

Data analysis for Seebeck coefficient measurements

Cite as: Rev. Sci. Instrum. **84**, 065102 (2013); <https://doi.org/10.1063/1.4807697>

Submitted: 03 April 2013 • Accepted: 10 May 2013 • Published Online: 03 June 2013

J. de Boer and E. Müller



View Online



Export Citation



CrossMark

ARTICLES YOU MAY BE INTERESTED IN

[A setup for measuring the Seebeck coefficient and the electrical resistivity of bulk thermoelectric materials](#)




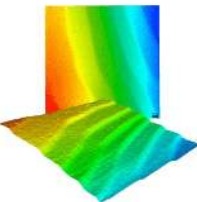

Review of Scientific Instruments **88**, 095111 (2017); <https://doi.org/10.1063/1.4990634>

[Using the Seebeck coefficient to determine charge carrier concentration, mobility, and relaxation time in InAs nanowires](#)

Applied Physics Letters **104**, 012113 (2014); <https://doi.org/10.1063/1.4858936>

[Measurement of Seebeck coefficient using a light pulse](#)

Review of Scientific Instruments **56**, 719 (1985); <https://doi.org/10.1063/1.1138213>

	<p>Nanopositioning Systems</p> 	<p>Modular Motion Control</p> 	<p>AFM and NSOM Instruments</p> 	<p>Single Molecule Microscopes</p> 
---	--	--	---	--



Data analysis for Seebeck coefficient measurements

J. de Boor^{1,a)} and E. Müller^{1,2}

¹*Institute of Materials Research, German Aerospace Center, Linder Höhe, 51147 Köln, Germany*

²*Institute for Inorganic and Analytical Chemistry, Justus-Liebig-Universität Gießen, Heinrich-Buff-Ring 58, 35392 Gießen, Germany*

(Received 3 April 2013; accepted 10 May 2013; published online 3 June 2013)

The Seebeck coefficient is one of the key quantities of thermoelectric materials and routinely measured in various laboratories. There are, however, several ways to calculate the Seebeck coefficient from the raw measurement data. We compare these different ways to extract the Seebeck coefficient, evaluate the accuracy of the results, and show methods to increase this accuracy. We furthermore point out experimental and data analysis parameters that can be used to evaluate the trustworthiness of the obtained result. The shown analysis can be used to find and minimize errors in the Seebeck coefficient measurement and therefore increase the reliability of the measured material properties.

© 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4807697>]

I. INTRODUCTION AND MOTIVATION

Thermoelectric materials can convert heat directly into usable electrical energy. Since there are ubiquitous sources of waste heat readily available thermoelectric generators have numerous potential applications; they can, e.g., enhance the fuel efficiency of cars or power sensors.^{1,2} With respect to the widely-discussed energy crisis thermoelectric materials have the potential to be a valuable part of the solution. The attractiveness of thermoelectric generators is coupled to their heat to electrical energy conversion efficiency. This efficiency is linked to the thermoelectric figure of merit ZT , which itself is composed of basic material properties:

$$ZT = \frac{\sigma S^2}{\kappa} T, \quad (1)$$

where σ is the electrical conductivity of a material, κ is the thermal conductivity, S is the Seebeck coefficient, and T is the absolute temperature. If ZT is to be determined and optimized, these three quantities have to be measured. Of these three the Seebeck coefficient is the most prominent in Eq. (1) and perhaps the most difficult to measure. First, the Seebeck coefficient enters ZT quadratically while all other quantities enter only linearly. Furthermore the Seebeck coefficient is the ratio of the potential difference U that arises due to a temperature difference ΔT and thus the determination of S combines the challenges of correct electrical and thermal measurements.

Many systematic errors of the Seebeck coefficient measurement are related to hardware issues such as thermal contact resistances between sample and thermocouples, parasitic heat flux through the thermocouples, and other sources. A lot of insight on this issue can be found in the literature.^{3,4} Besides that, there is also some uncertainty on how to extract the Seebeck coefficient best from the raw measurement data. In this paper we will focus on a suitable data analysis for the Seebeck coefficient, present consistency checks that can be done to evaluate the trustworthiness of the obtained data and point out parameters that reveal problems in the measurement.

^{a)}johannes.deboor@dlr.de

II. EXEMPLARY SETUP

We will shortly introduce the employed setup. It shares a lot of general features with other setups and might therefore serve as a typical example. The focus here is not on the actual design details of hardware; a brief introduction is nevertheless useful for the following discussion. The setup is capable of measuring the electrical conductivity and the Seebeck coefficient simultaneously from room temperature to 1000 K. A more detailed description of this setup and its accuracy can be found in Ref. 5; further examples of measurement systems for the Seebeck coefficient can be found in the literature.^{3,6-14} A schematic picture of the employed sample holder is presented in Figure 1, only the details necessary for the Seebeck coefficient measurement are shown.

The sample is subject to a variable temperature gradient that can be created using the gradient heaters that are positioned close to the sample. The temperatures as well as the voltage difference resulting from the temperature gradient are measured using sheathed thermocouples of type N. The two thermocouples are used to measure the temperatures T_1 and T_2 as well as the thermal voltages, see Figure 2. The voltage measured across the negative pair of wires U_{neg} is given by

$$U_{neg} = - \int_{T_1}^{T_2} (S(T) - S_{neg}(T)) dT \\ \approx -(T_2 - T_1) * (S(\bar{T}) - S_{neg}(\bar{T})), \quad (2)$$

where S is the Seebeck coefficient of the sample and S_{neg} the Seebeck coefficient of the negative leg of the thermocouple; for type N this is NiSiI. If the temperature difference is sufficiently small, the integral can be replaced by a simple product with $\bar{T} = (T_2 + T_1)/2$. Correspondingly, the voltage across the positive legs is given by

$$U_{pos} = -(T_2 - T_1) * (S(\bar{T}) - S_{pos}(\bar{T})). \quad (3)$$

The two temperature signals and the two voltages are feed to a Keithley 2700 digital multimeter (DMM) via a switch card (Keithley 7700) which is used for the concurrent measurement of the signals. The sample Seebeck coefficient is

