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$1/f$ Noise from Systems in Thermal Equilibrium

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The power spectra of fluctuations in the mean square of the Johnson-noise voltage across small semiconductor and metal films in thermal equilibrium were measured down to 10^{-4} Hz. The spectra have a $1/f$-like behavior that matches the resistance-fluctuation spectra obtained by passing a current through the samples. These measurements contribute strong evidence that $1/f$ noise is due to equilibrium resistance fluctuations.

In this Letter we report the observation of a $1/f$-like power spectrum for low-frequency fluctuations of the mean square of the Johnson-noise voltage across a very small sample of semiconductor or discontinuous metal film in thermal equilibrium. The $1/f$ spectrum is shown to be due to resistance fluctuations in the sample, and closely matches the resistance-fluctuation spectrum obtained by passing a current through the sample. Our measurements are the first observation of $1/f$ noise from a system in thermal equilibrium. The fact that $1/f$ noise had until now been observed only under nonequilibrium steady-state conditions led some authors[1,2] to propose nonequilibrium theories for its origin. Our present results, however, together with earlier work showing that a theory based on equilibrium temperature fluctuations quantitatively predicts the magnitude of $1/f$ noise in continuous metal films,[3] superconducting films[4] biased at T_c, and Josephson junctions,[5] constitute strong evidence that $1/f$ noise is an equilibrium effect.

Consider a resistance, R, of total heat capacity C_v shunted by a capacitance, C, and in thermal contact with a reservoir at temperature T_0. The voltage across the capacitor, $V(t)$, represents a single degree of freedom that can exchange energy with the resistor via the charge carriers in the resistor. This exchange takes place on time scales of order $\tau = RC$. In thermal equilibrium the average energy of the capacitor, $\langle E_c \rangle = \frac{1}{2}C\langle V^2\rangle = \frac{1}{2}k_B T_0$. These voltage fluctuations (Johnson noise) are limited to a bandwidth of $1/4\tau$, and consequently have a spectrum of the form $S_V(f) = 4k_B T_0 R/[1+4\pi^2 f^2\tau^2]$. If the resistor is assumed to exchange energy with the reservoir on a time scale of order τ_R that is much greater than τ, the capacitor is able to reach equilibrium with the internal degrees of freedom of the resistor before the internal energy of the resistor can change. The temperature of the capacitor is then the same as the temperature of the resistor. $V^2(t)$, like $V(t)$, is a rapidly fluctuating quantity in time due to this exchange of energy between the resistor and capacitor. However, the average of $V^2(t)$ over a time, θ, such that $\tau \ll \theta \ll \tau_R$, $\langle V^2(t)\rangle_\theta = k_B T/C$ (T is now the instantaneous temperature of the resistor), is sensitive to slow energy or temperature fluctuations in the resistor on time scales τ_R or longer.

Experimentally, the Johnson-noise voltage, $V(t)$, is passed through a filter with a band pass from f_0 to f_1, squared, and averaged over a time $\theta > 1/f_0$ to give $P(t)$, a slowly varying signal proportional to the Johnson-noise power in the band width f_0 to f_1. Thus,

$$P(t) \approx 4k_B TR \int_{f_0}^{f_1} df/(1+4\pi^2 f^2\tau^2) + P_0(t), \qquad (1)$$

where, if R and T are fixed, the first term on the right-hand side represents the average of $P(t)$, and $P_0(t)$ represents fluctuations in $P(t)$ about the average due to the rapid exchange of energy between capacitor and resistor. Because this exchange is so rapid, $P_0(t)$ has a spectrum, $S_{P_0}(f)$, that is independent of f for the low frequencies in which we are interested. S_{P_0} may be reduced by increasing the bandwidth or by moving the bandwidth to higher frequencies, but in practice $P_0(t)$ severly limits the accuracy of measurements of $P(t)$.

