, even when removing H should introduce strain to an equilibrated film. Finally, our previous observation in spatial cross-correlation experiments of large non-Gaussian noise from positively charged, mobile objects can only be explained if H itself, not just some large defect, is involved.

The most plausible objects in our films with such large fluctuating scattering cross sections would consist of inhomogeneities in the H distribution. The inhomogeneities could cause noise by fluctuating in position, or, if they break cubic symmetry locally, in orientation. There is an apparent discrepancy between our conclusion that such large-scale inhomogeneities exist and previous conclusions, based largely on the presence of unimodal x-ray-diffraction patterns, that in films the attractive po-

tential between the H atoms was suppressed by the mechanical constraint of binding to the substrate.<sup>9</sup> However, the noise technique is particularly sensitive to large objects, while x-ray techniques on polycrystalline samples are less sensitive to such inhomogeneities, although capable of detecting some hydride phase separations. Differences in the film properties, as manifest in different resistivities, could also account for different behavior.

The particular statistical properties of the noise give information on the dynamics of the fluctuations of the hypothetical inhomogeneities. Conductivity fluctuations in some other systems result from switching between several discrete states.<sup>5</sup> If the inhomogeneities made abrupt transition between discrete states, the resulting resistance changes would cause abrupt switching between discrete voltage levels. No such discrete switching was observed, suggesting the possibility that the fluctuations may be continuous. However, our inability to detect such discrete switching does not prove its absence.

There are more sensitive tests for discrete several-state systems. Such several-state systems can show nonwhite second spectra (unlike two-state systems), but they also show features in the first spectrum resulting from the superposition of a finite number of randomly distributed Lorentzian components. Our spectra showed no evidence of such features, unlike many other systems.<sup>5</sup>

There is at least one other system<sup>16</sup> (GaAs) which also showed large nonwhite second spectra without first-spectral features. Those results were interpreted as coming from the Lorentzian contributors which were active only a small fraction of the time. However, unlike in GaAs, the correlations between the noise-power fluctuations in separate octaves (see Fig. 6) fall off more slowly than would be found for a collection of independently modulated Lorentzian contributors. The implication is that the range of fluctuation frequencies in a fluctuating

unit is broader than in a single Lorentzian, implying that the units are not two-state systems, even when viewed for times on the order of the correlation time.

All these facts strongly suggest that the fluctuating objects cannot be cleanly divided into fairly simple independent units. Most likely, long-range-strain constraints together with a large random binding term from grain boundaries and other extended defects lead to a complicated set of low-energy configurations for the inhomogeneities in the H distribution. The anomalous noise arises from wandering in that complicated set of allowed configurations. Whether such effects would occur in true thermal equilibrium is unclear, since the presence of the non-Gaussian effects depends on sample history. However, it is clear that this fluctuating state can persist for times as long as days.

We do not believe that our conclusions about the behavior of dissolved H in Nb films are particularly surprising, although they are not in agreement with the simplest interpretation of previous experiments on similar systems.<sup>9</sup> However, they do indicate a mechanism for generating  $1/f$  noise that has little in common with those found in other metals. It seems to be an intrinsic property of this mechanism that the results are less reproducible than are those for noise in other metals.<sup>17</sup> However, if that were to be taken as grounds for not reporting them, the overall picture of the variety of sources of  $1/f$  noise in metals would be incomplete.

#### ACKNOWLEDGMENTS

We wish to thank H. Birnbaum and H. Zabel for very instructive conversations and N. M. Zimmerman for discussions of his unpublished data. This work was funded by the U.S. National Science Foundation, under Grant No. NSF-DMR-86-17941.

<sup>1</sup>J. H. Scofield and W. W. Webb, Phys. Rev. Lett. **54**, 353 (1985).

<sup>2</sup>N. M. Zimmerman and W. W. Webb, Phys. Rev. Lett. **61**, 889 (1988).

<sup>3</sup>G. B. Alers, M. B. Weissman, R. S. Averback, and H. Shyu, Phys. Rev. B **40**, 900 (1989).

<sup>4</sup>N. M. Zimmerman and W. W. Webb, Bull. Am. Phys. Soc. **34**, 839 (1989).

<sup>5</sup>M. B. Weissman, Rev. Mod. Phys. **60**, 537 (1988); M. J. Kirton and M. J. Uren, Adv. Phys. **38**, 367 (1989).

<sup>6</sup>P. J. Restle, M. B. Weissman, and R. D. Black, J. Appl. Phys. **54**, 5844 (1983).

<sup>7</sup>G. A. Garfunkel (unpublished).

<sup>8</sup>T. Schober and H. Wenzel, in *Hydrogen in Metals II*, edited by G. Alefeld and J. Völkl (Springer-Verlag, Berlin, 1978), p. 11.

<sup>9</sup>S. Moehlecke, C. F. Majkrak, and M. Strongin, Phys. Rev. B **31**, 6804 (1985).

<sup>10</sup>Several papers discuss the effects of long-range mechanical constraints and of defects on the hydrides of Nb, e.g., H. Zabel and H. Peisl, Phys. Rev. Lett. **42**, 511 (1979); H. Wagner,

in *Hydrogen in Metals I*, edited by G. Alefeld and J. Völkl (Springer-Verlag, Berlin, 1978), p. 5; H. Peisl, *ibid.*, p. 54; Ch. A. Wert, in Ref. 8, p. 305.

<sup>11</sup>H. Zabel (private communication and demonstration).

<sup>12</sup>G. Pfeiffer and H. Wipf, J. Phys. F **6**, 167 (1976).

<sup>13</sup>A. H. Verbruggen and R. Griessen, Phys. Rev. B **32**, 1426 (1985).

<sup>14</sup>J. Völkl and G. Alefeld, in *Hydrogen in Metals I*, edited by G. Alefeld and J. Völkl (Springer-Verlag, Berlin, 1978), p. 321.

<sup>15</sup>D. M. Fleetwood and N. Giordano, Phys. Rev. B **28**, 3625 (1983); D. M. Fleetwood, Ph.D. dissertation, Purdue University, 1984.

<sup>16</sup>P. J. Restle, G. A. Garfunkel, M. B. Weissman, P. Pearah, and H. Morkoç, Phys. Rev. B **34**, 4419 (1986).

<sup>17</sup>N. M. Zimmerman (private communication) has observed similar complications in ( $1/f$ )-noise measurements in Nb films, unlike his observations of well-behaved H noise in Pd films.

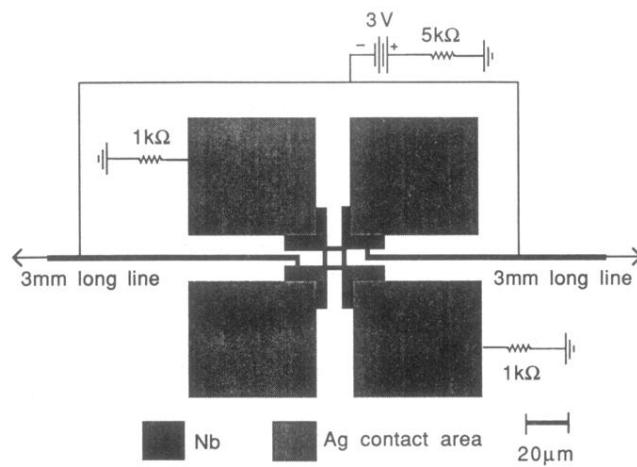


FIG. 1. Bridge sample geometry, including extra arms for introducing dc bias. Typical choices for removing hydrogen were 3 V in series with a 5-kΩ resistor. This caused a voltage drop of approximately 1 V across the long line of niobium.