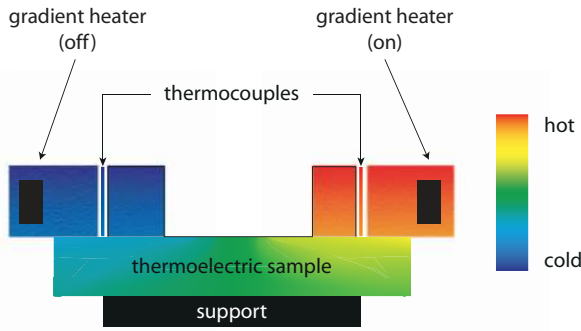


FIG. 1. Sample holder for the measurement of the Seebeck coefficient. The sample is sandwiched between the holder and a support. The temperature gradient along the sample is established using one of the gradient heaters. The resulting thermoelectric voltages and temperatures are recorded using two thermocouples. The whole sample holder is situated in an oven; this allows for temperature dependent measurements.

determined in a measurement sequence as shown in Figure 3. First gradient heater 1 is powered and a temperature difference between TC₁ and TC₂ establishes. This causes U_{neg} and U_{pos} to differ from zero, the ideal equilibrium value. After a certain time, typically 60 s, the heater is switched off, the temperature gradient relaxes, and the voltage signals slowly vanish. After the system has approximately returned to equilibrium heater 2 is powered and the step is repeated. Following the classification scheme by Martin the measurement routine is thus a quasi-stationary one.⁴ The measurement signals are recorded during both steps in the order $T_1, T_2, U_{neg}, U_{pos}, T_1, \dots$. To prevent cross talk between the recorded voltage signals and the power supplied to the gradient heaters only the data obtained after the heaters are switched off is used for the subsequent analysis.

Since the setup comprises only two thermocouples, one multimeter, and a switch card it is one of the simplest systems for a Seebeck coefficient measurement. Therefore, many things that are discussed in the following are representative for other systems, even if details in hardware or electronics may differ.

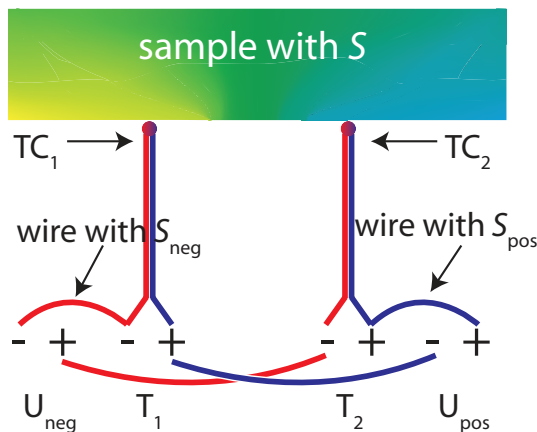


FIG. 2. Wiring scheme of the employed measurement setup. The two thermocouples are connected directly to the switch card and are used to obtain the temperatures T_1 and T_2 . Furthermore, the voltage U_{neg} across sample and negative legs of the thermocouples as well as the voltage U_{pos} across sample and positive legs are measured on the switch card; these are used to calculate the sample's Seebeck coefficient.

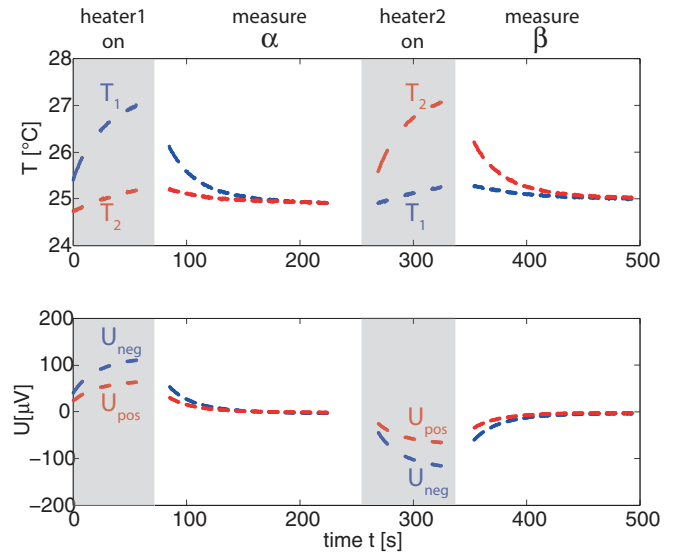


FIG. 3. Measurement routine for the determination of the sample's Seebeck coefficient. The figure shows the time resolved profiles of the temperatures (top) as well as the voltages during one measurement cycle. For later analysis, only the values recorded after the heaters are switched off are used.

III. FROM RAW MEASUREMENT DATA TO THE SEEBECK COEFFICIENT

We now want to evaluate several equations that can be used to obtain the sample's Seebeck coefficient. Rearranging Eqs. (2) and (3) yields the first two equations

$$S_A = -\frac{U_{neg}}{T_2 - T_1} + S_{neg}(\bar{T}), \quad (4)$$

$$S_B = -\frac{U_{pos}}{T_2 - T_1} + S_{pos}(\bar{T}). \quad (5)$$

The results of the two—in principal equivalent—equations are labeled S_A and S_B for better distinction. Equations (4) and (5) can be combined to a third equation for the Seebeck coefficient

$$S_C = \frac{-U_{neg}}{U_{pos} - U_{neg}} S_{TC}(\bar{T}) + S_{neg}(\bar{T}). \quad (6)$$

In contrast to the previous equations, Eq. (6) requires no explicit measurement of the temperatures T_1 and T_2 . They are still required to calculate the absolute measurement temperature \bar{T} , but for \bar{T} usually less precision is required compared to the measurement of $T_2 - T_1$. $S_{TC} = S_{pos} - S_{neg}$ is the Seebeck coefficient of the employed thermocouple.

Calculation of S_A and S_B requires exact knowledge of T_1 and T_2 . However, the typical accuracy of a thermocouple reading is of the order of 1 K, at best ≈ 0.2 K.¹⁵ This is due to the fabrication process of the thermocouples and cannot be avoided. On the other hand it is desirable that the temperature difference created across the sample during a measurement is small so that the simplification in Eq. (2) holds. Usually this temperature difference is therefore also of the order of 1 K. The calculation of $T_2 - T_1$ can thus be highly inaccurate which leads to incorrect values for the sample Seebeck coefficient. Hence in practice Eqs. (4)–(6) tend to give incorrect results and are rarely applied as such.

