PHYSICAL REVIEW VOLUME 111, NUMBER 4 AUGUST 15, 1958

Seebeck Effect Fluctuations in Germanium*

JAMES J. BROPHY
Armour Research Foundation of Illinois Institute of Technology, Technology Center, Chicago, Illinois
(Received January 9, 1958; revised manuscript received April 23, 1958)

Fluctuations in the Seebeck effect or thermoelectric power of germanium single crystals have been observed. The Seebeck noise power spectrum varies as reciprocal frequency and may be quantitatively predicted from current-noise measurements. Carrier density fluctuations responsible for $1/f$ noise are also the source of Seebeck noise. The present results indicate that carrier fluctuations having a $1/f$ spectrum persist even in the absence of net dc current flow. Seebeck noise is also observed in low-noise specimens having nonohmic, noisy electrodes.

I. INTRODUCTION

THE electrical fluctuations accompanying dc current flow in single-crystal semiconductor specimens are observed to have a component characterized by a noise power spectrum varying as reciprocal frequency.[1] It has been shown that this $1/f$ noise is due to conductivity modulations caused by carrier density fluctuations.[2] In many instances the noise power is observed to increase with the square of the average current, which implies that the magnitude of the carrier density fluctuations is independent of current.

This observation suggests that carrier density fluctuations having a $1/f$ spectrum may exist under suitable conditions in the absence of dc current flow. No attempts to detect this phenomenon have been reported in the literature, apparently because $1/f$ noise has always been considered a "current noise" effect. It is clear, however, that the white noise spectrum dictated by Nyquist's law for specimens in thermodynamic equilibrium has been experimentally established.

The thermoelectric power of single-crystal semiconductors is known to depend on the carrier density.[3] Thus, fluctuations in the carrier density would be expected to lead to fluctuations in the thermal emf and provide an experimental technique for detecting carrier density fluctuations in the absence of net dc current flow. This paper describes an experimental study of such "Seebeck noise" in germanium in which the fluctuations of the thermal emf of a sample in a thermal gradient are measured.

II. SEEBECK NOISE

For many single-crystal semiconductor samples in which electrode effects are negligible, the mean square $1/f$ noise voltage, $\langle \Delta V_I^2 \rangle$, may be written[2]

$$\langle \Delta V_I^2 \rangle / V_I^2 = \langle \Delta N^2 \rangle / N^2, \qquad (1)$$

where V_I is the dc potential drop across the specimen and N is the total number of carriers in the crystal. In this expression the $1/f$ behavior of $\langle \Delta V_I^2 \rangle$ is contained in $\langle \Delta N^2 \rangle$. Equation (1) is a convenient experimental method of determining the magnitude of the carrier fluctuations.

When the specimen is placed in a thermal gradient, a thermoelectric dc potential is built up across its terminals. One pictures that conduction currents flowing in response to this potential gradient are compensated by diffusion currents so that even with the external circuit arranged to prevent dc current flow, internal currents may exist. From this view, it is anticipated that an expression analogous to Eq. (1) may apply in this case where the voltages correspond to thermal emf's. That is,

$$\langle \Delta V_T^2 \rangle / V_T^2 = \langle \Delta N^2 \rangle / N^2, \qquad (2)$$

where V_T is the usual thermal emf and $\langle \Delta V_T^2 \rangle$, which is termed Seebeck noise, is the mean square thermal emf.

Seebeck noise levels may be predicted from Eqs. (1) and (2) and are very low for most specimens so that in general the effect is difficult to observe. For example, if the Seebeck noise power is to equal Nyquist noise, the current noise level must be three or four orders of magnitude above Nyquist noise under experimental conditions common in current noise studies on single-crystal semiconductors. While in principle this requirement can be satisfied by working at extremely low frequencies, it is not experimentally convenient to go below about one cycle per second. The most difficult aspect of the present work has been selection of stable, high-noise specimens.

III. EXPERIMENTAL TECHNIQUE

The samples used in this study were of 20-ohm-cm single-crystal n-type germanium roughly one by one millimeter in cross section and one centimeter long. To obtain large $1/f$ noise levels, they were plastically deformed[4,5] and chemically etched. They were provided with ohmic electrodes and soldered in a sample holder capable of establishing the necessary temperature gradient. The plastic deformation was carried out in air at temperatures of the order of 600°C after a rigid cleansing process to remove surface contamination.

* Work supported by the Office of Naval Research.
[1] H. C. Montgomery, Bell System Tech. J. **31**, 950 (1952).
[2] J. J. Brophy, Phys. Rev. **106**, 675 (1957).
[3] V. A. Johnson and K. Lark-Horovitz, Phys. Rev. **92**, 226 (1953).
[4] L. Bess, Phys. Rev. **103**, 72 (1956).
[5] J. J. Brophy, J. Appl. Phys. **27**, 1383 (1956).

The resistivity was increased somewhat by the deformation.

