

## Mechanical relaxations and $1/f$ noise in Bi, Nb, and Fe films

G. B. Alers\* and M. B. Weissman

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

(Received 4 March 1991)

Anelastic piezoresistance and  $1/f$  noise were measured in the same samples to compare mechanical relaxations with  $1/f$  noise. In bismuth below 200 K, both effects could be fitted to a model invoking one class of mobile defects. In niobium, both the anelastic piezoresistance and the noise scaled with the concentration of dissolved hydrogen. A well-defined peak in noise versus temperature was observed without any peak in the anelastic response. In iron, noise apparently from a carbon Snoek relaxation was observed at 220 K in a sample with high impurity concentration and at 300 K with low impurity concentration. No anelastic feature was found at 220 K in the high-impurity-concentration sample. The broad nature of  $1/f$  noise appears to arise not from a fundamental source but from the generally poor quality of thin films.

It is now fairly well known that  $1/f$  resistance noise in metals comes from the thermally activated motion of defects.<sup>1,2</sup> Several point-defect systems have been rather conclusively identified with the generation of resistance noise.<sup>3-6</sup> However, there are still some unanswered questions concerning the relation of the noise to the defect motions. First, the quantitative connection between noise and fluctuating electronic scattering by defects is not well established. Second, if noise does arise from defect motions then one would expect a correlation between noise magnitude and internal friction magnitude for a given material. However, to date no systematic study has been made for both noise and internal friction in the same samples. Only for the special case of dissolved hydrogen in amorphous metals have the noise in films and the internal friction of bulk shown a definite correspondence.<sup>3-5</sup>

The connection between internal friction and resistance fluctuations is a consequence of the fluctuation dissipation theorem.<sup>1,7</sup> The dissipation of mechanical energy (internal friction) will always be accompanied by thermally activated mechanical strain fluctuations. The spectral density of these strain fluctuations is proportional to  $Q^{-1}T/f$ , thus giving  $1/f$  strain noise for a frequency-independent friction background. If the defects with anisotropic strain tensors also have anisotropic resistivity tensors then the resistance should also fluctuate.<sup>1,7</sup>

In this paper we present measurements of the anelastic piezoresistance (AP) (see Berry and Orehtsky<sup>8</sup>) and  $1/f$  resistance noise in the same thin film samples. AP is the resistance change from stress-induced ordering of defects. The presence of AP implies a connection between resistance and anelastic relaxation because it only arises when the *same* defect motions cause both resistance changes and strain changes with rates in the appropriate frequency range. However, as will become apparent, large AP is a sufficient but not necessary condition for noise and friction to arise from the same motions. Noise and friction depend on the average (over defects) of the square of the resistivity and strain changes while AP depends on their

average product, which can be small when the sign of one or both effects varies between sites. Furthermore, the asymmetry of the strain may be different than the asymmetry of the resistivity tensors so that a certain defect motion couples to one better than it couples to the other. By comparing the noise and AP we may obtain information on whether the sites giving rise to the noise and the anelasticity are similar and homogeneous.

We shall see that the correspondence between the noise and the AP is weak. We report, surprisingly, that in each of the systems examined the noise magnitude showed sharper features as a function of temperature than did the AP. One implication is that the belief by some—that there is something more universal about  $1/f$  noise than about other low-frequency dynamical properties—is unjustified. That belief appears to be based on the experimental artifact that  $1/f$  noise is usually measured in poorly ordered films while most other properties, such as internal friction, are usually measured in bulk crystalline material.

### BACKGROUND

The model of  $1/f$  resistance noise from the thermally activated motion of defects with a large spread of rates has been developing for some time.<sup>1</sup> Specific defect systems that have been studied include dissolved hydrogen,<sup>3-5</sup> irradiation produced defects in Cu,<sup>6</sup> defects in Ag-Pd,<sup>9</sup> and grain boundary noise in gold<sup>10</sup> and aluminum.<sup>11</sup> However, there are still several open questions about this picture. These include the following.

(1) There is a lack of agreement between noise and internal friction studies of defects. Many metals that have been studied by noise, such as bismuth,<sup>12-14</sup> aluminum,<sup>11</sup> and silver,<sup>12</sup> show peaks in noise versus temperature when no such corresponding maximum exists for internal friction at the same temperature.<sup>15,16</sup> Conversely, many metals that show features in internal friction do not show features in noise.

(2) Defect states generally have well-defined charac-

teristic relaxation times as measured via internal friction, whereas 1/f noise, by definition, requires a very broad range of characteristic times. Resistance noise is generally measured in thin films which have a high density of defects that may cause a large amount of broadening of the distribution of characteristic rates. The important question then becomes whether internal friction in thin films is as broad as 1/f noise?

(3) Quantitative predictions for 1/f noise have been very rough because of uncertainties about the exact defect motions involved and uncertainties about their coupling to electron scattering. For defects produced by irradiation of copper films, Pelz and Clarke<sup>6</sup> found that a simple picture of diffusing vacancies could not explain the noise (by symmetry considerations). Other extended defects such as grain boundaries, etc., had to be invoked to explain the magnitude of the noise per defect. Zimmerman and Webb<sup>5</sup> also found that the noise from hydrogen diffusion in palladium could not be explained without invoking some other unspecified defects which made little net contribution to the resistivity. Other attempts to make quantitative predictions for 1/f noise magnitudes have been even less successful, with the unique exception of the spin reorientation noise<sup>17</sup> in the spin-glass copper-manganese. Noise from point-defect relaxations such as Snoek and Zener relaxations should be observable in most metals, but examples of such relaxations have not been studied.

The following experiments attempt to address these questions. The first two questions may be addressed by measuring mechanical relaxations and 1/f noise in the same thin-film samples. Many of the differences between noise and internal friction might be due to the differences between bulk samples and thin film samples. The third question may be addressed by measuring the coupling between mechanical relaxations and resistivity, i.e., AP,<sup>8</sup> for specific defect systems.

Anelastic piezoresistance (AP) may be described by a complex frequency-dependent piezoresistance,  $M(f)$ , for isotropic materials

$$E\delta\rho(f)/\rho\sigma_m(f) = M(f) = M_R(f) + iM_I(f), \quad (1)$$

where  $\rho$  is the resistivity,  $\sigma_m(f)$  is the applied mechanical stress at frequency  $f$ , and  $E$  is the Young's modulus. The real part,  $M_R(f)$ , is ordinarily dominated by the intrinsic elastic piezoresistivity and by the changes in geometry due to the applied stress. The imaginary part of  $M(f)$ ,  $M_I(f)$ , is usually due to the relaxation of defects with characteristic rate near  $f$ .