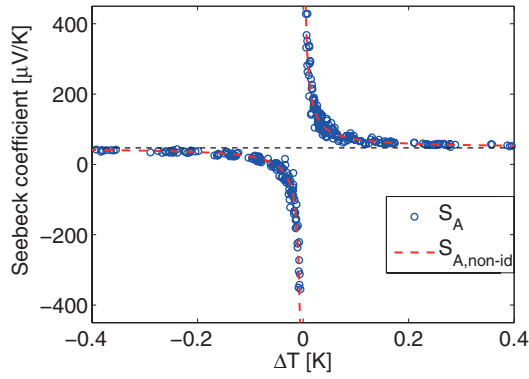


FIG. 4. Seebeck coefficient as obtained from Eq. (4) for the data shown in Figure 3. The result is not independent of ΔT as would principally be expected. The reason for the behavior is a combination of offsets between the thermocouples and spurious voltages from within the measurement system. The effects of these offsets can be expressed in a simple model (using Eq. (7)) and the result fits the experimental data reasonably well.

The second reason why Eqs. (4)–(6) are questionable is the existence of small spurious voltages from within the measurement system. These can stem from temperature differences at any electrical connection between different materials or inhomogeneities in the thermocouples and can usually not be completely avoided.^{4,10,12} These voltages will affect the results for S_A , S_B , and S_C . In order to illustrate this point we have calculated S_A for every set of T_1 , T_2 , and U_{neg} shown in Figure 3. The result is shown vs. $T_2 - T_1$ in Figure 4.

The results for S_A are not at all constant vs. ΔT ; in fact, the values diverge for small ΔT and converge for large $|\Delta T|$. If differences between the two thermocouples and spurious voltages in the measurement system are taken into account, Eq. (4) can be rewritten for these non-ideal conditions as

$$S_{A,non-id} = -\frac{U_{neg} + \delta U}{T_2 - T_1 - \delta T} + S_{neg}(\bar{T}). \quad (7)$$

Here δT is the temperature difference in the two thermocouple readings if they are at the same temperature and δU represents the spurious voltages that affect the U_{neg} reading. The result of Eq. (7) is plotted in Figure 4 for $\delta U = 2.5 \mu\text{V}$ and $\delta T = 0.001 \text{ K}$; U_{neg} is calculated from $U_{neg} = (S - S_{neg1})(T_2 - T_1)$, where S is the convergence value for large ΔT , the “true” sample’s Seebeck coefficient. It can be seen that the obtained measurement data can be represented well by Eq. (7) using the given parameters.

The magnitudes of δU and δT are quite small and will be comparable or larger in most measurement systems. The example illustrates that Eq. (4) should only be used to obtain a rough estimate for the Seebeck coefficient of a sample. Similar reasoning holds for Eqs. (5) and (6).

The well-known approach to eliminate the effect of offsets is to obtain the Seebeck coefficient not from a single set of data points but rather from a linear fit of voltage vs. temperature difference. In this case Eqs. (4) and (5) can be rewritten as

$$S_D = -\frac{\partial U_{neg}}{\partial \Delta T} + S_{neg}(\bar{T}), \quad (8)$$

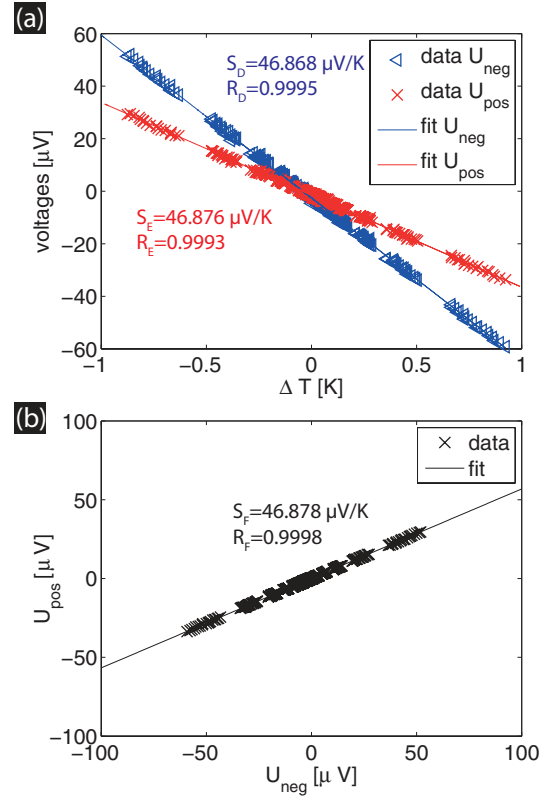


FIG. 5. (a) Seebeck voltages U_{pos} and U_{neg} vs. temperature difference ΔT and (b) U_{pos} vs. U_{neg} . All three data sets show a linear behavior as indicated by the good agreement between measurement data and the corresponding linear fits. Also indicated are the results for the Seebeck coefficient (Eqs. (8)–(10)), which agree with each other within 0.1%. The linear correlation coefficient R of the fit gives an indication about the agreement between raw data and linear fit; here R is very close to unity for all three data sets.

$$S_E = -\frac{\partial U_{pos}}{\partial \Delta T} + S_{pos}(\bar{T}), \quad (9)$$

where $\Delta T = T_2 - T_1$. Equation (6) can be differentiated with respect to one of the voltages, yielding, e.g.,

$$S_F(\bar{T}) = \frac{S_{TC}(\bar{T})}{1 - \frac{\partial U_{pos}}{\partial U_{neg}}} + S_{neg}(\bar{T}). \quad (10)$$

It is clear that the results for S_D , S_E , and S_F are not affected by constant spurious voltages or thermocouple differences that lead to incorrect results for S_A , S_B , and S_C . For Eqs. (8)–(10) to be correct it is only necessary that the offsets are constant during the measurement time, which can be experimentally fulfilled much easier than having no offsets at all. U_{neg} and U_{pos} vs. ΔT are shown in Figure 5(a), while Figure 5(b) shows U_{pos} vs. U_{neg} . The figures show the raw measurement data, the corresponding linear fits to the data as well as the linear correlation coefficients (Pearson’s correlation coefficient), and the Seebeck coefficients which were calculated from the fit.

