Seebeck effect of a conducting germanium surface

V. N. Zavaritskiĭ and N. V. Zavaritskiĭ
Institute of Physical Problems, Academy of Sciences of the USSR

(Submitted 4 June 1981)

Pis'ma Zh. Eksp. Teor. Fiz. **34**, No. 1, 45–48 (5 July 1981)

The Seebeck voltage has been measured over the temperature interval 1.7–17 K in bicrystals and cleaved single crystals of pure germanium having a high-conductivity surface. The observed effect is large and is shown to result from a drag of surface charges by volume phonons.

PACS numbers: 72.20.Pa, 72.80.Cw

The conductivity of single crystals of pure germanium is known to fall off exponentially with the temperature below 20 K, and at 4.2 K the volume conductivity is $\sigma_v < 10^{-8}$ mho/cm. In germanium, however, surfaces with a high conductivity $\sigma_s \sim 4 \times 10^{-4}$ mho, nearly independent of the temperature, can form. These surfaces are bicrystal joining planes (with a joining angle of 20–30°)[1)] or the surfaces formed by cleaving a single crystal parallel to a (111) plane.[1]

We have carried out measurements of the thermoelectric properties of such systems with the goal of studying the interaction of phonons with charges on a high-conductivity surface. Figures 1 and 2 show the results on the Seebeck voltage ($E = \alpha \Delta T$) of cleaved single crystals and of bicrystals of pure germanium with a high-conductivity surface. The temperature dependence $\alpha = \alpha_s(T)$, which is similar for all the samples studied at $T \lesssim 6$ K, can be approximated by a power law $\alpha_s \sim T^M$, where $M \approx 3$ at $T < 3$ K. As the temperature is raised, M falls off smoothly, reaching values $M \sim 1.5$ at $T = 4$–6. The absolute value of α_s differs from sample to sample (the difference reaches a factor of three in the case of the bicrystals) and is, in a first approximation, inversely proportional to the surface charge density n_s. The charge density n_s was determined from measurements of the Hall voltage U_H. The signs of the Hall and Seebeck voltages show that the charge carriers in the surface layer are holes, in agreement with Ref. 1.

Two mechanisms contribute to the Seebeck effect[2]: diffusion, represented by the component α^h, and phonon drag of charges, represented by α^p. To estimate the magnitudes of these effects, we first note that since the holes are distributed over a surface layer of thickness $\delta \sim 4 \times 10^{-7}$ cm (Ref. 1) their volume number density is $n_v \sim n_s \delta^{-1} \sim 3 \times 10^{19}$ cm^{-3}. The metallic temperature dependence of σ_s and the values of n_s and n_v show that the holes form a degenerate system with $\epsilon_F \sim 40$ MeV and $\mathbf{k}_F \sim 6 \times 10^6$ cm^{-1} (for the heavy holes we are adopting the customary assumption that $m_h \approx 0.4\, m_0$). From the Fermi energy we can estimate the diffusion component of the voltage:

$$\alpha^h \approx \frac{\pi k}{e \epsilon_F} T \sim 2 \cdot 10^{-6}\, T \cdot \mathrm{V/K}.$$

 0021-3640/81/10043-05$00.60

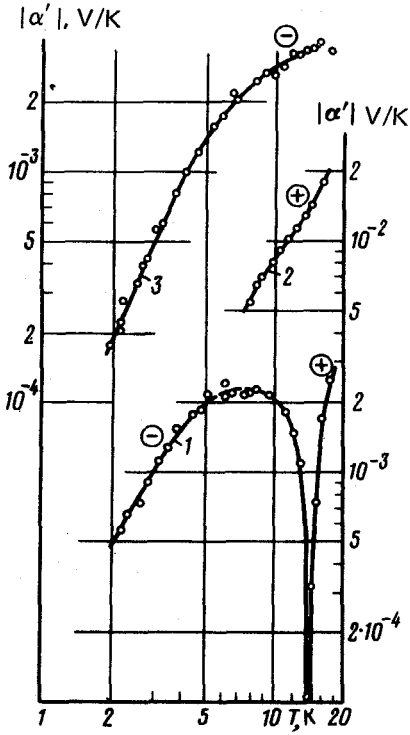

FIG. 1. 1, 3–Seebeck effect in two *n*-Ge samples with a high conductivity at the cleavage surface; $1-\sigma_S \approx 2 \times 10^{-4}$ mho; 2–the same sample after annealing, with $\sigma_{4K} < 10^{-7}$ mho; $3-\sigma_S \approx 4 \times 10^{-4}$ mho. The signs of α are shown in circles.