The origin of the AP may be most easily understood for the case in which a specific defect type breaks the local crystal symmetry and thus has an anisotropic strain and resistivity tensor. Stress-induced partial ordering of the defects changes the resistivity tensor at the sites that rearrange and therefore causes an overall resistance change.<sup>8</sup> Sites that have relaxation rates comparable to the frequency of the applied stress will produce an out-of-phase response in both the strain and the resistance giving both internal friction and AP.<sup>18</sup> Thermal fluctuations in the orientations will also occur giving rise to

resistance noise at the same frequency.

The magnitude of the out-of-phase response may be calculated for a density  $n_d(f, T)$  of mobile defects. Here  $n_d(f, T)$  is defined as the density of defects thermodynamically able to fluctuate with characteristic rate within a factor of  $e$  about  $f$ . An applied mechanical stress  $\sigma_m$  at frequency  $f$  will cause a density  $[\sigma_m n_d(f, T) \langle \delta\lambda \rangle] / n_a kT$  to rearrange<sup>16</sup> where  $n_a$  is the concentration of atoms and  $\langle \delta\lambda \rangle$  is the associated average elastic dipole asymmetry per atomic volume of the defects. Each defect rearrangement will have a corresponding change in effective electronic scattering cross section given by  $\delta\sigma_e$ .<sup>7</sup> The fractional change in resistivity from defect relaxations per unit strain will then be

$$M_I(f) = \frac{El}{\Omega kT} \sum_i (\delta\lambda \delta\sigma_e)_i \quad (2)$$

where  $l$  is the mean free path,  $\Omega$  is the sample volume, and the summation is over each mobile defect. The important point to emphasize about this expression is that it is bilinear and depends on the correlation between the stress-induced ordering and the resistive change of each defect. Random interference terms in the resistivity tensor will average out, and only systematic resistivity changes will contribute to give an overall anelastic response of

$$M_I = \frac{n_d(f, T) E \langle \Omega_m \Omega_e \rangle}{kT} \quad (3)$$

where  $\Omega_e = (l \delta\sigma_e)$  is the effective electronic coupling volume averaged over all defect motions, and  $\Omega_m = (\delta\lambda / n_a)$  is the effective mechanical volume.

Resistance noise power, in contrast to the anelastic piezoresistance, is proportional to the *square* of the resistance change of each defect and is therefore sensitive to random interference effects. The power spectrum of the fractional changes in the resistance  $S(f, T)$  can be expressed in terms of  $\alpha_a$ , a dimensionless number defined by<sup>1</sup>

$$S(f, T) = \alpha_a(f, T) / (n_a \Omega f). \quad (4)$$

In terms of the above-mentioned coupling constants, the magnitude of the fractional resistance fluctuations may be expressed as

$$\alpha_a(f, T) = (2/\pi) n_a n_d(f, T) \langle \Omega_e^2 \rangle. \quad (5)$$

In the above expressions, there are effectively three quantities of interest: the density of active defects  $n_d(f, T)$ , the average product of the mechanical and electronic coupling  $\langle \Omega_e \Omega_m \rangle$ , and the average squared electronic coupling  $\langle \Omega_e^2 \rangle$ . If a uniform mechanical coupling constant is taken from measurements of internal friction in similar systems and we further assume that  $\langle \Omega_e^2 \rangle = \langle \Omega_e \rangle^2$  then only two unknowns remain—the density of mobile defects and  $\langle \Omega_e \rangle$ . These may be determined from the combined noise and AP measurements. If one obtains unreasonable numbers for these two quantities then one of the assumptions is wrong, most likely indicating that the expected product of the mechanical and electrical coupling factors is highly inhomogeneous,

either because there are more than one type of defect or because random interference terms<sup>3</sup> dominate the electronic coupling. Alternatively, if enough is known about the concentration of defects then useful limits on  $\langle \Omega_e \Omega_m \rangle$  and  $\langle \Omega_e^2 \rangle$  can be obtained without necessarily invoking assumptions about  $\langle \Omega_m \rangle$ .

To gain more information on the coupling constants, it can be useful to examine the ratio of the AP to the noise:

$$\frac{M_I}{\alpha_a} = \frac{\pi E}{2kTn_a} \frac{\langle \Omega_m \Omega_e \rangle}{\langle \Omega_e^2 \rangle} \approx \frac{\langle \Omega_m \Omega_e \rangle}{\langle \Omega_m \rangle \langle \Omega_e \rangle} \frac{\langle \Omega_m \rangle}{\langle \Omega_e \rangle} \frac{\langle \Omega_e \rangle^2}{\langle \Omega_e^2 \rangle} \quad (6)$$

An exceptionally small ratio of  $M_I/\alpha_a$  then implies one of the following.

(1)  $\langle \Omega_m \Omega_e \rangle / \langle \Omega_m \rangle \langle \Omega_e \rangle \ll 1$ , i.e., the mechanical and electronic asymmetries are not correlated.

(2)  $\langle \Omega_m \rangle / \langle \Omega_e \rangle$  is smaller than for typical defects. The mechanical coupling may be unusually small because of a small internal strain or a small elastic asymmetry.

(3)  $\langle \Omega_e \rangle^2 / \langle \Omega_e^2 \rangle \ll 1$ , i.e., the random interference terms in the electronic coupling greatly exceed the systematic term. This condition will be true in films with a high degree of disorder or electronic interference with extended defects.

Therefore, by combining measurements of the AP and the noise in the same sample we can gain insight into the electronic coupling of the defect motion as it pertains to resistance noise. We can determine whether the scattering that determines  $\langle \Omega_e^2 \rangle$  is dominated by systematic scattering terms which are the same for each defect or by random interference terms from neighboring defects. The quantitative details of the electronic scattering for a specific defect motion are beyond the scope of this paper, but determining if the scattering is random or systematic is important to any future attempt to quantify  $1/f$  noise. The only details of the electronic scattering that we will be concerned with here are contained in the average change of scattering section ( $\delta\sigma$ ) when a defect motion occurs.

