Apparatus for the high temperature measurement of the Seebeck coefficient in thermoelectric materials

Joshua Martin^{a)}

Material Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA

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The Seebeck coefficient is a physical parameter routinely measured to identify the potential thermoelectric performance of a material. However, researchers employ a variety of techniques, conditions, and probe arrangements to measure the Seebeck coefficient, resulting in conflicting materials data. To compare and evaluate these methodologies, and to identify optimal Seebeck coefficient measurement protocols, we have developed an improved experimental apparatus to measure the Seebeck coefficient under multiple conditions and probe arrangements (300 K–1200 K). This paper will describe in detail the apparatus design and instrumentation, including a discussion of its capabilities and accuracy as measured through representative diagnostics. In addition, this paper will emphasize the techniques required to effectively manage uncertainty in high temperature Seebeck coefficient measurements. [http://dx.doi.org/10.1063/1.4723872]

I. INTRODUCTION

The Seebeck effect is a thermoelectric (TE) phenomenon that enables the conversion of an applied thermal gradient into an electric potential. This effect can be quantified through a constant of proportionality termed the Seebeck coefficient, $S_{ab} = \Delta V_{ab} / \Delta T$, under the assumptions in the differential technique,¹ where ΔV_{ab} is the electric potential between two different materials a and b, and $\Delta T = T_2 - T_1$ is the applied temperature difference.¹⁻⁷ According to this definition, the measured Seebeck coefficient Sab requires the correction Sab $= S_b - S_a$, where S_b is the contribution of the second conductor, to obtain S_a, the Seebeck coefficient of the sample (hereafter referred to as S). In n-type (p-type) semiconductors, the electric potential establishes in the opposite direction (same direction) of the thermal gradient resulting in a negative (positive) Seebeck coefficient. This convention ensures agreement between the Seebeck coefficient and the sign of the carriers. However, measurements of n (carrier concentration) and R_H (Hall coefficient) are often required to fully evaluate the electronic structure,^{8,9} as the Seebeck coefficient is not explicitly indicative of the majority carrier.

Materials that exhibit large absolute Seebeck coefficients (S $\approx 100 \ \mu$ V/K–200 μ V/K at their target operation temperature), in addition to other optimal physical properties, are considered candidates for use in thermoelectric applications.^{3–7} These applications include automotive engine waste heat recovery, power generation, spot cooling, and solid-state refrigeration. The dimensionless figure of merit, ZT = S² σ T/ κ , defines the effectiveness of a TE material, where σ is the electrical conductivity. To absolute temperature, and κ the total thermal conductivity. However, optimizing these interdependent physical parameters to achieve commercially practical efficiencies is challenging, requiring a tailored combination of properties not readily available in nature.

The continued development of higher efficiency TE materials requires thorough characterization of the electrical and thermal transport properties. Due to its intrinsic sensitivity to the electronic structure, the Seebeck coefficient is one physical parameter that is routinely measured to identify a material's potential thermoelectric performance. However, researchers employ a variety of techniques, conditions, and probe arrangements to measure the Seebeck coefficient,^{1,10–14} resulting in conflicting materials data and further complicating the confirmation of reported higher efficiency thermoelectric materials. In an effort to compare and evaluate these methodologies, and to identify optimal Seebeck coefficient measurement protocols, we have developed an improved experimental apparatus¹⁵ to measure the Seebeck coefficient under multiple conditions and probe arrangements, and the electrical resistivity at high temperature (300 K-1200 K). Electrical resistivity measurements will be presented separately in a forthcoming publication. This paper will include a general overview of thermoelectric metrology, the apparatus design and instrumentation, and a discussion of its capabilities and representative diagnostics. We will further emphasize the techniques required to effectively manage uncertainty in high temperature Seebeck coefficient measurements.