The calculated value of α^h turns out to be two or three orders of magnitude smaller than the value of α found experimentally. Clearly, the Seebeck effect in our case is caused primarily by phonon drag of the holes. To estimate an upper limit on α^p, we can use[2]

$$\alpha^p \sim \frac{C_L}{en_v}, \tag{1}$$

Substituting in the value of C_L, the lattice heat capacity of germanium, we find from (1) the result $\alpha^p \sim 1.2 \times 10^{-6} T^3$ V/K, which is one and one-half orders of magnitude smaller than the experimental value. Relation (1) is customarily used to evaluate phonon drag in metals, but in our case, with a phonon momentum $\mathbf{P}_p$ comparable to the hole momentum $\mathbf{P}_F \sim 6 \times 10^{-21}$ even at 20 K, the nature of the $\mathbf{P}$–h interaction is more "metallic," with $\mathbf{P}_F \gg \mathbf{P}_p$, than semiconducting, with $P_F < P_p$, over the entire measured temperature range $T < 6$ K. Allowance for the fact that the phonon system transfers to the holes only a fraction of their momentum proportional to $\tau_{ph}^{-1}/(\tau_{ph}^{-1} + \tau_p^{-1})$ (from measurements of the thermal conductivity of the samples we find that $\tau_p \sim 2 \times 10^{-7}$ s) can only reduce the calculated value of α^p further.

We believe that the anomalously large phonon drag of the holes at the conducting surface can be explained in the following manner. Relation (1) presupposes that only phonons of the conducting surface layer participate in the drag, but actually there is nothing to distinguish this layer in the phonon system, and phonons from a

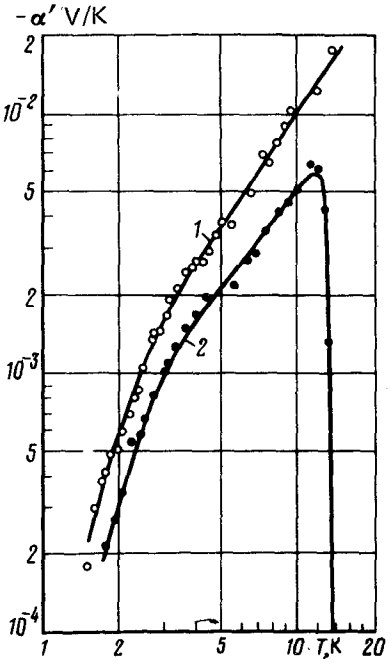

FIG. 2. The Seebeck effect in Ge bicrystals. 1–p-type; 2–n-type.

considerably larger region, $\sim l_p$ in size interact with the charges of the surface layer. The result should clearly be an increase in the phonon drag. A final resolution of this question will require a more detailed analysis.

Up to this point, we have been ignoring the volume component α_v of the Seebeck coefficient α. The quantity measured experimentally is actually

$$\alpha = \frac{\alpha_s R_v + \alpha_v R_s}{R_v + R_s}, \tag{2}$$

where R_s and R_v are the resistances of the conducting layer and of the volume. At $T<6$ we have $R_s \ll R_v$, and the measured value is $\alpha \equiv \alpha_s$; starting at 4.5 K, however, and up to 10 K, the resistance R_v falls off by three or four orders of magnitude, and at $T>6$ we must consider the component α_v in α. At sufficiently high temperatures the sign of α is determined by the sign of α_v, i.e., by the volume carriers. This effect is responsible for the change in the sign of α observed for several of the n-type samples (Figs. 1 and 2).

