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# Measurement of the electrical resistivity and Hall coefficient at high temperatures

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The implementation of the van der Pauw (VDP) technique for combined high temperature measurement of the electrical resistivity and Hall coefficient is described. The VDP method is convenient for use since it accepts sample geometries compatible with other measurements. The technique is simple to use and can be used with samples showing a broad range of shapes and physical properties, from near insulators to metals. Three instruments utilizing the VDP method for measurement of heavily doped semiconductors, such as thermoelectrics, are discussed. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4770124>]

## I. INTRODUCTION

The electrical resistivity and Hall coefficient are important materials properties. They play an important role in any field of research concerned with the electronic transport properties of materials such as semiconductors and metals. From the Hall coefficient, the charge carrier concentration can be directly calculated. By simultaneous measurement of the resistivity, the carrier mobility can also be inferred. The temperature dependence and magnitude of the carrier mobility makes it possible to extract information about the scattering mechanisms.<sup>1</sup> This cannot be done with separated measurements of the resistivity and Hall coefficient.

With the traditional bar shaped samples, six contacts are needed for simultaneous measurement of the resistivity and Hall coefficient. Additionally, all dimensions of the sample and the distance between the contacts for resistance measurement need to be known. With the van der Pauw (VDP) technique, only four contacts are needed and only the sample thickness is necessary to calculate the resistivity.<sup>2</sup> The sample geometry is also suitable for other transport measurements such as flash diffusivity.

Few systems implement the VDP technique for combined high temperature resistivity and Hall coefficient measurements.<sup>3-5</sup> A number of reports exist on systems utilizing other methods and sample geometries for both direct current (dc)<sup>6-8</sup> and alternating current (ac)<sup>9-15</sup> measurements. In this paper, we describe some of the challenges encountered when designing a high temperature resistivity and Hall effect apparatus based on the VDP geometry and outline general solutions that greatly facilitate the use of this method at high temperatures. Specific implementation of these solutions is assessed for three high temperature systems at NASA-JPL,

Caltech, and Aarhus University. All of these systems were designed for thermoelectric research; nevertheless, the general design rules are expected to hold regardless of application.

## II. MEASUREMENT BACKGROUND

Traditional measurements of the electrical resistivity utilize a four-point bar geometry (Figure 1(a)), where an electrical current is applied at or near the ends and the voltage is measured between two points where the current is uniform. Here, the distance between the contacts and cross-sectional area are critical geometric parameters in converting the measured resistance to resistivity. As virtually no current flow through the voltage contacts when such a four-point method is used, there is normally no error due to contact resistance.

### A. Van der Pauw method

Alternatively, van der Pauw showed that the resistivity of an isotropic, homogeneous flat sample could be determined from four probes located arbitrarily around the edge through conformal mapping mathematics.<sup>2,16</sup> Here, the specific probe location is less critical to reliable measurements, but the sample thickness remains important. Instead of measuring the distance between the contacts, the in-plane geometric factor is determined by switching the probes used for current and voltage.

When measuring the resistivity using the van der Pauw approach, current between two adjacent probes on the sample edge induces a voltage between two additional probes on the edge of the sample. This is shown in panel (c), a current is passed from contact  $p$  to  $o$ , while the voltage is measured between contacts  $m$  and  $n$  resulting in a resistance  $R_{po,mn} = V_{mn}/I_{po}$ . Due to symmetry, reversing the polarity of both the voltmeter and current source or interchanging the voltmeter and current source results in the same resistance.

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This resistance is called  $R_A$ . Measuring all four resistances and using the average reduces the effect of imperfect contacts and inhomogeneous samples but is not strictly necessary.<sup>17,18</sup> Likewise, using the contact arrangement in panel (d),  $R_B = R_{no,mp}$  and its three analogs can be measured.  $R_B$  is in general different from  $R_A$ . The two resistances fulfill the VDP relationship,<sup>2</sup>

$$\exp\left(-\frac{\pi d R_A}{\rho}\right) + \exp\left(-\frac{\pi d R_B}{\rho}\right) = 1. \quad (1)$$

Here,  $\rho$  is the sample resistivity and  $d$  its thickness. The VDP relationship cannot be solved analytically for  $\rho$  except for the special case where  $R_A$  and  $R_B$  are identical. Instead, a standard numerical method such as binary search or the Newton-Raphson method is used.