If the defect motion coupled to resistance solely via universal conductance fluctuations<sup>14</sup> then  $M_I(f, T)$  would be zero because the conductance change produced by any particular defect motion is random, depending on the relative positions of other scatterers within a coherence volume. The resistance noise would remain because each defect motion still produces a resistance change, though with a sign not predictable from purely local considerations. Therefore, a measurable  $M_I$  would imply that the electronic coupling is not dominated by universal conductance fluctuations.

Three materials were examined in this experiment: bismuth, niobium-hydrogen and iron-carbon. These materials were chosen because they have been studied previously by resistance noise and/or internal friction, and in each case there was reason to believe that noise and/or friction arises from a relatively uniform set of sites.

Resistance noise in the semimetal bismuth has been studied extensively, mainly because the high resistivity and high  $\alpha$  make noise measurements easy.  $\alpha(10 \text{ Hz}, T)$

has a peak as a function of temperature at roughly 200 K, the origin of which is still unknown.<sup>12-14</sup> It is this peak region that we are primarily interested in because no corresponding peak has been observed in the internal friction of bulk bismuth.

Iron is one of the materials most extensively studied by internal friction. There is a very well-studied peak in the attenuation at 290 K from a Snoek rotation of carbon impurities.<sup>15,16</sup> Noise in iron thin films has not been studied systematically.

A great deal of work has been done studying both internal friction and resistance noise from dissolved hydrogen in metals.<sup>3-5,18</sup> These systems have the advantage that the concentration of defects can be controlled by either hydrogen sorption or electrically sweeping<sup>19</sup> the hydrogen in and out of the sample. In niobium films the low frequency resistance noise has been seen to peak in the 50–120 K temperature range, depending on the concentration of hydrogen.<sup>20</sup> Similarly, a peak in internal friction has been observed in single crystals of niobium with oxygen impurities.<sup>18</sup> The peak in both has been attributed to the hopping of hydrogen between interstitial sites. In the case of internal friction, it was possible to identify the hydrogen involved as those trapped at oxygen impurities. For the noise, however, the exact sites involved are still uncertain. Because this is one of the few systems that has been studied by both internal friction and noise, it is a very well-suited candidate in which to study the anelastic piezoresistance.

## EXPERIMENT

To make a comparison between anelastic relaxations and  $1/f$  noise it is necessary to measure the anelastic response in thin films or perhaps whiskers. Some work on internal friction in films has been done by Berry and Pritchett<sup>21</sup> using thin vibrating reeds. We chose to apply periodic stress to the film by depositing it on a piezoelectric substrate. The film was strained with a periodic voltage applied to the piezoelectric substrate at a frequency low relative to the resonance of the substrate and the anelastic piezoresistance was measured by phase sensitive demodulating the low frequency resistance change. With this technique, unlike vibrating reed techniques, there is no anelastic background from the substrate to subtract. The phase shift from the piezoelectric substrate should be negligible because the straining frequency (5–10 Hz) was much lower than the mechanical resonance of the substrate (5–10 MHz). Any out-of-phase response from defects in the substrate would almost certainly be unimportant considering the high  $Q$  of the crystals and the size of the observed out-of-phase piezoresistance, which exceeded 2% of the in-phase response in all cases.

The piezoelectric substrates were PZT-5a ceramic with a thickness of 100–200  $\mu\text{m}$ . This piezoelectric ceramic had roughly a factor of 100 higher piezoelectric constant than quartz. The substrates were glued with conductive epoxy to either a glass or silicon base for rigidity with a thin metal film (usually Cr) as a conductor on the base. A 100–200 nm thick electrode of Cr was deposited on the top of the crystal and patterned using standard photol-



There is a very apparent feature in the temperature dependence of  $\alpha_a$  at 170 K as has been noted before.<sup>13,14</sup>  $M_I(5 \text{ Hz}, T)$  shows a strong temperature dependence in the region below 170 K. In the region of the noise peak and at lower temperatures, there appears to be some qualitative agreement between the anelastic response and the noise, with exceptions discussed below.

**Niobium.** The samples studied were deposited by rf magnetron sputtering onto room-temperature substrates at a rate of 5 Å/s and 250 W of input power. Higher deposition rates caused degradation of the polyimide layer and shorting of the sample to the upper pole of the piezoelectric substrate. Impurities in similar films were found to be roughly 2% oxygen and 4% carbon as determined by Auger analysis. An oxidized sample of niobium was used as a standard for oxygen concentration, but no standard was available for the carbon concentration which gives this quantity an uncertainty of about a factor of 2. The grain size was on average 50 nm by TEM. The resistivity of the films was 25  $\mu\Omega$  cm, compared to a bulk resistivity of 14.5  $\mu\Omega$  cm and the elastic piezoresistance was  $M_R = 1.0 \pm 0.3$ .

The sample was patterned by liftoff into a six-probe line with two center probes and dimensions 15  $\mu\text{m} \times 600 \mu\text{m} \times 0.05 \mu\text{m}$  for each side of the bridge. Contact was made by briefly milling the niobium surface and then depositing 50 nm of silver onto a contact region of the niobium. One of the silver center probes was used to apply a positive dc potential between the center of the line and the large niobium contact areas at each end of the line to electrically sweep out the hydrogen from the sample.<sup>19</sup> By varying this potential at room temperature, allowing time to equilibrate (roughly 1 day), and then cooling down, it was possible to control the average concentration of hydrogen in the sample. The concentration of the hydrogen could be estimated by the change in resistivity relative to that found when a field large enough to remove all the mobile hydrogen (3 V/cm) was applied.

Figure 3 shows  $\alpha(5 \text{ Hz}, T)$  for three concentrations of hydrogen over the temperature range in which a peak is observed. At higher temperatures, long-range diffusion of the hydrogen starts to become important. Figure 4 shows the  $M_I(5 \text{ Hz}, T)$  in the temperature range of the peak for the same three concentrations of hydrogen. The  $M_I(5 \text{ Hz}, T)$  was found to be somewhat hysteretic ( $\pm 15\%$ ) and the data in Fig. 4 is averaged over this hysteresis. Above 200 K the hysteresis became larger and the  $M_I(5 \text{ Hz}, T)$  drifted with time.  $\alpha(5 \text{ Hz}, T)$  was reproducible within 5% at all temperatures.  $\alpha(5 \text{ Hz}, T)$  shows a definite peak at 110 K whose size scales with hydrogen concentration, as shown in Fig. 3.  $M_I(f, T)$  also scales with hydrogen concentration, yet does not show any dramatic peak. The scaling of  $M_I(f, T)$  with hydrogen concentration strongly suggests that hydrogen motion is in fact the source of the anelastic response.

