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Reliable measurement of Seebeck coefficient in semiconductors

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Abstract. Reliable measurement of the Seebeck coefficient requires painstaking precautions. Unfortunately, these requirements are not met even in commercially available equipment, and therefore the obtained data often contain systematic errors. We describe equipment for reliable Seebeck measurements and present results on YB$_{66}$ and B$_{4.3}$C boron carbide as an example.

1. Introduction
The temperature gradient $\delta T$ in a solid implies a gradient in the density of mobile carriers, and accordingly, an electric potential gradient $\delta V$. Their relation yields the Seebeck coefficient $S = \delta V/\delta T$. Preliminary information on this material parameter, in particular on its sign, can be easily obtained using simple probe tips held at different temperatures. In contrast to the Hall effect, the sign of the Seebeck effect unambiguously corresponds to the prevailing type of charge carriers, irrespective of the mechanism of their transport. However, painstaking precautions must be taken if reliable values of the Seebeck coefficient are required, e.g., for quantitative characterization of charge transport. Unfortunately, even some commercially available equipment does not meet these requirements and hence introduces systematic errors [1-3].

The following requirements must be considered in reliable Seebeck measurements:
• Temperature and potential must be taken at the same point inside the sample. Mechanically attached probes cause a temperature jump between the probe and sample.
• The high Seebeck effect of semiconductors is particularly important for elucidating the electronic transport or for technical applications. Pressing metal probes creates Schottky barriers, whereas only ohmic contacts are appropriate for semiconductor measurements.
• Contact potentials occur at any junction between conducting solids. They are inevitable even in soldered probes. Theoretically, sign and value of contact potential depend on the position of the Fermi levels, potentially shifted or bended near the contact. In practice, the conditions are much more complicated, because there are additional, hardly controllable surface effects. Reliable Seebeck measurements require elimination of the contact potentials.
• In general, the Seebeck coefficient $S$ depends on temperature. Accordingly, the measured potential difference $\delta V$ usually varies nonlinearly with $\delta T$. Therefore, $S(T_0)$ must be determined for $S(T)_{T\rightarrow T_0}$. 
2. Problems of Seebeck effect measurements

Usually the Seebeck coefficient \( S = \Delta V/\Delta T \) is determined measuring \( V(T) \) at two temperatures. For this case, figure 1 demonstrates the possible influence of the contact potential; linear variation of \( S(T) \) presumed. As shown, even the sign of \( S \) can be incorrect at unfavorable conditions.

![Figure 1](image1.png)

**Figure 1.** Possible effects of the contact potential \( \Delta U \) if \( S = \Delta V/\Delta T \) is obtained from measurements at two different temperatures. (a) positive contact potential; (b) negative contact potential. Circles correspond to the measured data; arrows to contact potential \( \Delta U \); broken lines to Seebeck effect curves shifted by \( \Delta U \); solid red line to false Seebeck effect and dash-dotted line to the true Seebeck measurements unaffected by the contact potential.

In most cases, the Seebeck coefficient depends on temperature. Then, when the measurements are taken at two temperatures only, another problem arises. This is demonstrated in figure 2. Choosing small \( \Delta T \), would solve this problem, but then the \( \Delta V \) becomes too small for reliable measurement.

![Figure 2](image2.png)

**Figure 2.** Problems in obtaining temperature dependent Seebeck coefficients by measuring at two different temperatures. (a) \( T = T_0, \ T > T_0 \); (b) \( T_1 > T_0, \ T_2 > T_0 \). Circles correspond to the experimental data; arrows to contact potential \( \Delta U \); dash-double-dotted black line to real Seebeck effect shifted by \( \Delta U \); solid red line to false Seebeck effect and dash-dotted line to the true Seebeck effect at \( T_0 \) without contact potential.

Therefore, measurements at two temperatures are not sufficient for determining qualitatively and quantitatively reliable Seebeck coefficients. As demonstrated in figure 3, more or less continuous data \( U_{\text{Seebeck}} (\pm T) \) are needed for deriving the accurate asymptote representing \( S(T_0) = \lim (\Delta V/\Delta T) \) for...
$T \rightarrow T_0$. A reversal of the sign of $\Delta T$ is useful.

![Figure 3](image)

**Figure 3.** A reliable Seebeck measurement. Black dash-double dotted curve is measured thermoelectric voltage $V(T)$; arrows present contact potential $\Delta U$ and solid red line an asymptote to the black curve at $T_0$.