If the bandwidth in Eq. (1) is either totally above or totally below the knee at $1/2\pi\tau$, $P(t)$ is sensitive to slow resistance as well as temperature fluctuations. These resistance fluctuations, ΔR, may either be driven by temperature fluctuations with a spectrum $S_T(f)$ so that $\Delta R = \bar{R}\beta\Delta T$, where $\beta \equiv (1/R)\partial R/\partial T$; or be temperature independent fluctuations, ΔR_0, with a spectrum $S_{R_0}(f)$ (such as number or mobility fluctuations of the charge carriers). Thus, from Eq. (1), $\Delta P(t)/\bar{P} = (1 \pm \beta T_0)\Delta T/T_0 + \Delta R_0/\bar{R} + P_0(t)/\bar{P}$, and the relative power spectrum for fluctuations in $P(t)$ is of the form

$$\frac{S_P(f)}{\bar{P}^2} = (1 \pm \beta T_0)^2 \frac{S_T(f)}{T_0^2} + \frac{S_{R_0}(f)}{\bar{R}^2} + \frac{S_{P_0}}{\bar{P}^2}, \qquad (2)$$

where the plus sign corresponds to $f_0 < f_1 \ll 1/2\pi\tau$, and the minus sign corresponds to $f_1 > f_0 \gg 1/2\pi\tau$. If, however, most of the noise power and the knee frequency, $1/2\pi\tau$, are included in the bandwidth (i.e., $f_0 \ll 1/2\pi\tau \ll f_1$), from Eq. (1) we find $P(t) \approx k_B T/C + P_0(t)$ and $S_P(f)/\bar{P}^2 = S_T(f)/T_0^2 + S_{P_0}/\bar{P}^2$. In this limit, $P(t)$ is not sensitive to resistance fluctuations. Thus, with an appropriate choice of bandwidth, the low-frequency spectrum of $P(t)$ is an equilibrium measurement of $S_T(f)$ or $S_{R_0}(f)$ provided the temperature or resistance fluctuations are large enough to dominate S_{P_0}.

Our initial measurements were on evaporated InSb films with a thickness of 1000 Å and a resistivity of about 1 Ω cm. Previous measurements on similar InSb films[3] had shown that the $1/f$ noise did not arise primarily from temperature-induced fluctuations; the noise was too large in magnitude, and spatially uncorrelated. Therefore, we expected to observe only the resistance fluctuations $\Delta R_0(t)$. In order to make the relative resistance-fluctuation spectrum, $S_{R_0}(f)/\bar{R}^2$, large enough to dominate $S_{P_0}/\bar{P}^2$, the samples were made as small as possible. The resistance of a strip of InSb was monitored while the strip was cut transversely with a diamond knife until only a small bridge containing typically about 10^6 atoms remained. In the presence of a direct current, I, there are voltage fluctuations across the sample, $\Delta V(t) = I\Delta R_0(t)$, which have a relative spectrum $S(f) = S_V(f)/\bar{V}^2 = S_{R_0}(f)/\bar{R}^2$, where $\bar{V}$ is the average voltage across the sample. The solid line in Fig. 1 shows $S(f)$ for a 20-MΩ bridge of InSb measured with a direct current. The noise voltage was amplified, digitized, and analyzed by a PDP-11 computer using a fast-Fourier-transform algorithm to determine the power spectrum.

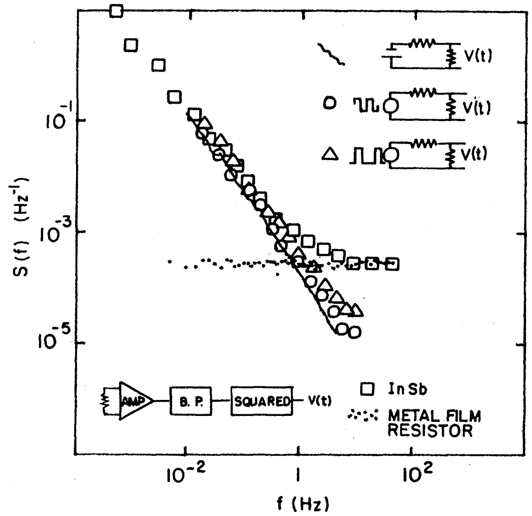

FIG. 1. InSb bridge: $S_V(f)/\bar{V}^2$ using dc bias (——), ac bias (○), pulsed current bias (△); Johnson-noise measurement, $S_P(f)\bar{P}^2$ (□). Background $S_P(f)/\bar{P}^2$ from metal-film resistor (•••).

We also measured the $1/f$ noise in two other ways. The spectrum was remeasured using an ac technique in which a square-wave current of zero mean value was applied to the sample. The frequency was about 10^3 times higher than the lowest frequency to be measured in the spectrum. The PDP-11 was used as a digital lock-in detector to measure the spectrum of the amplitude fluctuations of the induced voltage. The relative spectrum is plotted with open circles in Fig. (1). In a third technique the current was supplied as a series of positive-going pulses to reduce the power dissipated in the sample. The pulses were typically 1 msec long with a period of 10 msec. The relative spectrum is shown in Fig. 1 as open triangles. All three techniques measure the same resistance spectrum, $S_{R_0}(f)/\bar{R}^2$. The agreement of the three spectra demonstrates that neither a direct current nor a constant dissipation of power is the cause of the $1/f$ spectrum.