The measurement data can be represented excellently by a linear fit as clear from the figure and quantitatively supported by the obtained values for R_D , R_E , and R_F that are close to the ideal value of unity. The Seebeck coefficient values

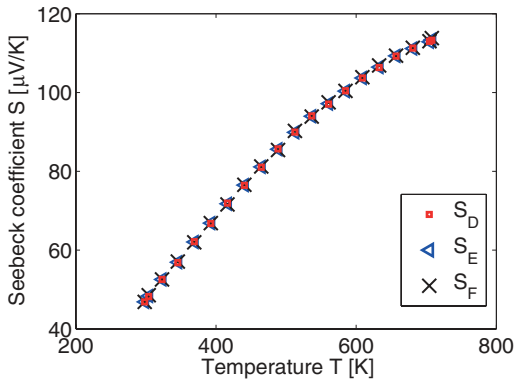


FIG. 6. Seebeck coefficient over temperature for a skutterudite sample. The plot compares the results of Eqs. (8)–(10) which basically lie on top of each other. The relative difference between S_D , S_E , and S_F is smaller than 0.6% for the whole temperature range.

obtained from the three linear fits are very similar and differ by less than 0.1%.

The results for S_D , S_E , and S_F are shown for a complete measurement over temperature for a skutterudite sample in Figure 6. The agreement between S_D , S_E , and S_F is excellent, the values differ by less than 0.6%.

The remaining differences can be caused by statistical noise in the measurement signals (a deviating measurement value in, e.g., T_1 will affect the result for S_D and S_E but not S_F) and by small inaccuracies in the Seebeck coefficient of the wire material.

The linear correlation coefficients for all three data sets have been calculated for each temperature. For better visibility not R itself but the difference to unity is plotted in Figure 7.

It can be seen that the linear correlation coefficients R_D , R_E , and R_F are very similar, always better than 0.999 and approximately independent of temperature.

In summary Eqs. (8)–(10) yield very similar results for the Seebeck coefficient and are equivalent. This might not be too surprising since they are derived from the same basic equations and describe the same physical situation. However, as will be shown in the following, the observed good agree-

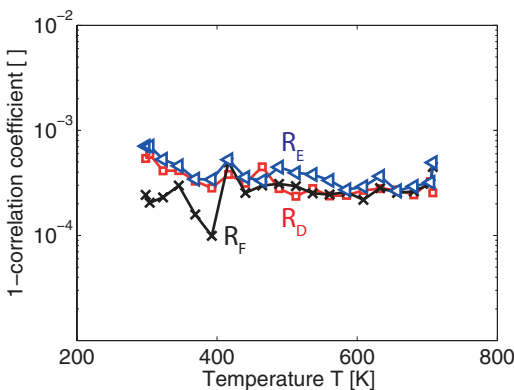


FIG. 7. Linear correlation coefficient for the results shown in Figure 6. The linear correlation coefficients and thus the quality of the fits used to obtain the Seebeck coefficient are approximately independent of temperature and close to unity over the whole temperature range.

ment is not self-evident and can be violated easily. For the results shown so far the temperatures used in Eqs. (8)–(10) are *not* obtained from a temperature reading of the multimeter. Instead, the voltages corresponding to T_1 and T_2 are measured directly and converted into temperatures externally using the controlling personal computer. The relation between the voltage from a thermocouple and the corresponding temperature at the junction (T_{hot}) is given by

$$T_{hot} = \sum_{m=0}^n d_m U^m, \quad (11)$$

where U is the recorded voltage. The coefficients d_m can be found for various thermocouple types and temperature ranges¹⁵ under the assumption that the cold end of the thermocouple is at $T_{ref} = 0^\circ\text{C}$. If this is not the case, the cold side temperature has to be measured and Eq. (11) adapted accordingly. In our case the temperature of the reference junction inside the multimeter can be determined directly from the Keithley DMM and is approximately $T_{ref} \approx 37^\circ\text{C}$. Using the inverse equation to Eq. (11) one can calculate the voltage U_{ref} due to the reference junction not being at 0°C

$$U_{ref} = \sum_{m=0}^n c_m T^m, \quad (12)$$

and modify Eq. (11)

$$T_{hot} = \sum_{m=0}^n d_m (U_{meas} + U_{ref})^m, \quad (13)$$

to be able to employ the standard tabulated coefficients. For the employed standard switch card the reference temperatures can be determined at six different positions of the card. These temperatures are very similar and vary only very slowly during the course of the measurement as shown in Figure 8. It is, therefore, sufficient to determine the temperature of the reference junction closest to the used slot prior to the measurement of the Seebeck coefficient, i.e., before the routine shown in Figure 3.

It should also be noted that small inaccuracies in the temperature measurement do virtually not affect the result for the Seebeck coefficient as long as they remain constant. In fact, if

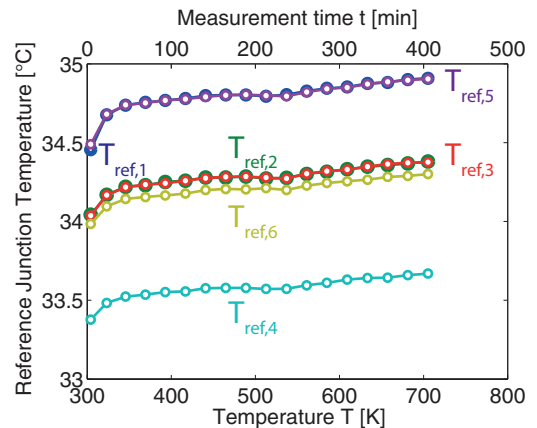


FIG. 8. Temperature of the six internal cold side temperature sensors of the employed switching card in the multimeter vs. measurement temperature and time. All temperatures are similar and vary only slowly over the course of the measurement. For the voltage to temperature conversion the temperature of the sensor closest to the respective thermocouple measurement channel is employed.

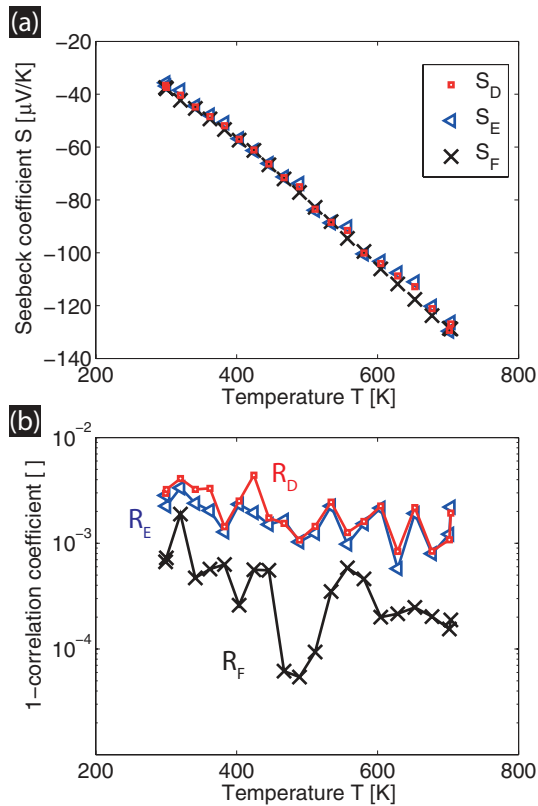


FIG. 9. (a) Seebeck coefficients calculated from (8)–(10). In contrast to the results shown in Figure 6 in this case the internal voltage to temperature conversion of the multimeter has been used to obtain the employed temperature differences. While all three curves follow the same trend it can be seen that S_D and S_E show some scattering and partially deviate significantly from S_F . The linear correlation coefficients of the underlying linear fits in (b) show that the fits are better for S_F .