II. SEEBECK COEFFICIENT METROLOGY

Measurement of the relative Seebeck coefficient, especially at high temperature, requires a minimum of three voltage measurements: one for the thermoelectric voltage ΔV and one each for the hot and cold thermocouple voltage for T_2 and T_1 , respectively, that determine the temperature difference ΔT . Acquisition protocols for these parameters must adhere to the following criteria, defined previously¹ as 1. the measurement of the voltage and temperature at the same locations and at the same time; 2. probe interfaces with the sample that are Ohmic and isothermal; and 3. the acquisition of small voltages with minimal extraneous contributions. Under these

^{a)}E-mail: joshua.martin@nist.gov. Fax: 301-975-5334.

conditions, the electric potential emergent under an applied thermal gradient is given by¹

$$\begin{split} V_{ab}(\mathrm{T}_{1},\mathrm{T}_{2}) &= \int_{\mathrm{T}_{1}}^{\mathrm{T}_{2}}\mathrm{S}_{ab}(\mathrm{T})\mathrm{d}\mathrm{T} \\ &= \int_{\mathrm{T}_{1}}^{\mathrm{T}_{2}}\mathrm{[S}_{b}(\mathrm{T}) - \mathrm{S}_{a}(\mathrm{T})]\mathrm{d}\mathrm{T}, \end{split} \tag{1}$$

where $S_a(T)$ is the absolute Seebeck coefficient of the sample being measured and $S_b(T)$ is the known Seebeck coefficient of the reference wires. It is assumed that materials a and b are chemically and physically homogeneous and isotropic, such that V_{ab} is explicitly a function of (T_1,T_2) and is independent of the temperature distribution between the interfaces.¹⁶

Historically, there exist two primary probe arrangements. In the axial-flow arrangement (2-probe), the temperature difference and the electric potential are measured on the probes which are in direct contact with the ends of the specimen (Figure 4). This is the arrangement preferred by Goldsmid and Tritt¹² for improved thermal and electrical contact. However, many Seebeck coefficient apparatus also concurrently measure resistivity, requiring additional voltage contacts away from the ends of the sample. In the potentiometric arrangement (or 4-probe), the temperature difference and the voltage difference are measured at two points on the sample (or inserted within the sample) equidistant from the hot and cold sinks and on the axis parallel to the thermal gradient. To maintain accuracy, the diameter of each temperature/voltage probe must be much smaller than the effective distance between them.

There is little comparative evidence to substantiate which arrangement provides the most accurate determination of temperature and voltage difference at the same points. We have therefore developed an apparatus capable of *in situ* comparison. An apparatus developed by Bowers¹⁷ in 1959 averaged the results obtained by both of these arrangements. The Seebeck coefficients were consistent within 10% up to 800 °C. However, there was no estimation made of the overall measurement uncertainty, so this result may be regarded as pre-liminary. Wood¹⁸ also compared the results of thermocouples pressed on the ends of a sample with those obtained by inserting them in holes drilled in the sample. For the temperature and the material evaluated, the results were consistent within the measurement uncertainty.

III. INSTRUMENTATION

Figure 1(a) is a photograph of the instrumentation cabinet for the apparatus. Bosch extruded aluminum framing provides the support infrastructure. This houses the furnace and control instrumentation, the vacuum system, the probe vacuum chamber, the probe assembly, the voltage measurement/temperature measurement instrumentation, the computer interface instrumentation, and the 24 V electrical subsystem. The primary components are described below.

The local thermal environment is modulated through a 7.2 kW ULVAC RHL-P65C tube furnace, consisting of a concentric series of 6 infrared (IR) emitting tungsten elements,



FIG. 1. (a) Photograph of the instrumentation cabinet for the high temperature thermoelectric apparatus. (b) Photograph of the sample probe. (c) Photograph of an individual probe arm without the heater coil detailing the machining of the tungsten component. (d) Four-probe thermocouple spring mounts.

each mounted at the focal point of a parabolic gold reflector. This geometry provides axial and radial thermal profiles that are temporally and spatially consistent. The temperature is tuned via a Eurotherm 7100A power controller and a Eurotherm 3508 temperature controller. Since the emitted IR frequencies are dependent on the voltage supplied, the power controller is placed between a 144 V output centertap transformer and the IR furnace, and is further equipped with an auxiliary power supply that is in phase with the transformer input voltage. Infrared elements typically operate under phase angle firing modes which can result in the generation of significant radio frequency interference with the voltage measurement instrument. Therefore, the selected power controller operates under advanced single cycle firing. In this mode, the power is only active between multiples of zero-voltage crossings that track the input line frequency, effectively eliminating radio frequency noise. The furnace temperature is monitored through a custom spark welded 0.125 mm Pt-Pt + 13% Rh bare wire thermocouple mounted in an extruded alumina twin bore tube and wrapped in a molybdenum radiation shield. Once the setpoint has stabilized, the thermal oscillations as observed from the furnace thermocouple are below 50 mK throughout the stated temperature range.