## B. Hall coefficient

In an isotropic material, the Hall coefficient is a measure of the induced voltage orthogonal to both an electric current and magnetic field.<sup>19</sup> The typical four-point bar geometry is shown in Figure 1(b), with the magnetic field normal to the sample surface. Thus, in a traditional bar geometry, five or six leads are required to measure both the resistivity and Hall coefficient. The ratio of the induced transverse voltage to the current can be described as a resistance  $R_{mn,qr} = V_{qr}/I_{mn}$ . The Hall coefficient is generally described as  $R_H = R_{mn,qr}/d/B$  where  $d$  is the sample thickness (in direction of magnetic induction  $B$ ); however, care must be taken to avoid Ohmic voltage signal and the magnetic response may not be linear in  $B$  (both discussed below).

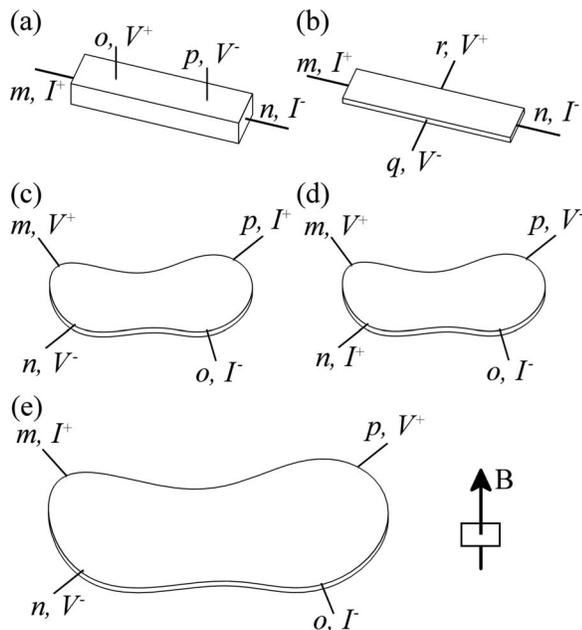


FIG. 1. Common sample geometries. (a) Preferred geometry for four-probe resistivity measurements, (b) common geometry for a Hall effect measurement, resistance measurements, (c) and (d) arbitrarily shaped lamella for VDP measurements showing contact arrangements for two resistance measurements, and (e) contact arrangement for a Hall effect measurement with the VDP method. The arrow in the bottom right corner indicates the positive direction of the magnetic field in panels (b) and (e).

With the van der Pauw geometry, the Hall coefficient can be obtained from the same four contacts used in the resistivity measurement. A current is passed diagonally across the sample, which is in a magnetic field perpendicular to the sample plane. For example,  $R_H = R_{mo,np}/d/B$  (Figure 1(e)) is used for Hall effect measurement. Four identical measurements can be made with the current in both directions along both diagonals. The measurements are repeated for at least two field strengths, such as positive and negative fields to subtract the Ohmic voltage signal.

## III. INSTRUMENT SETUP AND MEASUREMENT PROCEDURES

### A. Instrument geometry

A high temperature van der Pauw system requires a sample stage, heater, magnet, and associated electronics. However, the geometry and high temperature material selection can pose a challenge. This is further exacerbated when the sample must be kept under vacuum or a controlled environment via an enclosure. The following describes general design requirements for each of these components and the specific implementations which have been chosen in the three systems reviewed here.

#### 1. Magnet

The magnet can be either a cryostat magnet or an electromagnet. A cryostat magnet usually has a narrow, cylindrical sample space within the superconducting coil where the magnetic field is directed along this cylindrical axis. This gives very limited space in the sample plane perpendicular to the magnetic field and limits space for contacts, which is unsuitable for large samples. In an electromagnet, there is more space perpendicular to the magnetic field but the pole gap should be small to allow for a high magnetic field, and hence restricts the space perpendicular to the sample plane. The electromagnet has the advantage that the direction of the field is more easily changed and the total accessible volume for the sample holder can be made larger.