one assumes the same cold junction temperature for two thermocouples which in reality do have different cold side junction temperatures, one or both of the calculated temperatures will differ from its “true” value. However, this offset will not affect the result for S_D and S_E because the slope of a linear fit is employed to calculate the Seebeck coefficient.

With this kind of temperature measurement we found the described good agreement between Eqs. (8)–(10). If instead directly the temperature readings from the multimeter are used, the agreement is less good. The results of S_D , S_E , S_F and the corresponding linear correlation coefficients are plotted in Figure 9. Here a PbTe sample was used with a Seebeck coefficient comparable to the skutterudite sample shown in Figure 6.

While S_D , S_E , and S_F follow the same trend they show significant deviations from each other; these can exceed 5%. It can also be seen that S_D and S_E show some scattering, while S_F is relatively smooth. This impression can be confirmed by Figure 9(b), where it can be seen that the linear correlation coefficient is better for S_F than for S_D and S_E . Since S_F is calculated directly from the voltages while S_D and S_E are calculated using the temperature readings, S_F is virtually not affected by inaccuracies in the voltage-temperature conversion in contrast to S_D and S_E .

The external voltage-temperature conversion has another advantage beside the improved accuracy. If both voltages and temperatures are recorded by a single DMM, the instrument has to switch between the voltage and the temperature sensing modes. This switching requires some time (≈ 5 s) due to internal stabilization procedures and restricts the number of measurable data points in a non-steady-state measurement routine as is employed in our setup. If only voltages are recorded, more data points can be obtained in the same measurement time which reduces statistical uncertainties of the obtained results.

If for some reason one has to rely on the temperature reading of the measurement device and cannot employ an external voltage-to-temperature conversion, the linear correlation coefficients for S_D , S_E , and S_F can give an indication which equation gives the most reliable result. We found that S_F from Eq. (10) shows less scattering than Eqs. (8) and (9). Since S_F furthermore does not require an accurate temperature reading and therefore no voltage-to-temperature switching it can be used to obtain measurement data at a faster rate.

IV. SIMULTANEOUS MEASUREMENTS

Independent of the particular formula all equations for the determination of the Seebeck coefficient require in principal the simultaneous measurement of several voltages (and temperatures). The exceptions are true steady state measurements, however, these have very long measurement times which is why quasi-stationary or transient measurement conditions are often employed.⁴ True simultaneity can only be achieved using several properly linked multimeter which might not always be possible or feasible. We will first show here that correct results can also be obtained with a single multimeter by data interpolation and second that this interpolation is important even for fast data acquisition rates.

From the raw data shown in Figure 3 interpolation curves for the two temperatures and voltages are calculated. From these curves the values at certain points of time can be obtained; we chose the time where U_{neg} is recorded as reference, but this is a more or less arbitrary choice. Since the measurement data show monotonic behavior with relatively large time constants the interpolation represents the measurement data very well. To avoid extrapolation the first and the last data points are excluded from the interpolation. The time difference between a measurement of U_{neg} and U_{pos} is around 0.11 s, one might therefore suspect that no temporal data interpolation is necessary as the measurements are taken relatively quick after each other. Figure 10 shows the plot of U_{neg} vs. U_{pos} for the raw and the interpolated data. For the raw data the first measurement for U_{neg} corresponds to the first measurement of U_{pos} (ignoring the small mismatch in time), while for the interpolated data the time difference between the two measurements has been taken into account.

On first glance the effect seems to be very small, with a good match of the data sets. However, the inset in Figure 10 shows both the differences in the individual data points as well as in the corresponding fits that are used to obtain the Seebeck coefficient. In this particular case the value

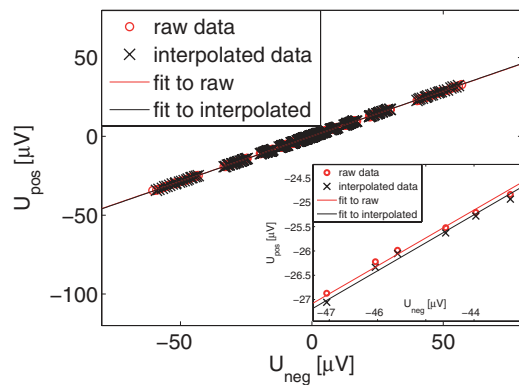


FIG. 10. U_{pos} vs. U_{neg} with and without temporal interpolation. For the raw data each measurement of U_{neg} is related to the subsequent measurement of U_{pos} . For the interpolated data the value is calculated from the temporal interpolation of the measurement data such that there is temporal match between U_{neg} and U_{pos} . Although the effect appears to be small and is hardly visible in the overview plot, the zoom in shows that the interpolation to the same time changes the values of U_{pos} and thus the calculated Seebeck coefficient.

from the raw data and from the interpolated data differs by $\approx 2\%$.

The severity of this effect depends on data acquisition as well as thermal properties of sample and system. Whether the Seebeck coefficient is determined too large or too small depends on the measurement order. We typically find a slow increase of the relative error with increasing temperature. This is probably due to the thermal relaxation time constants of the sample holder which decrease with absolute temperature due to increasing radiation coupling. The Seebeck coefficient over temperature calculated from raw and interpolated data is shown in Figure 11.

The significance of a correct data interpolation has been shown for the case that the Seebeck coefficient is determined from Eq. (10), i.e., from U_{pos} and U_{neg} , but the same holds true for Eqs. (8) and (9) as well. The significance of this effect also depends on the measurement routine and the setup, but we wanted to point out here that this can indeed play an important role.