The furnace encloses a 100 mm diameter (DIA) single ended quartz tube that mates to the vacuum chamber through a series of water cooled O-ring connecting flanges. The sample probe is centered within this quartz tube and supported through an opening in the vacuum chamber. To maintain an inert and contaminant free environment, the sample chamber is typically evacuated below 10^{-2} Pa (10^{-4} Torr) using a magnetic bearing Pfeiffer TMH 071P turbomolecular drag pump, roughed in line by an oil-free Pfeiffer MVP 015 diaphragm pump. In addition, the sample chamber can be backfilled with a variety of inert gases including helium. The vacuum



FIG. 2. Schematic diagram of the sample probe and probe assembly mechanism.

system is controlled through a series of timing relays to prevent turbo pump exposure to a high foreline pressure. The vacuum chamber houses the isothermal terminal block, the probe support, and assembly mechanisms, and serves to connect the measurement instrumentation with the sample probe.

The sample probe (Figures 1(b) and 1(c)) is uniquely machined with relief features to accommodate multiple sample configurations, including parallelepiped (2 mm–18 mm height) and disk geometries (6.35 mm radius), both in transverse and longitudinal orientation. In addition, the probe design enables measurement of the Seebeck coefficient in both 2- and 4-probe arrangements (Figure 2). This allows for routine comparison of both arrangements and expands the practical range of sample size and geometry. For the 2-probe arrangement, thermocouples are spark welded to the upper and lower electrodes; 4-probe measurements are accomplished by means of two small diameter thermocouples pressed onto the sample between the top and bottom probes used in the 2probe arrangement. The upper and lower probes are inverse configurations.

Selection criteria for probe materials are discussed in Ref. 1. Tungsten was selected for the electrode probe material due to its low electrical resistivity (52.8 nOhm \cdot m), high thermal conductivity (174 $W \cdot m^{-1} \cdot K^{-1}$), and desirable physical properties (molybdenum is an excellent alternative). Each tungsten electrode (19.05 mm DIA) features a corresponding alignment relief notch to enable straightforward sample mounting (centered for a 2.5 mm \times 2.5 mm cross section area sample and perpendicular to the 4-probe thermocouples) and to maintain a consistent furnace immersion depth for the 4probe thermocouples that press onto the sample (Figure 1(c)). In this way, any chemical inhomogeneity signature that develops in the thermocouples as a function of thermal profiles will remain consistent between measurements. Electrical connections between the electrodes and the Keithley 2400 bipolar current source (for resistivity measurements) are formed by soldering copper wires to nickel electroplated tungsten wires using bismuth indium solder, and then by spark welding the bare tungsten wires to the tungsten electrodes using a nickel jumper (the jumper is mediatory: the weld is essentially tungsten to nickel to tungsten). Since tungsten wires form microcracks when cut, they were instead sectioned using a narrow grinding wheel. A coil was formed in the end of the tungsten wire prior to welding to the electrode for strain relief and to ease assembly. Since the coil is located inside the aluminum nitride (AIN) mounting cylinder (discussed below), it is compressed onto the tungsten electrode, serving to maintain electrical contact in the unlikely event the tungsten-nickeltungsten weld ever fails.

Each tungsten electrode is precisely fitted within electrically insulating support mounts (Figures 1(b) and 1(c)). These are fabricated from advanced AIN ceramic cylinders (25.4 mm DIA \times 28.58 mm tall) and bonded to the tungsten using AlN-based adhesive (Aremco 865C). Aluminium nitride has a high thermal conductivity $\approx 180 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ with an average thermal expansion coefficient identical to tungsten. Controlled thermal gradients for Seebeck coefficient measurements are formed by passing current through either of two heater coils, each bonded to the upper and lower aluminum nitride probe mounts using a thin layer of aluminum nitride adhesive. These coils are comprised of custom bifilar wound (non-inductive) tungsten-rhenium alloy wires electrophoretically coated with alumina for electrical isolation. Bipolar heating allows for zero-gradient resistivity measurements as well as toggled Seebeck coefficient measurements to conduct thermal offset checks. Current is sourced to each heater coil using a NI PXI-4110 triple output precision direct current power supply (current sensitivity 0.4 μ A), mounted in a NI PXI-1033 chassis. Electrical connections between the coils and the current source are formed in a manner similar to that of the tungsten electrodes.