The Caltech and JPL magnets are nearly identical electromagnets with different pole caps. The pole caps on the JPL magnet have much space between them (7.5 cm) to accommodate the sample stage, heater, and vacuum enclosure but do not focus the magnetic flux down as much as the Caltech magnet (2.5 cm between pole caps). The larger distance between the pole caps on the JPL magnet decreases the maximum field (approximately 1.0 T for JPL vs 2.0 T for Caltech). The Aarhus setup uses a different electromagnet with a 3.0 cm pole gap. This gives a 1.2 T field when the pole shoes are adjusted to give a homogeneous area (change less than 1.5%) of 3.0 cm in diameter.

#### 2. Controlled atmosphere vessel

In order to prevent sample oxidation and sublimation, a controlled atmosphere vessel is needed. The atmosphere can either be vacuum or an inert cover gas. At high temperatures,

thermally insulating the heater from the walls of the vessel is necessary to maintain the vessel's mechanical strength and stabilize the sample temperature. Choice of atmosphere (vacuum or an inert cover gas) is a critical decision. In a vacuum there is no convection, which facilitates insulating the vessel from the heaters. However, compared to a cover gas, the vacuum can increase evaporation from high vapor pressure samples. To counteract this, a layer of boron nitride spray can be applied after mounting the sample. A final consideration is the gap between the electromagnet pole caps. In both cases, the vessel and associated insulation will significantly decrease the available spaces between the pole caps.

In the systems described here, all three use vacuum atmosphere within the vessel. Radiation shielding is employed to minimize heat flow from the sample to the vessel.

### 3. Heating

There are in general three different strategies to heating the sample and probe: embedded heaters in the sample holder, radiative heating of the holder from inside the vessel, or heating the controlled atmosphere vessel from the outside. Heating from the outside is less efficient, requiring higher heater temperatures and requires more space for insulation. If outside heating is chosen, an inert gas atmosphere allows for better heat transfer to the sample than a vacuum.

When using resistance heaters, the field generated from the current should be reduced around the sample. If heating coils are used, a double helix with antiparallel current can be used to cancel out the generated field. A low current dc source is preferred since this minimizes the magnetic field in the heaters. An ac source will generate oscillating magnetic moments, which can cause vibrations when interacting with the field from the electromagnet. These vibrations can both damage the sample holder and increase the measurement noise due to changing capacitances of the leads and voltages induced by the oscillating magnetic field.

When using embedded heaters, it is particularly important to avoid temperature errors associated with radiative losses from the stage/sample. A thin metal sheet or foil (without electrically contacting the sample or electrical wiring) or equivalent insulation efficiently inhibits radiation from the sample and reduces the heat loss. In Figure 2(a), the heat shield around the stage is represented as a box with one end open. Several layers may be needed to improve the insulation, especially at high temperatures. If the innermost layer is in good thermal contact with the stage, the shielding will be close to the stage temperature and further stabilize the sample temperature.

The wider pole gap of the NASA-JPL system permits radiative heaters to surround the sample and a maximum temperature of 1000 °C. The heaters are simple resistive heaters. In contrast, the Caltech and Aarhus systems use heaters directly embedded into the sample stage. The Aarhus design uses a heater wire embedded into a ceramic binder within the stage while the Caltech heater is the size of a commercial cartridge heater and replaceable. Both systems exhibit a maximum temperature of 600 °C; this value is expected to increase with improved radiation shielding.