**Iron.** The following is the first examination of 1/f noise from impurities in iron. Results from two samples will be reported here, "clean" iron and "dirty" iron.

The iron films were prepared by the electron-beam evaporation with rates of roughly 1 Å/s in a background pressure of  $10^{-6}$  to  $10^{-7}$  Torr onto room-temperature

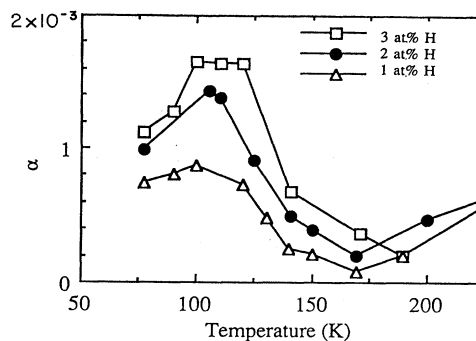


FIG. 3. Resistance noise magnitude  $\alpha_a$  at 5 Hz in a thin-film sample of niobium for three concentrations of hydrogen. Hydrogen concentration was controlled with a dc electric field applied to the center of the line sample.

substrates. Films made in parallel to the sample films were examined by SIMS for contamination. No standard was available for the iron films, so all absolute concentrations have an uncertainty of about a factor of 2. Relative concentrations between the two films discussed should be much more precise. The clean iron films were 100 nm thick and found to contain on average 1.5% oxygen and 0.03% carbon. The room-temperature resistivity was 28  $\mu\Omega$  cm (compared to a bulk value of 9.8  $\mu\Omega$  cm) and the residual resistance ratio was  $\mathcal{R} = 2.0$ . The "dirty" iron films were 70 nm thick and were evaporated from a composite source of iron, manganese, and carbon and had a concentration of 10% manganese, 2% oxygen, and 0.5% carbon. The room-temperature resistivity was 65  $\mu\Omega$  cm and  $\mathcal{R} = 1.3$ . The dirty and clean iron had a measured elastic piezoresistance of  $M_R = 2.0 \pm 0.5$  and  $M_R = 1.5 \pm 0.5$ , respectively, without any annealing. For the dirty iron films, a 500 nm layer of thermally evaporated  $\text{SiO}_x$  was used as an insulating layer between the substrate and the sample instead of polyimide because dirty films deposited on polyimide were found to crack, most likely due to the large residual stress in the films.

Large amounts of manganese were necessary in the films to act as pinning sites for the carbon.<sup>15</sup> If no man-

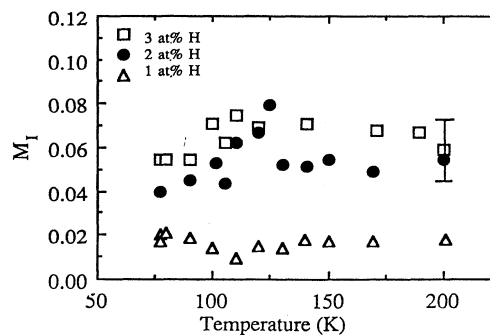


FIG. 4. Out-of-phase piezoresistance for the niobium film sample of Fig. 3 with the same hydrogen concentrations.

ganese was present then the sample noise and anelastic response were observed to be very large and nonstationary within hours after deposition, but would drop dramatically after about a day and no peak in the anelastic response or the noise would be observed. This behavior is presumed to arise from the diffusion of carbon atoms to trapping centers such as grain boundaries or clusters where the carbon would no longer be mobile. Samples with smaller concentrations of manganese did not show a stable peak in the noise. Use of such large amounts of the manganese complicates the analysis of the results because the environment of the carbon atoms is highly disordered.

Figure 5 shows  $\alpha_a(5 \text{ Hz}, T)$  in the clean and dirty iron samples. A well-defined peak is observed in the noise of the dirty sample at 225 K which is roughly two orders of magnitude above the noise in the clean sample. The peak in  $\alpha_a(f, T)$  for the dirty sample is also observable in the spectrum as shown in Fig. 6. The change in frequency of this peak with changes in temperature can be used to calculate an activation energy and prefactor for this feature. We found an activation energy of  $0.7 \pm 0.1 \text{ eV}$  with a prefactor of  $f_0 = 10^{16} \text{ Hz}$ . This activation energy is slightly smaller than  $0.83 \text{ eV}$  observed in bulk samples.<sup>15,16</sup> Shifts in activation energy may result from internal strain such as caused by large amounts of impurities.

$M_I(f, T)$ , as shown in Fig. 7, does not show a peak for the dirty iron.  $M_I(f, T)$  is even observed to be smaller in the dirty sample than in the clean sample, although part of this reduction is simply due to the normalized form of  $M_I(f, T)$  and the factor of 2.3 difference in resistivity of the two samples. It appears then that there is no correspondence between the noise and the AP in the dirty iron. In the clean iron, however, a plateau in both the AP and the noise at roughly 280 K might be attributable to carbon, though it is difficult to say conclusively without a well-defined feature in the spectrum.

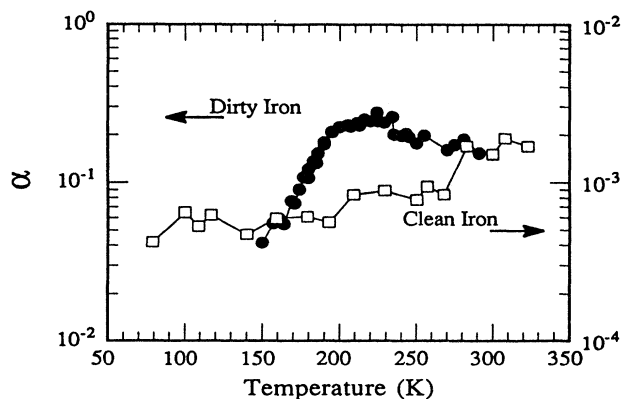


FIG. 5. Resistance-noise magnitude  $\alpha_a$  at 5 Hz for two thin film sample of iron. The dirty iron contained roughly 10 at. % manganese and 0.5 at. % carbon. The clean iron contained roughly 0.03 at. % carbon.