The sample holder consisted of two flexible copper terminals between which the sample was soldered. One terminal was attached to a copper strip which dipped into a liquid nitrogen bath, and the other terminal was similarly attached to a strip connected to a blackened absorber which was heated with an infrared lamp. The entire assembly was contained in a small Dewar. By cooling and heating opposite terminals in this fashion, a temperature differential of 40°C was maintained across the sample while the mean temperature was slightly below ambient. Electrical leads were brought through standard connectors such that both current noise and Seebeck noise could be examined without disturbing the specimen. In most experiments, two-terminal samples were studied in which the electrodes served to pass the electrical (or thermal) current while the noise level was observed across them. In other experiments, four-terminal, bridge-type samples were examined in which the current and potential electrodes were separate. Thermal emf's were measured with a breaker amplifier and found to be in approximate agreement with published data.[3] The temperature differential across the specimen was determined in separate experiments by means of small thermocouples attached to the ends of the sample.

The current or Seebeck noise voltages were examined by connecting the sample to a high-gain, low-noise amplifier-voltmeter system employing a tunable filter and a true-rms vacuum tube voltmeter. The input of the amplifier was blocked for dc with a capacitor so that no dc current could flow in the probe circuit. The amplifier system was periodically calibrated by measuring the Nyquist noise level of known resistances.

IV. RESULTS

The observed Seebeck noise spectrum of a typical sample is shown in Fig. 1 together with the current-noise spectrum. The results are plotted by using the interpretations of Eqs. (1) and (2) so that the experiments may be directly compared. The agreement is quite satisfactory. The current noise characteristics of this sample are similar to those often observed in specimens having high noise levels. The noise power exhibits a "bursting" effect which appears to be short intervals of higher noise level and which leads to a total power spectrum which falls faster than f^{-1}, as shown in the figure. These characteristics are similarly reproduced in the Seebeck noise.

The current noise level of this sample at a frequency of 10 cycles per second is shown in Fig. 2 as a function of dc voltage. At low currents the noise power varies approximately as the square of the voltage, as usually observed in $1/f$ noise, while at higher currents a higher power law is observed, as previously noted for deformed samples.[5] These data may be interpreted in terms of carrier fluctuations by using Eq. (1), which results in a fluctuation nearly independent of current over the square-law region as shown in the figure. Also shown is the magnitude of carrier fluctuations calculated from Seebeck noise data using Eq. (2). Both the Seebeck noise level and the magnitude of the carrier fluctuations determined from the thermal gradient experiment are in good agreement with current noise measurements. The increase at higher currents is also observed in non-deformed samples[1] at somewhat greater electric fields.

Seebeck noise data for a deformed bridge-type specimen are shown in Fig. 3 together with the observed noise spectrum in the absence of a thermal gradient. In the second case a white spectrum is observed, as

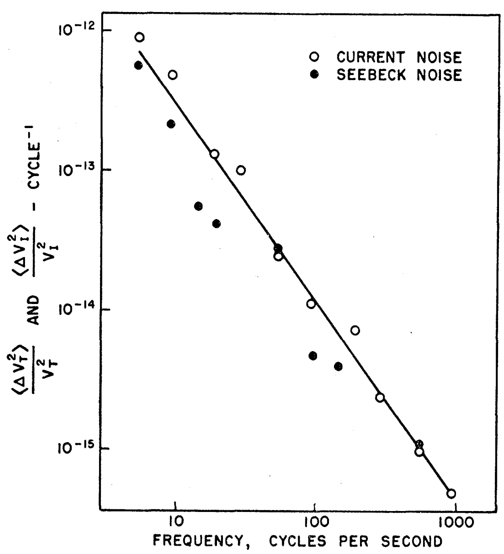

FIG. 1. Comparison of Seebeck noise spectrum and current noise spectrum for an *n*-type plastically deformed germanium crystal.

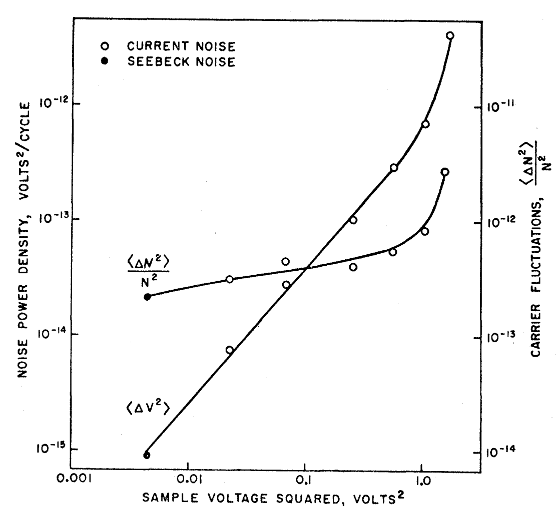

FIG. 2. The observed noise voltage and magnitude of carrier fluctuations as a function of dc voltage at 10 cycles per second for the same sample as Fig. 1. The Seebeck noise data points for both curves are in good agreement with current noise measurements.