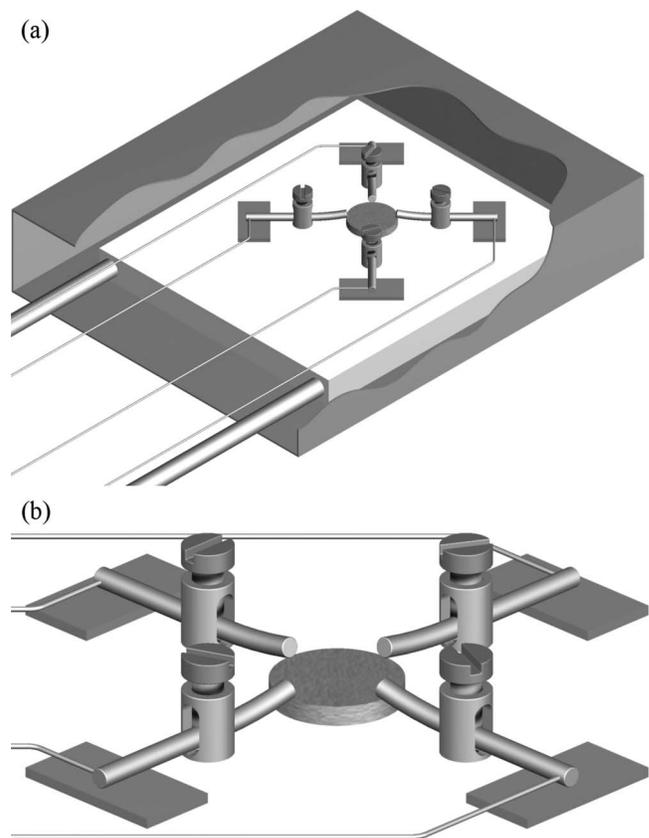


FIG. 2. Illustration of the sample holder. (a) The sample is mounted on a heated plate inside a heat shield. Two rods can be used to fix the sample holder between the poles of the electromagnet (not shown). (b) Zoom on the post-and-screw design. When the metal rods are pressed against the sample they bend elastically. This ensures good electrical contact during thermal expansion. The other end of the rods are either pressed against metal pads or connected directly to wires, in which case the pads are unnecessary. Both methods are shown for comparison.

### 4. Thermocouples

Thermocouples are critical for both controlling the heater response and for accurately measuring the sample temperature while data are being collected. Thermocouples (not shown) can be embedded in the sample holder below the sample. The thermocouple wires cannot be in direct contact with the sample since this interferes with the measurements.

In the Caltech and Aarhus systems, both the thermocouple and heaters are embedded in the stage. As the stage is a good thermal conductor, the heater PID control is quite good for these systems. The NASA-JPL system uses a thermocouple next to the sample that is attached to the stage. Thus, the thermocouple is radiatively coupled with the heaters, much like the sample.

### 5. Sample holder

The sample holder can be made from any electrically insulating material that can sustain the desired maximum temperature. It should also have sufficiently high thermal conductivity to reduce temperature gradients across the sample holder. Possible materials are ceramics such as boron nitride, alumina, and silicon carbide. Boron nitride is easily machin-

able and has a high thermal conductivity but a low mechanical strength. Alumina and silicon carbide are hard to machine but can be purchased as cements, which can be cast to the desired shape. Figure 2(a) shows the principal components of a sample holder with embedded heaters for use in an electromagnet. The same general design can be used with radiated heaters in which case the heat shield is replaced by the heaters. The sample holder is rigidly mounted to fix the sample holder between the poles of the electromagnet.

Different approaches to the sample holder have been chosen. At Caltech, boron nitride is used for its machinability although it is expensive and the low mechanical strength has led to it requiring replacement after about 1000 uses. Holes bored into the boron nitride are used to contain custom cartridge heaters. The sample holder is rigidly attached by means of two rods. In Aarhus, the sample holder is cast from silicon carbide cement. Since silicon carbide cement is inexpensive, the heating coils are cast directly into the sample holder. This gives good heat transfer and eases temperature control but they cannot be changed if they break. To prolong the lifetime, thicker heating wire and higher currents are used to keep the wire temperature low. The wires are spatially separated from the sample to minimize the magnetic field and the coils are kept parallel to the sample plane. At JPL, refractory metal bolts are used to hold thick alumina plates together. The initial fabrication is not trivial, as the alumina requires a multitude of holes, but the stage is quite robust.

The stage can be designed to hold a sample on each side. In practice, the temperature control is typically the source of increased measurement time and a dual sample stage can double system throughput. If designed well, this will only increase the probe thickness slightly. The two sample design is best implemented in systems where the time required for a single measurement is low to keep the number of measurements high. Such a dual-stage has been implemented at NASA-JPL.

## 6. Electrical contacts to sample

The connections to the sample are made with four pressure contacts<sup>19</sup> as seen in Figure 2(b). Screws and posts are used to press metal rods against the top edge of the sample making electrical contact and keeping the sample in place. This geometry allows for many sample sizes to be used, from a few millimeters in diameter to almost the diameter of the post arrangement as well as from thin films to  $\sim 3$  mm in thickness. This eliminates the need for contact glue or paste, thus decreasing the contact area. Contact glues and pastes can additionally react with or diffuse into the sample at high temperatures, leading to offset voltages and bad measurements. The post and screw design is additionally attractive, as it does not significantly increase stage thickness.