The AlN support mounts are supported and connected to a probe assembly mechanism in the vacuum chamber through 11.43 mm DIA, 305 mm long extruded SIALON rods (a silicon nitride/aluminum oxide composite). This material has a low thermal expansion coefficient and high flexural strength. The AlN support mounts feature a notch to relieve any expansion strain or stress. The SIALON rods are hollow to accommodate passage of the thermocouple and heater wires between the probes and the vacuum chamber.

The probe assembly features simultaneous multi-axis movement for adjustment to the upper and lower probe distance (for variation in sample height), and for movement of the 4-probe thermocouples to and from the sample (Figure 2). A magnetic spring-balanced, linear bearing assembly performs automatic adjustment of the 4-probe thermocouples' vertical spacing in a continuum, optimally selected for various sample heights. The ratio of the probe spacing to sample height is also adjustable. Vertical movement of both the upper and lower probes and the 4-probe thermocouples is accomplished using a Velmex UniSlide twin lead screw slider for dual opposing motion connected with a bellows coupling to a rotary vacuum feedthrough (Thermionics, Inc.). The upper and lower SIALON tubes are mounted to either of the two coaxial dovetail slider mounts. A NEMA 23, 1.8° bipolar step motor with a resolution up to 1/256 step is used to adjust the twin slider positions, where the pressing force is modulated by adjusting the motor current and velocity (along the torque curve). The 4-probe thermocouple alumina tubes are mounted external to the furnace using independent sliders fitted with compression springs (k = 1.91) to maintain the pressure of the thermocouple interface (Figure 1(d)). These sliders are mated through a series of vacuum compatible linear bearings to a rotary-to-linear vacuum feedthrough, also fitted with a bipolar step motor for horizontal positioning.

IV. TEMPERATURE MEASUREMENT

Bentley¹⁹ provides a thorough discussion of thermocouple theory, error reduction, and methods to estimate the total uncertainty. Temperature measurement for each of the 2and 4-probe location pairs is accomplished using 0.125 mm Pt-Pt + 13% Rh thermocouples (Omega Engineering), with the entire length embedded in a twin bore alumina sheathing to avoid strain and contamination. This wire diameter minimizes heat sinking without significantly increasing contamination susceptibility or drift. Although R-type thermocouples in the stated temperature range are more oxidation resistant, have higher operating points, and are generally more reproducible than base-metal thermocouples, real thermocouples are not chemically or physically homogenous. Physical inhomogeneity includes variation in crystallite size and macroscopic strains from cold-working. This can contribute an error of 0.2 K + 0.1% of T.¹⁹ Since the voltage of noble metal thermocouples has been shown to depend on the thermal history, the thermocouples were cleaned with ethanol prior to assembly, then annealed in air at 1100 °C in a tube furnace and cooled over 2 h to 300 °C (Refs. 19 and 20) to ensure calibration. A thermocouple that is not in calibration can contribute an error of 0.3 K.¹⁹ The thermocouple tips are shielded from thermal radiation using two polished molybdenum radiation shields. One shield rests between the lower and upper probe to trace the temperature along the sample, while the second shield encloses the entire probe along the axis of the furnace.

In this embodiment, measurement of the Seebeck coefficient is explicitly relative (Eq. (1)). The measured value is proportional to the difference between the Seebeck coefficient for the material of interest and that for the reference wires. Therefore, the Seebeck coefficient of the reference material must be determined in a separate experiment throughout the temperature range of interest. The Seebeck coefficient has been calculated for a variety of pure materials by measuring the Thomson heat $\mu_{\rm T}$ (or Thompson coefficient) directly and using the relation

$$S(T) \int_0^T \frac{\mu_T}{T} dT,$$
 (2)

where T is the temperature. This technique established the absolute scales of thermoelectricity for common reference materials in TE measurements. The most accurate reference data have been obtained by Roberts for Pt between 273 K and 1600 K.²¹ Burkov²² provides an empirical interpolation function for the Seebeck coefficient of Pt between 70 K and 1500 K and estimates the uncertainty for this absolute thermoelectric scale as $\pm 0.1 \ \mu$ V/K at temperatures between 70 K and 900 K, increasing to $\pm 0.5 \ \mu$ V/K at 1500 K.