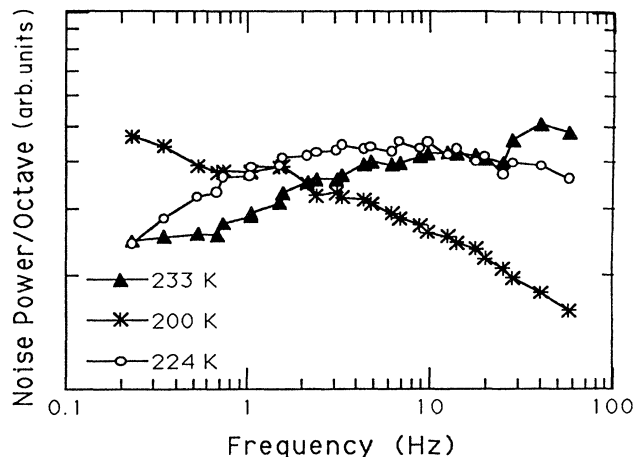


FIG. 6. Resistance noise power spectrum at three temperatures for the dirty iron film of Fig. 5. In this format,  $1/f$  appears flat. The shift of the spectrum with changes in temperature was used to calculate an activation energy.

## DISCUSSION

*Bismuth.* The plot in Fig. 2 shows both the anelastic response and the resistance noise in a logarithmic plot so that the relative scales differ only by the multiplicative constant. In the region 100–200 K there appears to be good agreement between the AP and the noise. At the lowest temperature,  $\alpha_a(f, T)/T$  does not drop as quickly as  $M_I(f, T)$  with lowering temperature. This effect is expected due to the “universal conductance fluctuation” phenomenon,<sup>14</sup> which does not appear in the anelastic response for reasons discussed above.

The anelastic response rises near room temperature, which is most likely due to annealing affects or the “high-temperature background”<sup>15,16</sup> of the mechanical relaxations. The melting point of Bi is low and mechanical relaxations are known to grow exponentially near the

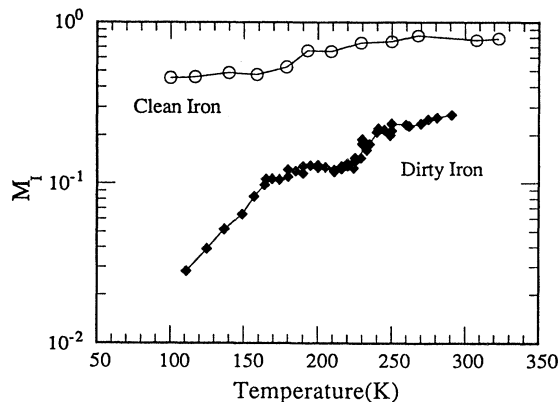


FIG. 7. Out-of-phase piezoresistance for the same iron films of Fig. 5.

TABLE I. Summary of measured quantities from the resistance noise and anelastic piezoresistance for the three systems studied. For calculations of  $n_d(f, T)$ ,  $\langle \delta\lambda \rangle$ , and  $\langle \Omega_e \rangle$ , one quantity had to be estimated from prior knowledge for the other two to be calculated. The estimated quantities are labeled by an asterisk. The other two derived quantities depend on the estimated one, as described in the text.

| Material        | $M_R$<br>(295 K) | Temperature<br>of peak (K) | $M_I$<br>at peak | $\alpha_a$<br>at peak | $n_d(f, T)$<br>(at. %) | $\langle \delta\lambda \rangle$<br>( $n_a \Omega_m$ ) | $\Omega_e$<br>( $\text{cm}^3$ ) |
|-----------------|------------------|----------------------------|------------------|-----------------------|------------------------|---|---------------------------------|
| Bi              | 20               | 170                        | 3.3              | 0.12                  | $5 \times 10^{-2}$     | 1*  | $7 \times 10^{-22}$             |
| Nb-3 at. % H    | 1.0              | 110                        | 0.07             | $3.6 \times 10^{-4}$  | 0.75*                  | 0.032   | $4.0 \times 10^{-24}$           |
| Nb-2 at. % H    | 1.0              | 110                        | 0.05             | $2.0 \times 10^{-4}$  | 0.5*                   | 0.038   | $3.6 \times 10^{-24}$           |
| Nb-1 at. % H    | 1.0              | 110                        | 0.02             | $0.8 \times 10^{-4}$  | 0.25*                  | 0.020   | $5.6 \times 10^{-24}$           |
| Fe-C<br>(Clean) | 1.5              | 310                        | 0.50             | $1.9 \times 10^{-3}$  | 0.07                   | 0.9*  | $3 \times 10^{-23}$             |
| Fe-C<br>(Dirty) | 2.0              | 220                        | 0.085            | 0.25                  | $1 \times 10^{-5}$     | 0.9*  | $3 \times 10^{-20}$             |

melting point in bismuth<sup>24</sup> as well as in other metals. This rise is not well understood, but it may occur from such effects as grain boundary sliding, etc. Only slightly above room temperature, the anelastic response was observed to grow very rapidly and become unstable, often preceding deterioration of the sample.

Comparisons of the magnitude of the AP and the noise given in Table I can be made in the region 100–200 K. The exact noise mechanism in bismuth is not known, but if we assume a defect model with a uniform mechanical coupling constant roughly equal to an atomic volume then we may obtain a density of active defects  $n_d(f, T)/n_a = 5 \times 10^{-4}$  and an electronic coupling of  $\langle \Omega_e \rangle = 7 \times 10^{-22} \text{ cm}^3$  using the values of  $M_I$  and  $\alpha_a$  in Table I. The mean free path has been measured<sup>13</sup> in similar films by the Hall effect to be 100 nm which would give a change in scattering cross section of  $\delta\sigma = 7 \times 10^{-16} \text{ cm}^2$ , a very reasonable number considering the small Fermi wave vector for bismuth. The density of mobile defects might seem somewhat low, but these films have very low levels of impurities (by SIMS) and large grains.

Unfortunately, with these results we cannot pin down exactly the mechanism of the noise. However, the qualitative agreement between the temperature dependence of the noise and the anelastic response strongly suggests a common mechanism for the two effects. The ratio of the elastic and electrical coupling obtained by assuming uniform sites is very reasonable for a defect model.