### 3. Equipment for reliable Seebeck measurements

The realization of a quasi-continuous curve $\Delta V(\Delta T)$ requires a dense sequence of simultaneously measured data for $\Delta V$ and $\Delta T$ tapped at exactly the same measuring points within the sample. Accordingly, the same probes must be used for both data.

We report on equipment for measuring Seebeck coefficients of boron-rich solids exemplary for high-ohmic semiconductors. Temperatures and potentials are determined at the very same small probes with ohmic contacts in samples with resistances up to $10^{12} \, \Omega$. Thermocouples of suitable metal combinations were used as probes. They were affixed to the sample by capacitor discharge. In this way, ohmic Cu and Pt contacts were realized to boron-rich solids.

![Figure 4](image)

**Figure 4.** Electronic circuits for measuring Seebeck coefficients. (a) complete circuit; $T_1$, $T_2$ are temperatures applied to the sample; $V_{in}$, $V_{out}$ are the input and output voltages, respectively, of the INA 110 amplifier. (b) wiring scheme of INA 110 amplifier (Burr-Brown corporation)

The electronic circuits are displayed in figure 4. The electrical leads for measuring temperature via thermocouples and for measuring the thermoelectric voltage must be electrically isolated from one another, in spite of using the same probes. This was realized with FET amplifiers INA 110 (Burr-Brown Corporation) having input resistances of $10^{15} \, \Omega$. Very important was the small drift of this amplifier ($2 \, \mu V/K$ only), largely avoiding the compensation of offset voltages after the equipment had reached thermal equilibrium (i.e., after about two hours). The lowest amplifier stage ($10 \times$) was...
sufficient for obtaining reliable data. The simultaneous recording of data was enabled by trigger impulses initiating the measuring devices integrated into a bus system.

The data recorded in a dense sequence were edited in a computer, were the calibration curves of the thermocouples had been approximated by high-order polynomials. The edited data were displayed on the computer screen, similar to figure 3, during several cycles of increasing and decreasing temperatures in the range ±1 to 3 K around the relevant temperature.

The central temperature was controlled in a thermostat, and the heating and cooling was provided by small internal heaters having small heat capacity. All the relevant data were displayed on the computer screen as well. This way the whole procedure was supervised, contact voltages were discerned, and reliable values for the Seebeck coefficient could easily be determined.

Pt/PtRh thermocouples are usually usable below ~2030 K. However, in boron-rich solids, a boron-platinum eutectic is formed at ~1070 K, destroying the thermocouple and modifying the sample. Hence, for measuring the Seebeck coefficient of boron carbide (melting point ~2720 K) up to about 2000 K, a modification of the equipment was required.

For determining the temperatures at the sample, we used the boron carbide itself as thermistor, whose temperature-dependent resistivity was thoroughly calibrated. Tungsten tips were used as contacts. As an example, the Seebeck coefficient of boron carbide was measured up to ~2000 K. This temperature limit was due to decomposition of the hexagonal BN sample holder.

4. Examples of measurement
The high input resistance of the amplifier allows measurements even on highly-resistive samples. As an example, in figure 5 the Seebeck coefficient of YB$_{66}$ is displayed, whose resistivity at low temperatures is about $10^9 \, \Omega^{-1} \, \text{cm}^{-1}$[4].

Figure 5. Seebeck coefficient of YB$_{66}$. ▲ $T$ increasing; ▼ $T$ decreasing.

Figure 6 presents the results obtained on B$_{13}$C boron carbide by both methods described above (for moderate and high temperatures, respectively). In spite of a somewhat greater error margin, the Seebeck data obtained by the modified high-temperature method satisfactorily fit to the data measured with the method for moderate temperatures. For more details of the Seebeck coefficient of boron carbide see [5,6], and references therein. The measured prismatic samples had ~12 mm length and 4 mm thickness. The probe distance was ~8 mm and the probe size was <1 mm.
Figure 6. Seebeck coefficient of B$_{4.3}$C boron carbide. ◆, method as described above, T = 75 - 350 K; ▲, method as described above, T = 350 - 1000 K, T increasing; ▼, method as described above, T = 350 - 1000 K, T decreasing; ■ modified method for high T, T = 450 - 1950 K

5. Summary
We have described a method of reliable measurement of the Seebeck coefficients in semiconductors, including high-resistivity materials. The method avoids systematic errors caused by contact potential, irrespective of its sign and quantity. Electric potential and temperatures are obtained at the very same probes, and therefore their distance does not need to be measured.

References