A simplified version of data interpolation is the so-called “delta method.” In this approach the data are taken in a certain

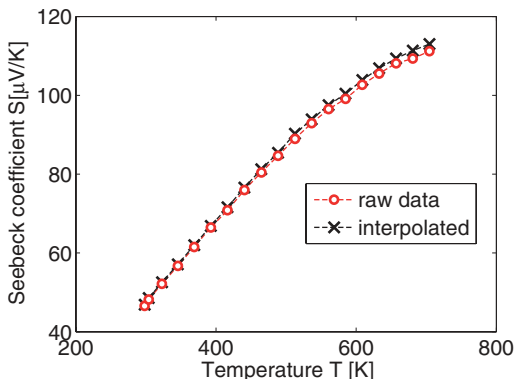


FIG. 11. Seebeck coefficient over temperature obtained from raw measurement data and interpolated data. Here the relative error is about 2%, depending on sample properties and geometry it can vary between 1% and 5%.

order (e.g., T_{c1} , T_{h1} , $U1$, T_{h2} , T_{c2} and then averaged, i.e., $T_c = (T_{c1} + T_{c2})/2$, $T_h = (T_{h1} + T_{h2})/2$).¹⁰ While this is certainly an improvement to no interpolation it is not necessarily correct as it implicitly assumes that the switching times between the readings are identical and that the time gap between the first two temperatures and the voltage is the same as the time gap between the voltage and the second set of temperatures. For our multimeter we found that switching from voltage to temperature takes longer than the other way round (7 s–5 s), i.e., the delta method would be an incorrect linear interpolation in this case. The alternatives to data interpolation are steady state measurements or the use of several multimeters for simultaneous data acquisition.¹² Steady state measurements require equilibration times which inherently prolongs the measurement time and are usually acquired from less data. Comparing the effort/complexity of a simple data post treatment and synchronizing several measurement devices one might find the former a feasible approach.

V. CONSISTENCY CHECKS AND ERROR INDICATIONS

In the following we want to list and discuss consistency checks that can be used to find errors in the measurement, data acquisition, or data analysis.

The first opportunity for consistency checks are the different, but equivalent equations to determine the Seebeck coefficient. As discussed above equations based only on a single measurement of temperatures and voltages (Eqs. (4)–(6)) cannot be expected to be accurate due to ubiquitous spurious thermal voltages within a measurement system. However, the equations based on a series of temperature and voltage measurements can be used as a consistency check. If Eqs. (8)–(10) do not give very similar results, this may point out errors in the used values for the thermocouple Seebeck coefficients, the temperature measurement, or the voltage-to-temperature conversion as well as the temporal data interpolation if employed. A further advantage of employing all three equations arises when the Seebeck coefficient of the material is comparable to either of the thermocouple wire Seebeck coefficient. In this case $\partial U_{pos}/\partial U_{neg}$ cannot be calculated accurately and Eqs. (8) and (9) will give more reliable results than Eq. (10).

Indications for experimental errors can be obtained by some data analysis. When calculating the Seebeck coefficient the linear fits as shown in Figure 5 will usually have an absolute term that is different from zero, i.e., the linear fit will not run exactly through the origin. In the case of fitting U_{pos} vs. U_{neg} the absolute term of the fit is the offset between the two voltages. The offset arises from non-ideal connections or material inhomogeneities in the measurement path and is a measurement system specific quantity and should not depend on the sample under investigation. Figure 12 shows the absolute term from the linear fit of U_{pos} vs. U_{neg} over measurement temperature for two different samples. One is a low-doped LAST-18 sample with a Seebeck coefficient between $-300 \mu\text{V/K}$ and $-400 \mu\text{V/K}$ in the plotted temperature range while the other is a doped skutterudite sample with the Seebeck coefficient between -120 and $-200 \mu\text{V/K}$. Although the sample properties are highly different, the offsets are

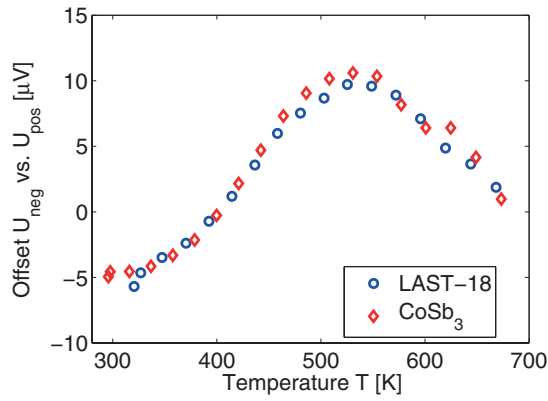


FIG. 12. Offset of the fit U_{pos} vs. U_{neg} with respect to measurement temperature. The offset is shown for two samples with different Seebeck coefficients; nevertheless resulting in similar offsets.

comparable. Therefore, monitoring this quantity during the measurements allows for detection of changes in the setup that might otherwise remain undiscovered. An example is a change in the connection of a thermocouple wire to a connecting plug. It should also be noted that the offset is of the order of $10 \mu\text{V}$ over the whole temperature range and thus relatively small compared to the measurement signals. Equations (8)–(10) for the calculation of the Seebeck coefficient are based on the assumption that offsets are constant over the measurement time at one particular temperature. The observation that these offsets are indeed small therefore justifies this assumption in our case; in the literature values up to 1 mV as offsets have been reported.¹⁰

Another quantity to judge the quality of the measured data is the linear correlation coefficient of the linear fits. It quantifies how good a linear relation between two variables (e.g., ΔT and U_{pos}) is fulfilled. It is, therefore, a measure for the quality of a linear fit and should be very close to unity. Linear correlation coefficients significantly smaller than unity (say <0.999) indicate severe problems with the measurements: poor signal quality, temperature drifts affecting the measurement, offset voltages that change during the measurement time, etc. If such problems are generally solved for a system, the correlation coefficients can also be used to detect alteration of a sample during a measurement. While most thermoelectric materials are intended to be stable one often has to deal with thermally unstable materials, especially in the early stages of the material development. In Figure 13 we show the Seebeck coefficient measurement for Zn_4Sb_3 , a material well known for its thermal instability.¹⁶ The blue circles correspond to the Seebeck coefficient values obtained from the complete measurement routine as shown in Figure 3 and are labeled “ $\alpha + \beta$.” At lower temperatures the Seebeck coefficient of the sample increases slowly with increasing as typical for a degenerate semiconductor. Above 420 K the Seebeck coefficient increases much more rapidly with increasing temperature up to a temperature of 470 K beyond which the increase in temperature is comparable to the low temperature regime. In the temperature interval between 420 K and 470 K the material undergoes degradation which causes the observed rapid rise in the Seebeck coefficient; further details on the ma-