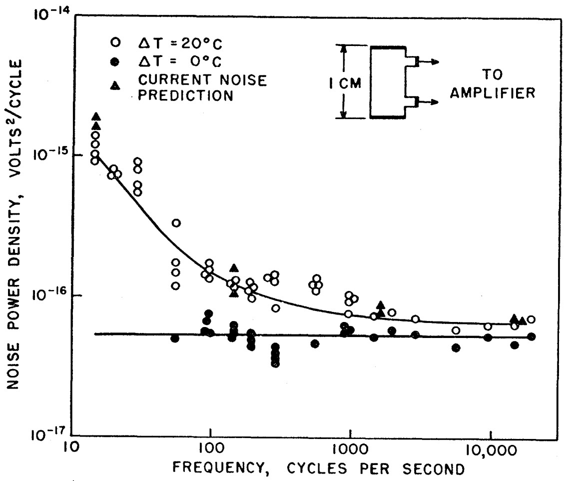

FIG. 3. Observed noise voltage spectra of a deformed germanium bridge-type specimen with and without a temperature gradient. Only Nyquist noise is observed in the absence of a gradient.

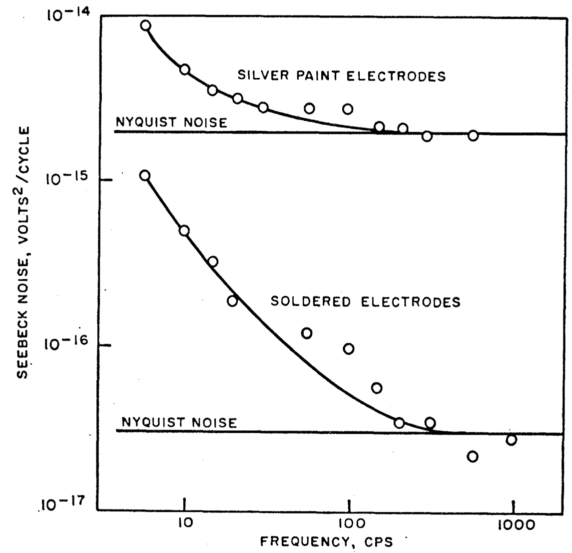

FIG. 4. Seebeck noise spectra of low-noise, nondeformed germanium crystals having noisy electrodes.

expected from Nyquist's law. The white noise level with the sample in the gradient is somewhat greater because the mean temperature was slightly below ambient and the sample resistance increased. Both white noise levels are in good agreement with Nyquist's law and sample resistance measurements. Also shown are several data points predicted from current noise measurements using Eqs. (1) and (2).

It is found that nonohmic electrodes also lead to Seebeck noise on otherwise quiet specimens. Figure 4 shows the Seebeck noise spectra of two undeformed germanium samples with poor electrodes. The lower curve is for a sample which was later found (by current-noise measurements) to have poorly soldered contacts. Considerable $1/f$ Seebeck noise is noted. Identical samples with satisfactory electrodes exhibited no Seebeck noise. A similar sample with simple silver paint electrodes, which are known to be extremely noisy, is also shown in Fig. 4. Here again considerable Seebeck noise is observed on an otherwise quiet specimen. In this case the Seebeck noise is partially obscured by the increased Nyquist level due to the electrode barrier. No attempt has been made in these data to compare predicted and observed levels because of the nonlinear characteristics of the specimens and the obvious inhomogeneous origin of the noise.

Several undeformed samples having $1/f$ current-noise levels such that by Eqs. (1) and (2) the Seebeck noise was below Nyquist noise were examined under identical conditions. In every case only Nyquist noise was observed. A carbon resistor, for which straightforward application of Eqs. (1) and (2) did not predict an observable Seebeck noise (because the thermal emf was very small) did not yield noise in excess of the Nyquist value in the thermal gradient. A commercial point-contact diode, type 1N90, exhibited no excess thermal noise, even though one was predicted. In this experiment, however, the actual temperature differential across the contact itself was uncertain.

The fluctuations in the thermoelectric voltage observed in these experiments have been termed Seebeck noise because of the similarity of the experimental conditions to the standard technique of measuring the Seebeck emf. However, as already pointed out, it is possible to account quantitatively for the results by considering only fluctuations in the conduction currents. It appears that fluctuations in the diffusion currents, which are associated with fluctuations in the Fermi level, are negligible compared to the conduction-current effects.

V. SUMMARY

These experiments show the existence of fluctuations in the thermoelectric emf of single-crystal germanium which have not previously been reported. The Seebeck noise power spectrum has a $1/f$ character and may be quantitatively predicted from current-noise measurements on the same sample. The noise levels are quite low and are observable only on specimens having rather high $1/f$ current-noise levels. The results appear to indicate that carrier fluctuations responsible for $1/f$ noise in semiconductors are also the source of Seebeck noise. Noisy electrodes on normally quiet specimens also result in Seebeck noise, showing the presence of a contact effect similar to that observed in current noise.

ACKNOWLEDGMENTS

The author expresses his appreciation to W. W. Cranford and A. R. Reinberg who carried out many of the experimental measurements.