Errors arise in the measurements if the contacts have large areas or are far from the periphery.<sup>20</sup> The use of cylindrical metal wires at an angle to the sample plane can help to form point contacts just on the sample edge. Here, the top surface of the sample is higher than the contact pads surrounding the sample. The sample height can be adjusted with alumina plates to ensure the wires have the right angle. Alternatively,

line contacts can be used on the side of the sample.<sup>3</sup> Such contacts will limit the flexibility when placing the contacts and gives higher restrictions on the sample geometry.

In the Hall effect measurement, when the contacts are not placed exactly opposite of each other with respect to the current direction, the sample resistance will contribute to the measured voltage. While in principle this effect is subtracted it should be avoided as much as possible to reduce the measurement uncertainty and noise. Errors also arise if the distance between two contacts becomes comparable to the sample thickness. For square and rectangular samples, the contacts should be made to the corners rather than the sides.<sup>21</sup> The measurement error is expected to be proportional to sample thickness over diameter.

The correct choice of material for the metal contacts is crucial for obtaining high accuracy measurements.<sup>19</sup> The metal should be inert, maintain good mechanical and electrical properties in the used temperature range, and have a low Seebeck coefficient (low thermopower). Typically used metals such as silver and copper, and even nickel and platinum, can give reactions with many materials. Additionally, nickel is ferromagnetic and not preferred for Hall effect measurements. Instead metals with high melting points that are inert to most materials should be used. Some possible choices are niobium, molybdenum, tantalum, and tungsten. For the contacts to remain good during thermal expansion, the metal rods should be flexible and act as springs. This means that they cannot be too thin or thick, and should keep their mechanical strength and elasticity in the used temperature range. When the screws are tightened the rods should bend before the sample breaks.

If the pressure screws and posts are made from the same material, they will fuse during high temperature operation. Possible materials are inert and non-magnetic metals including stainless steel and the above mentioned elements, among others. Since screws of stainless steel are cheap and easy to replace another material can be chosen for the posts.

We have found 1.0–1.5 mm molybdenum or tungsten wire have good electrical and mechanical properties and works well for thermoelectric measurements. It is strong and flexible and maintains its strength to very high temperatures, allowing for thin rods to be used. This minimizes the contact area.

The usual procedures for electrical wiring, insulation, and shielding should be used to reduce noise and stray voltages to acceptable levels.

## B. Measurement strategy

For accurate measurement of the resistivity and Hall coefficient, a number of measurement offsets need to be removed. In the resistivity measurement, these include zero point offsets in the voltage versus current curve due to thermal voltages from the sample, measurement leads, and electronics. In a Hall coefficient measurement, offsets resulting from the sample resistance additionally arise when the contacts are not perfectly aligned.

When using dc measurements, the offset from thermal voltages can be removed by measuring the offset voltage before and after the resistance measurement, with the current turned off. By measuring it twice and using the average off-

set, linear changes in the voltage offset are taken into account. The average offset voltage is subtracted from the voltage measurement before calculating the resistance.

If the current source has the ability to reverse the direction of the current, the delta method can be used instead. Here, the current is turned on in the positive direction, switched to negative and then back to positive. In each step, the current and voltage are measured as  $V_1^+$  and  $I_1^+$  for positive current,  $V^-$  and  $I^-$  for negative current, and finally  $V_2^+$  and  $I_2^+$  for positive current. The resistance is then calculated as  $R = (V_1^+ + V_2^+ - 2V^-)/(I_1^+ + I_2^+ - 2I^-)$ . This both removes the offset voltage and combines one resistance measurement with its equivalent with reversed polarity of the current source and voltmeter. It is important to note that the circuit has to be the same for the measurements with positive and negative current for the offset voltage to be constant. Hence, the current should be reversed in the current source and not by switching a matrix card or other instruments between the current source and sample. Thermal offsets are removed automatically when using ac measurements, provided an appropriate frequency is chosen.