The most anomalous feature of bismuth noise has been that it is larger (at least at and below room temperature) in better annealed, thicker films. Together with the nearly traceless noise symmetry, these facts strongly suggest that the noise comes from regions with good crystal symmetry. The relatively sharp peak in  $\alpha_a(f, T)$  also fits with a picture in which the noise comes from sites in a uniform crystalline environment. Thus the obvious mechanism to suspect would be some rotating defect in the crystal, e.g., an interstitial impurity. However, the very good reproducibility of the noise, as measured by several groups, suggests that impurities are not required. Likewise the independence of the noise on annealing, once moderately large grains have formed, suggests that many simple defect types, which could anneal out, are

not involved. Single-crystal whiskers, however, are quieter, indicating that some defect is responsible for the noise. Peculiarities of diffusion in bismuth at twinning boundaries may account for why some defect remains trapped under any practical annealing protocol for films.<sup>25</sup>

*Niobium.* In niobium, it was found that both  $M_I(f, T)$  and  $\alpha_a(f, T)$  scaled with hydrogen concentration implying that hydrogen motion was the primary mechanism for both effects. However,  $\alpha_a(f, T)$  showed a peak as a function of temperature while  $M_I(f, T)$  did not. These results suggest that there are two types of sites—sites that have a small ratio of  $M_I/\alpha_a$  in the region of the peak, and sites that have a larger  $M_I/\alpha_a$  but do not show a maximum density. The question is then, in relation to Eq. (6), whether the sites giving the noise peak fail to show up proportionally in  $M_I(f, T)$  because they have anomalously large  $\langle \Omega_e^2 \rangle$  values, anomalously small  $\Omega_m$  values, or because the correlation coefficient between  $\Omega_e$  and  $\Omega_m$  is small for these sites.

Precisely because the sites give rise to a peak in  $\alpha_a(f, T)$ , it is most reasonable to assume that they are more homogeneous than the sites giving the background. Thus there are unlikely to be more nearby random scattering sites near this homogeneous set than near the sites giving the broad background, so  $\langle \Omega_e^2 \rangle$  is unlikely to be especially large. Likewise, it would not be reasonable to assume that for the peak sites the correlation coefficient between  $\Omega_e$  and  $\Omega_m$  is smaller than for sites in less homogeneous environments, unless it happens that  $\langle \Omega_e \rangle$  is relatively small through an accidental symmetry. The remaining possibility is that  $\langle \Omega_m \rangle$  is unusually small.

From previous measurements of internal friction, typical values for the mechanical coupling constants of hydrogen in niobium have been measured as  $\langle \lambda \rangle \cong 0.1$  with an asymmetry for Snoek relaxation of hydrogen trapped at an oxygen impurity of  $\langle \delta\lambda \rangle \cong 0.01$ .<sup>18</sup> The mechanical coupling of hydrogen is small relative to other impurity relaxations and the asymmetry for trapped hydrogen is even smaller. For comparison, the mechanical asymmetry of hydrogen in amorphous silicon-palladium has

been measured to be  $\langle \delta\lambda \rangle \cong 0.1$ .<sup>26</sup> It is therefore plausible that  $M_I$  is dominated by "background" sites in a more disordered environment that do not have the unusually low  $\langle \Omega_m \rangle$  of the more homogeneous sites. There is a significant amount of oxygen ( $\sim 2\%$ ) present in these films which can act as trapping sites for the hydrogen as found in internal friction studies of bulk niobium. We therefore believe that the peak which shows up in the noise but not the AP is most likely due to the Snoek mechanism for hydrogen rotating about oxygen, which has a suitably low  $\langle \Omega_m \rangle$ .

For a quantitative analysis of these results, it is possible to estimate the concentration of mobile hydrogen in the niobium from the resistance change with electrical sweeping of the hydrogen and determine the mechanical and electrical coupling factors from the noise and AP as given in Table I. Assuming an Arrhenius prefactor of  $10^{12}$  Hz, the width of the peak as a function of temperature (roughly 4 Debye widths)  $n_d(f, T) < n_d/4$  at the peak, where  $n_d$  is the total concentration of defects.<sup>16</sup> This maximum estimate for  $n_d(f, T)$  contributing to the noise peak, together with Eq. (5) gives  $(\langle \Omega_e^2 \rangle)^{1/2} > 4 \times 10^{-24}$  cm<sup>3</sup>. A mean free path of 10 nm gives a scattering-cross-section fluctuation of at least  $4 \times 10^{-18}$  cm<sup>2</sup>, which is small but plausible.

Since no peak is observed in  $M_I(f, T)$  we cannot calculate  $\Omega_m$  for these sites. However, if we assume homogeneous coupling factors then Eq. (3) can be used to estimate an upper limit on  $\Omega_m < 5 \times 10^{-25}$  cm<sup>3</sup> which corresponds to a mechanical coupling factor  $\langle \delta\lambda \rangle < 0.03$ . At 200 K,  $\alpha(f, T)$  is down by a factor of 10 from the peak. If the  $n_d(f, T)$  in this region is also down a factor of 10, which is the simplest assumption, then we obtain for the mechanical coupling of these background sites  $\langle \delta\lambda \rangle \cong 0.3$  for all concentrations.

Obviously, each of these numbers is obtained via some approximate assumptions. The point to be emphasized is simply that both the friction and the noise can be fit with reasonable parameters. The values obtained for  $\langle \Omega_e^2 \rangle$  and  $\langle \Omega_m \rangle$  are within range of what one would expect.  $\langle \Omega_e^2 \rangle$  does not seem exceptionally large. Most likely it is  $\langle \Omega_m \rangle / \langle \Omega_e \rangle$  which is unusually small for the sites that give the peak in the noise, accounting for their failure to show up against the background in the AP.

These results demonstrate the difference between mechanical anelasticity and resistance fluctuations which arises from the different coupling constants associated with each measurement. It is not true that a peak in internal friction versus temperature would necessarily imply an observable peak in the resistance noise at the same temperature, or vice versa. In this case, it appears that the larger mechanical coupling of the more disordered "background" sites would also obscure any peak in the internal friction for these particular films.