This proposed explanation for the change in the sign of α has been confirmed by direct measurements of the Seebeck voltage for one of the n-type samples with a cleaved surface, with a conductivity suppressed by annealing. It can be seen in Fig. 1 that α_v for this sample does in fact have the sign opposite that of α_s. On the other hand, the measurements reveal $R_v \approx R_s$ at 16 K. [The value of α_v and its temperature dependence $\alpha_v(T)$ agree with the results of previous measurements[3] for pure germanium.]

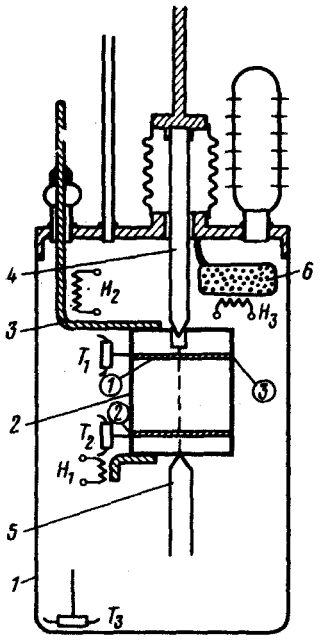

FIG. 3. The vacuum apparatus used for measuring the Seebeck voltage of cleaved samples.

All the measurements were carried out in a vacuum. Figure 3 is a diagram of the apparatus used for studying the cleaved samples. The sample (2) (11 × 10 × 1 mm in size), in which indium contacts have been sealed, is soldered to a copper heat sink (3) which is insulated from the housing of the apparatus. The sample is held between cleaving knife-edges 4 and 5 (4 is movable). Superconducting measurement leads 1-3 are soldered to the sample (the leads for measuring U_H are not shown). Also soldered to the sample are carbon resistance thermometers T_1 and T_2, which are used to measure T and the difference ΔT caused by the heater H_1. Cleavage is verified from the resistance between leads 1 and 3. The temperature of the wall (1) of the apparatus is inferred from the resistance of thermometer T_3. The sample is cleaved in pure He^4 at 4.2 K. A highly conducting surface is formed by heating (with heaters H_2 and H_3) to 40-60 K. During the heating, the carbon (6) warms to 50-70 K, while the bottom of the apparatus remains at the temperature of the helium bath. After the heating, the helium is pumped off by a diffusion pump at the given temperature of the carbon (6), which then (during cooling) adsorbs the gas remaining in the apparatus.

The value of α was measured by a comparison method from 1.7 K to 17 K. Measurements at lower temperatures were hindered by the sensitivity of the measurement apparatus (10^{-10} A), while measurements at higher temperatures were hindered by the errors in the measurement of ΔT. In the case of the bicrystals there could be a systematic error $\sim 30\%$ because of the small dimensions. The conducting layer was destroyed by heating for 10 h at 160 K. The Hall voltage U_H, from which n_s was inferred, was a linear function of the field up to 20 kOe. The thermal conductivity κ of the samples, which was calculated by us from our results for $T < 4$ K, can be de-

scribed by $\kappa = 8 \times 10^{-2}\ T^3$ W/(cm · K) and agrees well with the measurements of Ref. 4 for pure samples.

[1)]We did not observe a high conductivity at the (100) (111) twinning boundary.

1. B. M. Vul, É. I. Zavaritskaya, and E. G. Sokol, Zh. Eksp. Teor. Fiz. **80**, 1639 (1981) [Sov. Phys. JETP [to be published)].
2. J. M. Ziman, Principles of the Theory of Solids, Cambridge Univ. Press, 1964 (Russ. transl. Mir, 1974), Chapter 7.
3. H. P. R. Frederikse, Phys. Rev. **92**, 248 (1953).
4. J. A. Carruthers, T. H. Geballe, H. M. Rosenberg, and J. M. Ziman, Proc. R. Soc. **238a**, 502 (1957).

Translated by Dave Parsons

Edited by S. J. Amoretty