For the measurement of $P(t)$, the sample was capacitively coupled to a preamplifier to prevent any leakage current flowing through the sample. The input capacitance produced a knee frequency, $1/2\pi RC \approx 500$ Hz, in the Johnson-noise spectrum. After amplification the noise was filtered with a 10- to 300-kHz band pass filter, squared with an analog multiplier, and filtered to remove frequencies above the digitizing frequency. Since the bandpass is above the knee frequency the calculated relative spectrum of this signal is given by Eq. (2) (with the minus sign), while the measured relative spectrum is shown as the open squares in Fig. 1. The white spectrum above 1 Hz represents $S_{P_0}/\bar{P}^2$. The $1/f$ spectrum below 1 Hz closely matches the current-biased measurements. To insure that the $1/f$ spectrum was generated by fluctuations in the sample rather than by spurious effects from our electronics, the InSb was replaced by a metal-film resistor (which did not exhibit $1/f$ noise) of the same resistance. This relative spectrum is shown dotted in Fig. 1. The spectrum is white down to the lowest frequency measured, and represents only the term $S_{P_0}/\bar{P}^2$.

We have made similar measurements on metal films. Although the three current-biased techniques give identical relative spectra for continuous metal films in which the resistance fluctuations are temperature induced,[3] we were unable to make these films small enough for $S_R(f)/\bar{R}^2$ to dominate $S_{P_0}/\bar{P}^2$ at frequencies down to 10^{-3} Hz. Very thin (~100-Å) metal films however (in which current transport is probably partly via metallic conduction, and partly via a hopping process) exhibit much greater noise[6] than can be accounted for by temperature-induced resistance fluctuations.

In Fig. 2, the continuous curve is the relative spectrum of a very thin Nb film ($R \approx 200$ kΩ) measured with an ac current bias. The open squares are a Johnson-noise measurement with a bandwidth of 100 to 200 kHz above the knee frequency of 40 kHz. The agreement below 10^{-2} Hz is excellent. The dotted spectrum was obtained from the same sample using a bandwidth of 5 to 200 kHz, which includes the knee frequency and most of the Johnson-noise power. Although the low-frequency spectrum is substantially reduced [as expected when $P(t)$ is no longer sensitive to resistance fluctuations], it is still above the background spectrum of a large metal-film resistor. This residual noise is possibly due to the temperature-fluctuation term $S_T(f)/T_0^2$. Indeed, the assumption[3] of a $1/f$ spectrum for $S_T(f)$ for a sample of 10^6 atoms yields $S_T(f)/T_0^2 \sim 3\times 10^{-7}/f$ Hz^{-1}, a value that is consistent with the observed spectrum.

Our results strongly suggest that $1/f$ noise in semiconductors and discontinuous metal films arises from equilibrium resistance fluctuations. Current-biased measurements probe these resistance fluctuations, but in no way generate them. This idea is consistent with several current theories of $1/f$ noise that propose various mechanisms for the resistance fluctuations. These theories are, for example, surface traps modulating the number of carriers in semiconductors[7]; mobility fluctuations of the carriers in semiconductors and ionic solutions[8,9]; and temperature-induced resistance fluctuations in metal films,[3] superconducting films at the transition,[4] and Josephson junctions.[5] Our equilibrium measurements are, however, obviously inconsistent with theories that rely on nonequilibrium processes such as turbulence theories,[1] theories that require a long-term steady current or power,[2] and theories involving thermal feedback via the heat generated by an external current.

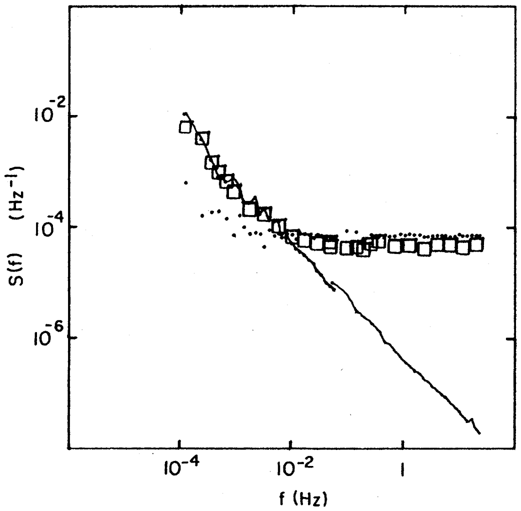

FIG. 2. Nb bridge: $S_V(f)/\bar{V}^2$ using ac bias (——); $S_P(f)/\bar{P}^2$ (□). $S_P(f)/\bar{P}$ including knee frequency (•••).