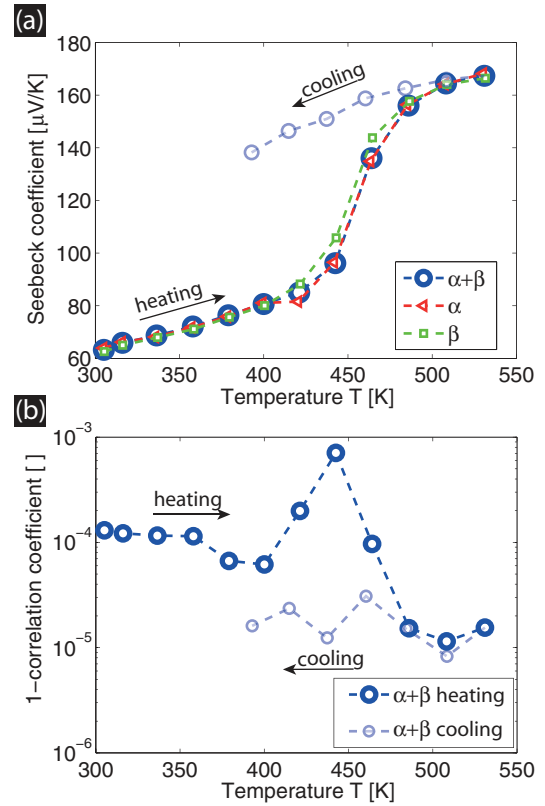


FIG. 13. (a) Seebeck coefficient of a Zn_4Sb_3 sample over temperature. “ $\alpha + \beta$ ” corresponds to the Seebeck coefficient that is obtained if the whole data from the measurement routine as shown in Figure 3 are employed. The result if only the first half of the data are employed is labeled “ α ,” while the result from the second half is labeled “ β .” For stable samples the three values should be very close to each other, but here it can be seen that between 420 K and 470 K “ α ” and “ β ” differ from each other. The reason is a change of the sample properties during the measurement, i.e., the sample has (on average) a different Seebeck coefficient during measurement “ α ” than at “ β ” at a given temperature. This is reflected in the correlation coefficient (b) that deviates stronger from unity in the region where the sample is thermally unstable. This shows that the linear correlation coefficient can be used to detect such changes.

terial are, e.g., given in Ref. 17. To illustrate the change of the sample the Seebeck coefficient of the sample upon cooling is also shown in Figure 13(a).

The deviation of the corresponding linear correlation coefficients from unity is plotted in Figure 13(b) and shows an interesting behavior. At low temperatures the difference is relatively small and approximately constant. In the temperature interval where the sample undergoes degradation the deviation from unity increases and decreases when the sample is stable again. In this case the linear correlation coefficient can therefore be used as an indicator where the sample is changing during the measurement.

To emphasize that the sample is indeed changing in the mentioned temperature window, Figure 13(a) shows the Seebeck coefficient values obtained from the complete measurement routine together with the values that are obtained if only the first half of the data is used for fitting (“ α ”), i.e., using only heater 1 as well as the result from the second half (“ β ”), using only heater 2, compare Figure 3. At low and at high temperatures the three curves agree well with each other as would be expected; in fact, this is another consistency check

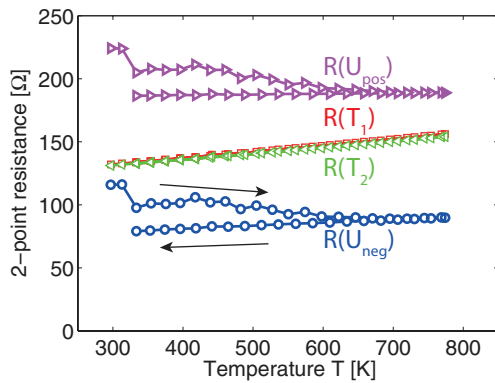


FIG. 14. Exemplary two-point resistances of the two thermocouple channels and the two circuits used to measure U_{neg} and U_{pos} over temperature. Drastic changes in $R(U_{neg})$ or $R(U_{pos})$ can indicate poor contact between the sample and the thermocouples while comparison of $R(T_1)$ and $R(T_2)$ between different measurements can reveal changes of the thermocouples, e.g., by contamination.

for the measurement data. However, in the temperature range between 420 K and 470 K there is a visible difference between “ α ” and “ β ,” corresponding to the temperature window in which the sample undergoes thermally induced changes resulting in a higher Seebeck coefficient. Since the “ β ” measurement is taken after the “ α ” measurement it will yield a higher Seebeck coefficient value. This comparison between the data from “ α ” and “ β ” visualizes the temperatures where the sample is unstable. We want to point out here that this can also be identified from the plot of the linear correlation coefficient. If the sample changes on a time scale comparable to the measurement time at a particular temperature, the linear fits to the raw used to obtain the Seebeck coefficient become poorer which in turn is visible in the linear correlation coefficients.

This is of course also visible if one closely examines the fits of the measurement data. However, due to the large amount of data that is produced during a measurement this is often not practical. Here, the correlation coefficient can be a very useful quantity to be automatically monitored as it can indicate setup problems or material changes, i.e., where a closer examination of the measurement data is appropriate.

Further quantities that can be used to detect measurement errors are the two-point resistances of the different measurement channels. We measure the two-point resistances across the two thermocouple channels and across the circuits used to measure U_{neg} and U_{pos} . The results vs. measurement temperature are shown in Figure 14 for a measurement on a Mg_2Si sample.

For the two thermocouple channels the measured resistance stems basically from the thermocouple wires, which are thin and therefore have a resistance of $\approx 140 \Omega$ at room temperature. Both thermocouples show a similar resistance and increase with increasing temperature as can be expected. The values are not related to the sample properties and should be very similar for every measurement. If the resistance values start to deviate from each other or, more importantly, if the measured resistances deviate from the result of previous runs this could be an indication of thermal aging of the thermocouples. Since temperature measurement as well as Seebeck coefficient calculation rely on an assumed temperature-to-voltage

relation thermal aging of the thermocouples can lead to erroneous results.