If  $R_H$  changes linearly with  $B$ , the resistive offset in the Hall effect measurement can be removed by measuring the Hall voltage for several magnetic field strengths and subtracting the offset at  $B = 0$ . This increases the measurement time significantly, and often it is more convenient and sufficiently accurate to use only two field strengths. Reversing the field direction is preferred over turning the field on and off since it doubles the measured Hall resistance and removes magnetoresistance effects (voltages proportional to even powers of  $B$ ) but still appropriate when the Hall effect is nonlinear (Hall voltages proportional to odd powers of  $B$ ). Using thinner samples results in higher effective resistances which improves resolution, especially for low-mobility samples. Both the relative effect of noise proportional to the current and current independent thermal noise are lowered, resulting in a larger signal-to-noise ratio.

To reduce the measurement uncertainty, the contacts should be Ohmic and there should be no Schottky barrier. This is generally the case for high charge carrier concentrations as in heavily doped semiconductors and metals, especially at room temperature and above. For very low carrier concentration, the contacts may not be Ohmic, and measuring the I-V curve is necessary.

### C. Other considerations

When making temperature varying measurements the temperature can either be continually ramped or increased in steps. Although increasing the temperature in steps makes the measurements more accurate, it also increases the measurement time considerably. If the temperature is ramped continually, the rate should be adjusted so the temperature does not change enough during measurements to substantially change the sample resistivity.

The measured resistivity is not affected much if the temperature changes slightly during the measurement; however, fine features in the resistivity versus temperature curve might be lost. If the contacts are slightly misaligned, the resistive

offset in the Hall measurement will be very large and the Hall resistance can reduce to only a few percent of the measured value. If the temperature changes considerably between measuring with positive and negative fields, the resistance of the sample also changes and the resistive offset may not be subtracted off correctly.

Both ac and dc measurements can be used with the method described here. Alternating current measurements are often considered to give more precise measurements but are also harder to implement as shielding and capacitance considerations are different. An ac magnetic field with an ac test current through the sample<sup>13-15</sup> can also be used for measurement of the Hall effect.

## IV. MEASUREMENT EXAMPLE

Figure 3 shows a two-point (current and voltage across the same two contacts) I-V curve for a material with a charge carrier concentration of  $2.8 \times 10^{-18} \text{ cm}^{-3}$ . The current range typically used is covered, 0-500 mA. The voltage is measured across a contact-sample-contact double junction and is hence antisymmetric when reversing the current direction. Therefore, only positive currents are shown. No Schottky anomaly is visible. The sample is a  $\text{Mg}_2\text{Si}$  intrinsic semiconductor and a slight decrease in resistance ( $\sim 5\%$  corresponding to  $\sim 2 \text{ K}$  temperature increase) can be ascribed to Joule heating at high currents (more than 1 W of Joule heating at the maximum current). Because this is a two-point measurement the resistance is a sum of the resistances of the leads, contacts, and the sample.

An example of a high temperature measurement is shown in Figure 4. A PbS sample was heated to  $\sim 600 \text{ }^\circ\text{C}$  and cooled to room temperature at a rate of 100 K/hr while continually measuring the resistivity and Hall coefficient. The measurement was performed on both the Caltech (squares) and Aarhus (line) setups. The measurements agree quite well at room temperature. The slight disagreement in resistivity and Hall carrier concentration is most likely due to errors in the temperature measurement. The hysteresis in the Hall carrier

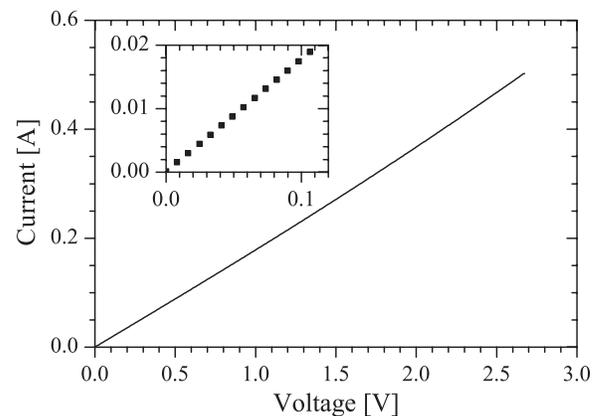


FIG. 3. I-V curve for metal contacts showing no Schottky anomaly. The current range, 0–500 mA, covers the currents typically used. The inset shows a zoom on the low current data to emphasize the absence of a Schottky anomaly. The sample used is n-type intrinsic  $\text{Mg}_2\text{Si}$  with  $n \sim 2.8 \times 10^{-18} \text{ cm}^{-3}$ . Molybdenum has been chosen for the contacts.