*Iron.* In iron,  $\alpha_a(f, T)$  was observed to increase by a factor of roughly 200 with the addition of carbon and manganese. We believe that this peak in noise versus temperature is due to the motion of carbon impurities trapped at manganese sites because the activation energy is close to what is expected and because a similar peak is

not observed in the clean iron. The peak in the dirty iron sample was very well defined, as a function of both temperature and frequency. The existence of such a well-defined peak implies that the rates are not too spread out and that there is some common environment for the carbon impurities.

It is possible that instead of carbon, it is oxygen that is trapped at the manganese and giving rise to the resistance noise. However, the solubility of mobile oxygen in iron is very low because of the strong binding energy between iron and oxygen. Secondly, the activation energy for oxygen interstitials in iron<sup>27</sup> is 1 eV which is less consistent with the observations than the activation energies for carbon or nitrogen in iron-manganese. Finally, to the knowledge of the authors, there have been no observations of an internal friction due to oxygen in iron-manganese. Therefore, we believe carbon to be a more likely source for the noise peak than oxygen, although the oxygen possibility cannot be completely ruled out.

In the clean iron, there was no clear peak seen. There was a plateau observed at 300 K in both the noise and the AP which might be from a Snoek relaxation. Without a definite peak, however, it is difficult to determine the exact mechanism, though carbon motions seem like a plausible source. Above 340 K in the clean iron, the noise and AP were unstable, most likely from annealing effects.

The mechanical coupling factor for the carbon Snoek relaxation in clean iron is known to be large  $\langle \delta\lambda \rangle \cong 0.9$ , from internal friction studies.<sup>16</sup> If we assume this value and further assume that the electronic coupling is homogeneous, then it is possible to estimate a density of active defects and electronic coupling from the noise and AP as summarized in Table I. For the clean iron at 310 K, we obtain a density  $n_d(f, T) \cong 7 \times 10^{-4} n_a$  and an electronic volume  $\langle \Omega_e \rangle \cong 3 \times 10^{-23}$  cm<sup>-3</sup> at 300 K, very reasonable numbers considering the uncertainties in the SIMS analysis and in the assumptions involved in comparing the AP and the noise. It is not certain that all the noise is from a carbon Snoek relaxation, but this assumption does not appear to be too unreasonable for the clean iron. However, for the dirty iron at 220 K, if we assume the same homogeneous mechanical coupling and a homogeneous electrical coupling we obtain  $n_d(f, T) \cong 10^{-7} n_a$  and  $\langle \Omega_e \rangle \cong 10^{-20}$  cm<sup>-3</sup>. The latter number is unreasonably large, and the former one is surprisingly small.

In the dirty iron the picture of the noise and AP from a carbon-manganese relaxation does not seem to work. We again find a noise peak without a corresponding AP peak, leading to the same alternatives we considered for the peak in niobium-hydrogen. In the case of carbon in iron, however, it is much less plausible that  $\langle \Omega_m \rangle / \langle \Omega_e \rangle$  could be small enough to account for the absence of a peak in the AP. However, it is possible for the systematic part of  $\langle \Omega_e \rangle$  to be very small in the homogeneous sites that give rise to the peak. As in other alloys for which AP has been studied,<sup>8</sup> the sign of  $\langle \Omega_e \rangle$  can change as a function of composition. An accidentally small  $\langle \Omega_e \rangle$  can occur.

However, a small  $\langle \Omega_e \rangle$  in iron does not imply a small  $\langle \Omega_e^2 \rangle$ . This is especially apparent in the increase by a



factor of 200 in the noise while the concentration of carbon increased by only a factor of 10. It is possible to calculate  $\langle \Omega_e^2 \rangle$  or  $\langle \Omega_e \rangle$  from assumptions of the carbon concentration (known to within a factor of 2 from SIMS analysis) and the noise magnitude using Eq. (5) or the AP magnitude using Eq. (3). The width of the peak as a function of temperature, assuming an Arrhenius prefactor of  $10^{16}$  Hz, is roughly 2.5 Debye widths, which implies that  $n_d(f, T) \approx n_d/2.3$  at the peak.<sup>16</sup> We then find  $\langle \Omega_e^2 \rangle^{1/2} \approx 2 \times 10^{-22}$  cm<sup>3</sup>, which, with an estimated mean free path of 5 nm, would imply a change in cross section of  $4 \times 10^{-16}$  cm<sup>2</sup>. The magnitude of  $M_I$  combined with the above carbon concentration and the presumed  $\langle \Omega_M \rangle$  of  $2 \times 10^{-23}$  cm<sup>3</sup> yields  $\langle \Omega_e \rangle \approx 1 \times 10^{-24}$  cm<sup>3</sup>. These data make sense only if the random contribution to the resistance change at each site substantially exceeds the systematic term. The same conclusion would hold if we assumed that oxygen was the mobile defect.

In the case of iron with 10% manganese, we would in fact expect a large random contribution. As noted by Pelz and Clarke,<sup>6</sup> significant interference terms between scattering sites appear in the resistivity tensor when the sites are closer than one or two Fermi wavelengths. In iron, the ratio of the Fermi wavelength to the spacing between atoms is unusually high and with 10% manganese we would expect each carbon motion to produce interference terms with several randomly placed neighboring manganese atoms. In this case the appearance of the noise peak without an AP peak is due not to an anomalously low mechanical coupling but to an anomalously large and random electronic coupling.

In clean iron, it is reasonable to consider systematic changes in electronic scattering of a carbon Snoek relaxation. In dirty iron, where there is a large peak in the temperature dependence of the noise from a (presumably) carbon-manganese relaxation, the scattering change is primarily in "random" interference terms, partially due to the defect pairing. In these films, it might well be possible that internal friction would show the same peak as is apparent in the noise because there does not appear to be any anomaly in the mechanical coupling.

### CONCLUSION

We have compared measurement of the anelastic piezoresistance and resistance noise in metal films to probe the coupling of resistance to the motion of defects. In so doing we have been able to test the analogy between mechanical anelasticity and  $1/f$  noise that has been presumed for some time. Results in bismuth films show good qualitative and quantitative agreement in the 100 to 200 K region of the noise peak. Above this the noise drops, whereas the AP grows with increasing temperature, demonstrating the "high-temperature background"

that appears in the mechanical properties but not in the resistance fluctuations. In niobium-hydrogen, there was a well-defined peak in the noise that did not appear in the AP even though both the noise and AP scaled with hydrogen concentration. This result is consistent with a small mechanical coupling to the hydrogen Snoek relaxation relative to the mechanical coupling of the more disordered "background." In iron, a well-defined peak appeared in the noise with the addition of carbon and manganese, which did not appear in the AP. In this case, the electronic coupling to the impurity motion was dominated by random interference terms, which enhanced the noise, yet reduced the systematic AP terms in the electronic scattering. For the clean iron, there was reasonable quantitative agreement between the AP and the noise even though there was no well-defined peak in either.