The measured two-point resistances across the circuits for U_{pos} and U_{neg} are basically the sum of the sample resistance, the resistance of the thermocouple legs, and the contact resistance between thermocouple and sample. For typical thermoelectric materials the sample resistance is orders of magnitude smaller than the remaining resistance and therefore usually not detectable. The resistance of the thermocouple legs can be estimated from the two-point resistance of the thermocouples and does vary only slowly with temperature. From the measured resistances across the channels for U_{pos} and U_{neg} one can therefore estimate the contact resistance between thermocouples and sample. We often observe some contact resistance at the beginning of the measurement which rapidly decreases with increasing temperature and stays small under subsequent cooling. This indicates that the contact between sample and thermocouple improves due to the heat treatment. If this effect is small, we do not observe any influence on the measured Seebeck coefficient, i.e., the result of the heating and the cooling curve is identical. On the other hand it is clear that a large contact resistance can indicate a contamination of the thermocouple which can lead to errors. We also note that large contact resistances increase the scattering of the raw voltage measurements. A similar analysis has been suggested by Martin who performed an I–V sweep instead of a two-point resistance measurement.¹² This actually might reveal even more information such as, e.g., the ohmic nature of contacts but it also requires further electronic equipment. The procedure suggested here might be an alternative if I–V sweeps are not feasible.

VI. SUMMARY

We have presented details about the data analysis of Seebeck measurements as well as consistency checks and parameters to check and increase the trustworthiness of the obtained results. Using a custom-build system as exemplary setup we have performed a thorough analysis of the data obtained from quasi-stationary measurements. Comparing different equations to calculate the Seebeck coefficient one easily finds that equations based on only one set of voltages/temperatures can easily lead to erroneous results as they are affected by spurious voltages inherent in all measurement systems. If measurements are obtained from a variable temperature gradient, we can experimentally show excellent agreement between three different equations for the Seebeck coefficient. This, however, is only true if the analysis is not based on the internal voltage-to-temperature conversion of the employed digital multimeter. Simultaneous acquisition of the measured temperatures and voltages is another point that is important for accurate non-steady-state Seebeck measurements. If this is not possible, we have shown that temporal data interpolation can also be applied to obtain correct results.

Finally, we discuss several quantities that can be used to evaluate the trustworthiness of the data or indicate experimental deficiencies. These are the linear correlation coefficient of the linear fits used to calculate the Seebeck coefficient, the offset of these fits, the agreement between different equations

to calculate the Seebeck coefficient and the two-point resistances of the different measurement circuits.

Within the last 5 years there have been considerable efforts to increase the quality of thermoelectric measurements in general and in the Seebeck coefficient measurements in particular.^{4,5,18–20} Many problems are hardware related and are addressed in other publications. However, several problems can also be identified and monitored by a thorough data analysis which increases the accuracy and the reliability of the obtained measurement results. This in turn is indispensable for efficient optimization of thermoelectric materials and their application.

ACKNOWLEDGMENTS

G. Karpinski is acknowledged for setting up the measurement routines, C. Stiewe and P. Ziolkowski for fruitful discussions about the paper. Financial support from the BMBF project INTEG (Grant No. 03X3555A) is gratefully acknowledged.

¹G. S. Snyder and E. S. Toberer, *Nature Mater.* **7**, 105 (2008).

²N. S. Hudak and G. G. Amatuucci, *J. Appl. Phys.* **103**, 101301 (2008).

³O. Boffoué, A. Jacquot, A. Dauscher, B. Lenoir, and M. Stölzer, *Rev. Sci. Instrum.* **76**, 053907 (2005).

⁴J. Martin, T. Tritt, and C. Uher, *J. Appl. Phys.* **108**, 121101 (2010).

⁵J. de Boor, C. Stiewe, P. Ziolkowski, T. Dasgupta, G. Karpinski, E. Lenz, F. Edler, and E. Müller, “High-temperature measurement of Seebeck coefficient and electrical conductivity,” *J. Electron. Mater.* (published online).

⁶J. de Boor and V. Schmidt, *Adv. Mater.* **22**, 4303 (2010).

⁷J. de Boor and V. Schmidt, *Appl. Phys. Lett.* **99**, 022102 (2011).

⁸A. T. Burkov, A. Heinrich, P. P. Konstantinov, T. Nakama, and K. Yagasaki, *Meas. Sci. Technol.* **12**, 264 (2001).

⁹C. Byl, D. Bérardan, and N. Dragoe, *Meas. Sci. Technol.* **23**, 035603 (2012).

¹⁰S. Iwanaga, E. S. Toberer, A. LaLonde, and G. J. Snyder, *Rev. Sci. Instrum.* **82**, 063905 (2011).

¹¹P. H. M. Böttger, E. Flage-Larsen, O. B. Karlsen, and T. G. Finstad, *Rev. Sci. Instrum.* **83**, 025101 (2012).

¹²J. Martin, *Rev. Sci. Instrum.* **83**, 065101 (2012).

¹³V. Ponnambalam, S. Lindsey, N. S. Hickman, and T. M. Tritt, *Rev. Sci. Instrum.* **77**, 073904 (2006).

¹⁴Z. Zhou and C. Uher, *Rev. Sci. Instrum.* **76**, 023901 (2005).

¹⁵See http://srdata.nist.gov/its90/main/its90_main_page.html for NIST ITS-90 Thermocouple Database.

¹⁶B. B. Iversen, *J. Mater. Chem.* **20**, 10778 (2010).

¹⁷T. Dasgupta, H. Yin, J. de Boor, C. Stiewe, B. B. Iversen, and E. Müller, “Thermal instability of β -Zn₄Sb₃: Insights from transport and structural measurements,” *J. Electron. Mater.* (published online).

¹⁸N. D. Lowhorn, W. Wong-Ng, Z.-Q. Lu, J. Martin, M. L. Green, J. E. Bonevich, E. L. Thomas, N. R. Dilley, and J. Sharp, *J. Mater. Res.* **26**, 1983 (2011).

¹⁹E. Lenz, S. Haupt, F. Edler, P. Ziolkowski, and H. F. Pernau, *Phys. Status Solidi C* **9**, 2432 (2012).

²⁰H. Wang, W. Porter, H. Böttner, J. Koenig, L. Chen, S. Bai, T. Tritt, A. Mayolet, J. Senawiratne, C. Smith, F. Harris, P. Gilbert, J. Sharp, J. Lo, H. Kleinke, and L. Kiss, *J. Electron. Mater.* **42**, 654 (2013).