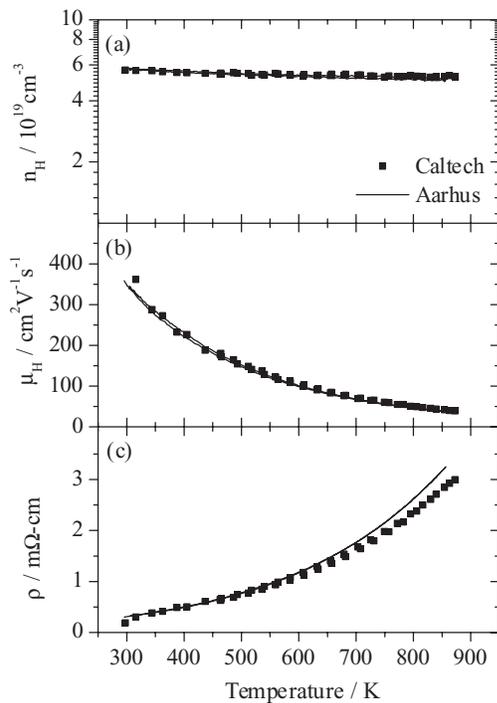


FIG. 4. Example of a measurement of (a) Hall carrier concentration, (b) Hall mobility and (c) electrical resistivity. The data were measured during heating and cooling to 600 °C on both the Caltech (squares) and Aarhus (line) setups. The sample is doped PbS.

concentration, most visible in the Aarhus data, is due to the sample resistivity changing during the measurement, as discussed above. The single parabolic band model is quite accurate for PbS and hence the change in Hall carrier concentration with temperature is small. With the method described herein the uncertainty in the resistivity and Hall coefficient is believed to be less than 5% for uniform samples. However, in the Hall effect measurement the noise can often exceed this, especially for low mobility or low carrier concentration samples. Additionally, bad alignment of the sample contacts or high heating rates may give systematic deviations in excess of this, as discussed in detail above. The error in the temperature measurements depends on the exact thermocouple placement, thermal resistance between sample and thermocouple and heat loss from the sample. In the apparatus described here, the error in temperature measurements is believed to be less than 15 °C, including the thermocouple precision.

## V. DISCUSSION

### A. Measurement approach

#### 1. Bar method

The most frequently used sample geometry for both resistivity and Hall effect measurements is the bar shape (Figs. 1(a) and 1(b)). For the measured resistivity to be accurate, the contacts  $o$  and  $p$  should be sufficiently far from contacts  $m$  and  $n$  to ensure parallel current paths. A primary source of uncertainty in these measurements is the ability to measure the geometric factors, namely, the distance  $l$  between contacts  $o$  and  $p$  as well as the cross-sectional area  $A$  of the

bar. Often the contacts are attached with an electrical conducting adhesive, paste or solder, thus increasing the contact areas and making measurement of the distance between the contacts,  $l$ , ambiguous, leading to a primary source of inaccuracy. Additional contacts are needed for simultaneous resistivity and Hall measurements where large contacts  $r$ ,  $q$ , may alter the current path for resistance measurements.

### 2. VDP method

In the VDP technique, explicit knowledge of the current paths is not needed, allowing for the resistivity and Hall coefficient to be measured on the same sample using the same contacts. The sample must be isotropic within the plane and of uniform thickness, may not contain any holes, and the contact areas have to be small compared to the surface area and ideally should be along the entire thickness at the edge. Like the traditional geometry, the sample is assumed to be homogeneous and without cracks. The sample can be polished to an even thickness, which can be measured sufficiently accurately not to lower the accuracy of the method significantly.