The results show only a weak correlation between mechanical anelasticity and resistance noise. There are important differences between the mechanical and electronic coupling factors for defect motions. In the case of niobium-hydrogen, the electronic coupling factors for the hopping of hydrogen were sufficient to give rise to a resistance noise peak, yet the mechanical coupling factors for these sites were too small to give a measurable anelastic response above a background. In contrast, for the noise peak in iron-carbon it was the electronic coupling factors that were dominated by random interference terms that did not give any systematic scattering term for the piezoresistance. Therefore, we have demonstrated three cases in this experiment: a correspondence between AP and noise in bismuth, a lack of correspondence in niobium because of a small systematic mechanical coupling of the peak sites, and a lack of correspondence in iron because of small systematic electronic coupling of the peak sites. Mechanical anelasticity studies and noise studies then provide distinct, not redundant, information on defect motions. The anelastic response observed was as broad, or broader, than the noise. That implies that resistance noise has a  $1/f$  spectrum because of the highly inhomogeneous nature of thin films, not because of a more fundamental reason.

### ACKNOWLEDGMENTS

We thank Judy Baker and Nancy Finnegan for assistance with the SIMS and Auger analysis, A. V. Granato for valuable discussions of internal friction, B. D. Nevins for discussions of hydrogen in niobium, and C. Keener for information on noise in bismuth whiskers and transport in bismuth films. This work was supported by NSF Grant No. DMR 89-22967 and through facilities of the Materials Research Laboratory under Grant No. DMR 89-20538.

\*Present address: Department of Physics and Astronomy, Michigan State University, East Lansing, MI 48823.

<sup>1</sup>M. B. Weissman, Rev. Mod. Phys. **60**, 537 (1988).

<sup>2</sup>K. S. Ralls, D. C. Ralph, and R. A. Buhrman, Phys. Rev. B **40**,

11 561 (1989).

<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. Zimmerman and W. W. Webb, Phys. Rev. Lett. **65**, 1040

- (1990).
- <sup>5</sup>N. Zimmerman and W. W. Webb, *Phys. Rev. Lett.* **61**, 889 (1988).
- <sup>6</sup>Jonathan Pelz, John Clarke, and Wayne E. King, *Phys. Rev. B* **38**, 10 371 (1988); *ibid.* **36**, 4479 (1987).
- <sup>7</sup>Sh. M. Kogan and K. E. Nagaev, *Solid State Commun.* **49**, 387 (1984).
- <sup>8</sup>B. S. Berry and J. L. Orehotsky, *Philos. Mag.* **9**, 467 (1964).
- <sup>9</sup>D. M. Fleetwood and N. Giordano, *Phys. Rev. B* **31**, 1157 (1985).
- <sup>10</sup>A. H. Verbruggen, R. H. Koch, and C. P. Umbach, *Phys. Rev. B* **35**, 5864 (1987).
- <sup>11</sup>R. H. Koch, J. R. Lloyd, and J. Cronin, *Phys. Rev. Lett.* **55**, 2487 (1985).
- <sup>12</sup>P. Dutta, P. Dimon, and P. M. Horn, *Phys. Rev. Lett.* **43**, 646 (1979); P. Dutta and P. M. Horn, *Rev. Mod. Phys.* **53**, 497 (1981).
- <sup>13</sup>R. D. Black, P. J. Restle, and M. B. Weissman, *Phys. Rev. Lett.* **51**, 1476 (1983); C.D. Keener and M. B. Weissman, *Phys. Rev. B* (to be published).
- <sup>14</sup>N. O. Birge, B. Golding, and W. H. Haemmerle, *Phys. Rev. B* **42**, 2735 (1990); *Phys. Rev. Lett.* **62**, 195 (1989).
- <sup>15</sup>R. De Batist, *Internal Friction of Structural Defects in Crystalline Solids* (North-Holland, Amsterdam, 1972).
- <sup>16</sup>A. S. Nowick and B. S. Berry, *Anelastic Relaxation in Crystalline Solids* (Academic, New York, 1972).
- <sup>17</sup>N. E. Israeloff, M. B. Weissman, G. J. Nieuwenhuys, and J. Kosiorowska, *Phys. Rev. Lett.* **63**, 794 (1989).
- <sup>18</sup>M. Nagano, E. A. Clark, and H. K. Birnbaum, *J. Phys. F* **18**, 863 (1988).
- <sup>19</sup>R. F. Mattas and H. K. Birnbaum, *Acta. Metall.* **23**, 973 (1975).
- <sup>20</sup>B.D. Nevins, dissertation, University of Illinois, 1991 (unpublished).
- <sup>21</sup>B. S. Berry and W. C. Pritchett, *J. Phys. (Paris)* **46**, 457 (1985).
- <sup>22</sup>R. Koike and H. Kurokawa, *Jpn. J. Appl. Phys.* **5**, 503 (1966).
- <sup>23</sup>Y. F. Komnik, E. I. Bukhshtab, Y. V. Nikitin, and V. V. Andrievskii, *Zh. Eksp. Theor. Fiz.* **60**, 669 (1971) [*Sov. Phys. JETP* **33**, 364 (1971)].
- <sup>24</sup>S. P. Nikanorov and A. D. Romanov, *Fiz. Tverd. Tela* (Leningrad) **17**, 180 (1975) [*Sov. Phys. Solid State* **17**, 105 (1975)].
- <sup>25</sup>W. P. Ellis and N. H. Nachtrieb, *J. Appl. Phys.* **40**, 472 (1969).
- <sup>26</sup>B. S. Berry and W. C. Pritchett, *Nontraditional Methods in Diffusion*, edited by G. E. Murch, H. K. Birnbaum, and J. R. Cost (Metallurgical Society of AIME, Warrendale, PA, 1984).
- <sup>27</sup>H. Schultz, *Mater. Sci. Eng.* **3**, 189 (1968).