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Mössbauer Studies of Oxygen-Stabilized Eu^{2+} in CaF$_2$†

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The thermal anneal of Eu^{2+} to Eu^{3+} in calcium fluoride injected with oxygen has been studied by means of the Mössbauer effect. Assuming a common frequency factor τ_0, four distinct ionization energies of 1.52 ± 0.02, 1.80 ± 0.02. 1.99 ± 0.01, and 2.14 ± 0.01 eV have been measured, with $\tau_0 = 10^{-(7\pm 0.1)}$ sec. A model of four complexes of the type $\mathrm{Eu}^{2+}\mathrm{O}_i^{2-}\mathrm{F}_j^{-}$ ($i = 1, 2, 3, 4$; $2i + j = 8$) is proposed, in analogy with previously identified trivalent rare-earth complexes in CaF$_2$.

The nature of the stabilization of divalent rare earths in CaF$_2$ has long been a subject of investigation. Intuitively one might expect the divalent Eu^{2+} to simply replace the Ca^{2+} at its body-centered positions surrounded by the cubic array of eight F$^-$ anions. This assumption was, for example, made in interpreting some earlier Mössbauer studies of Eu in CaF$_2$.[1-3] However, to stabilize Eu^{2+} at concentrations of several percent in CaF$_2$, techniques such as hydrolysis, or preparation in a hydrogen atmosphere, have been found necessary. Recent experiments have suggested that these preparation techniques in fact lead to the injection of oxygen into the calcium fluoride lattice, and indeed oxygen-compensated Gd^{3+} complexes have been observed in CaF$_2$ by Reddy *et al.*[4] and by Kitts and Crawford.[5] We report here a Mössbauer study of divalent europium, stabilized in CaF$_2$ through analogous oxygen-europium complexes.

In these studies we have used CaF$_2$ powder samples doped with Eu$_2$O$_3$ as well as a series of Optovac-prepared single crystals of CaF$_2$ doped with EuF$_3$ from 0.1 to 30 mole %. These samples gave equivalent results. In order to stabilize significant fractions of Eu^{2+} in these samples, they were heated under a hydrogen atmosphere in a quartz tube above 1100°C for about 24 h, followed by a reasonably rapid quench over typically 15 min. The fraction of Eu^{2+} obtainable by such preparation conditions can exceed 98%.

All evidence points to the injection of oxygen into the CaF$_2$ lattice as being critical for the Eu^{2+} production. It is known[6-8] that O^{2-} can be introduced into CaF$_2$ through the presence of water vapor, and that under the above hydrogen-atmosphere condition the introduction of oxygen proceeds particularly efficiently,[7] as HF is formed on the surface of the CaF$_2$ which etches the quartz to release water vapor. The Gd-doped CaF$_2$, found by Kitts and Crawford[5] to contain oxygen-compensated complexes, was prepared by us in just this manner. Further we have measured the rate of penetration of the Eu^{2+} conversion process into a single crystal of CaF$_2$:Eu. The colors we observed in these samples after quench are those of *F* centers; Sierro[8] had noticed the same phenomenon and had proposed that F$^-$ vacancies were introduced along with the O^{2-}. We found agreement of our diffusion rate with a similar experiment done by Muto and Awazu,[6] who had followed the progress of oxidation of Sm^{2+} in CaF$_2$ using the color change as a measuring device of the conversion front, and then associated this front with the penetration of O^{2-}.

Mössbauer analysis of the samples to measure the Eu^{2+} fraction was performed at room temperature using a standard constant-acceleration apparatus and a single-line source of Sm^{151} in an oxide matrix. The inset in Fig. 1 shows a typical Mössbauer spectrum with both Eu^{2+} and Eu^{3+}, accumulated in about 20 h. The resonances of the divalent and trivalent europium are clearly resolved. We have determined the Debye temperatures of the two europium ions to be the same within error, so the ratio of the resonance areas is equal to the ratio of Eu^{2+} to Eu^{3+} ions in the sample. This illustrates one of the advantages of the Mössbauer effect for such measurements, as both ionic species are measured simultaneously in an absolute way, so that there is an assurance that no unobserved species might