Like the traditional method, finite size of the contacts in the VDP leads to sources of error in the measurement. For a circular disc of diameter  $D$ , the error from a line contact extending a distance  $l$  along the sample periphery, away from the periphery, or a point contact placed away from the periphery, scales as  $\Delta\rho/\rho \propto l^2/D^2$  and  $\Delta R_H/R_H \propto l/D$ . If  $l/D \ll 1$ , the errors are to a first approximation additive<sup>16</sup> and the error from a contact of finite area scales according to the same relationships. Tests have shown that the sample thickness should not exceed half the diameter for the technique to remain accurate.<sup>17</sup>

### 3. Hall effect

Inspired by the free electron model, the Hall carrier concentration can be defined from the Hall coefficient as  $n_H = -1/eR_H$  for electrons or  $p_H = 1/eR_H$  for holes where  $e$  is the electron charge. For materials with more complex band structures,  $n_H$  simply becomes a measure of the Hall coefficient in units related to carrier concentration that can be negative or positive. Together with the resistivity, the Hall mobility can also be defined as  $\mu_H = 1/n_H e \rho$  or  $\mu_H = 1/p_H e \rho$  for electrons and holes, respectively. For complicated systems, we define  $\mu_H = 1/n_H e \rho = R_H/\rho$  as simply a measure of the Hall effect in units of mobility that would be negative for electrons and positive for holes. For materials where a simple single band model does not apply, the results should be used with care since they can be quite far from the real charge carrier concentrations and mobilities. This is frequently apparent when more than one carrier type is present. In this case, the Hall voltages of the two species partially cancel leading to low values of  $R_H$  and  $\mu_H$  or high  $n_H$  where the magnitude and sign of the values depend in a complicated way on the transport parameters of the individual species.<sup>19</sup>

### B. Application in thermoelectrics

In thermoelectrics, the electronic properties strongly affect the material performance. The efficiency of a

thermoelectric material is to first order proportional to the thermoelectric figure of merit given by  $zT = S^2T/\kappa\rho$ , where  $S$  is the Seebeck coefficient,  $\kappa$  is the thermal conductivity,  $\rho$  is the electrical resistivity, and  $T$  is the temperature. The Seebeck coefficient, electrical resistivity, and the electronic contribution to the thermal conductivity depend on the charge carrier concentration.<sup>22</sup> Hence, the charge carrier concentration, being calculated from the Hall coefficient, is also important for full characterization of the material. Additionally, charge carrier scattering impacts both the electronic mobility (and thus resistivity) and the Seebeck coefficient. The temperature dependence of the mobility is one way to identify the dominant charge carrier scattering mechanism.

Within thermoelectrics, one of the experimental challenges is to accurately measure properties contributing to the figure of merit at high temperatures. Measuring individual properties on different samples can reduce the accuracy due to variations between the samples. Cutting a single sample between individual measurements can give the same problem due to sample inhomogeneities. The development of techniques utilizing the same sample geometry can hence increase the accuracy of the figure of merit substantially.

Thermoelectric materials are often prepared as pressed pellets or as ingots made by the Bridgman-Stockbarger or Czochralski techniques. Polycrystalline pressed pellets of cubic materials are usually isotropic.<sup>23</sup> Polycrystalline pressed pellets of weakly anisotropic materials are often isotropic within experimental uncertainty.<sup>24</sup> Strongly anisotropic crystalline materials such as  $\text{Bi}_2\text{Te}_3$  can be expected to be isotropic within the plane perpendicular to the pressing direction but can have very different transport properties along the pressing direction.<sup>25</sup> The properties of melt-grown ingots may have properties that change along the length of the ingot, and each slice may make a different study.

In all these cases, these circular disks are frequently used directly for measuring the thermal diffusivity in the laser flash technique<sup>26</sup> and can also be used for measuring the Seebeck coefficient<sup>27,28</sup> along the same direction (parallel to the pressing direction). The same sample geometry can be used for measuring the resistivity and Hall coefficient in the VDP method but the measurements are performed in the plane of the disk. Hence, a complete characterization of a material can be obtained from the same sample without shaping it between individual measurements, provided the properties are isotropic.

These benefits reveal why the three thermoelectric research groups discussed herein have adopted the VDP method for high temperature measurements.

## VI. SUMMARY

We have discussed general design guidelines for successfully implementing the VDP geometry in combined measurements of the resistivity and Hall coefficient at high temperature. Three instruments that were specifically designed for

thermoelectric measurements are discussed in detail. The approach is convenient for measurements on thermoelectrics due to the compatibility of the sample geometry with other measurements. Several overarching design principles and guidelines discussed herein are also equally applicable to traditional bar measurements at high temperature.

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