Thermocouples provide a relative measurement of temperature that requires accurate knowledge of a reference temperature. Inaccurate measurement of this reference temperature therefore increases the uncertainty in the measurement of a thermocouple temperature by ≈ 0.05 K.¹⁹ The terminal block functions as the interface for each thermocouple lead wire to the voltage measurement device. The temperature of the interface between these thermocouple wires and the voltmeter is the reference temperature. Commercial terminal blocks are generally constructed from low thermal conductivity materials and do not ensure the uniform distribution of temperature between multiple terminals and the reference temperature measurement position. In addition, thermocouple extension wire and reference junction compensating circuits should be avoided where high accuracy is desired. Extension wires can contribute an error up to 0.4 K + 0.03% of T for noble metal thermocouples.¹⁹

To achieve uniform temperature distribution between all terminals with respect to this single reference temperature, a custom isothermal terminal block was constructed (Figure 3). This is composed of a high thermal conductivity AlN substrate with metalized surfaces, stack soldered to a 6.35 mm thick oxygen free (OF) copper base plate on the bottom and to individual OF copper screw terminal blocks on the top. The copper base provides additional thermal mass to reduce thermal fluctuations. The 88.9 mm \times 44.45 mm \times 1.02 mm aluminum nitride substrate was metalized first with a 100 nm titanium tungsten adhesion layer, then a 1.35 μ m Nickel layer, then a 1.7 μ m Au Angstrom layer. The copper base was bonded to the bottom of the metalized aluminum nitride using a SAC (95.5% Sn 3.8% Ag 0.7% Cu) alloy ribbon solder using organic acid flux and the copper screw terminal blocks were bonded to the top of the metalized AlN using indium ribbon, which has a lower melting temperature than the SAC alloy. Ribbon solders enable uniformly thick solder joints and consequently a uniform thermal profile. The copper film on the top surface was subdivided into individual



FIG. 3. (a) Diagram of the isothermal terminal block. (b) Photograph of the isothermal terminal block with the platinum RTD (resistance temperature detector) mounted.

electrically isolated copper contact pads by scoring grooves in the copper film 0.38 mm wide. Sixteen OF copper screw terminal blocks 6.35 mm \times 5.08 mm \times 19.05 mm were polished to a mirror finish in 6 stages using 3M brand aluminum oxide polishing paper (400, 600, 1200, 4000, 6000, and 8000 grit). This ensures uniform radiating properties and a smooth contact surface. Each screw terminal block features 3 mounting locations: one for thermocouple lead wire, one for the copper wire connecting it to the nanovoltmeter, and a third to measure the thermoelectric voltage between two distinct copper terminal blocks and thereby two distinct platinum thermocouple wires, for measurement of the 2- and 4-probe thermoelectric voltage, and the resistivity voltage. The reference temperature is measured using a calibrated (NIST traceable) platinum resistor (Lake Shore Cryotronics, Inc. Model PT-103-AM-70H) soldered and screwed to the surface of the center copper terminal blocks to best represent the temperature at each contact location. A 0.5 mA current is sourced through the platinum resistor using a NI PXI-4110 triple output precision dc power supply. The uncertainty at room temperature is 22 mK, where the temperature of the reference junction increases a only few Kelvin over the stated measurement temperature range.

V. CONTACT INTERFACES

The series of connections between the thermocouple wires and the nanovoltmeters are formed using only copper to copper pressure interfaces to minimize thermoelectric voltage offsets below 0.2 μ V.²³ All copper interfaces are polished and then cleaned prior to assembly using a Deoxit brand solution. Connections between the isothermal terminal block and the vacuum electrical feedthroughs are formed using custom interconnect wires fabricated from Ohno con-

tinuous casting (OCC, near monocrystalline >99.9997% purity) copper wire sheathed in Teflon insulation. Connections through the vacuum wall are formed using custom fabricated copper only thermocouple multipair feedthroughs with loop and screw connectors, providing 8 connection pairs in total (modified from Kurt J. Lesker part TFT4RN00008B). Connections between the thermocouple feedthroughs and the nanovoltmeters are formed using Keithely low-thermal input cables with a LEMO connector on one end and copper spade lugs on the other. The thermocouple voltage, thermoelectric voltage, resistance voltage, and platinum resistor voltage are all measured using three Keithely 2182A nanovoltmeters. At any given time, two of the meters are dedicated to the T_2 and T_1 thermocouples (2- or 4-probe) and the third is connected to an 8-channel 7168 Nanovolt Scanner Card inserted within a Keithely 7001 switch mainframe to scan between the thermoelectric voltage and other signals. The nanovolt scanner card does not degrade the noise and drift performance of the 2182A, nor does it increase the uncertainty. All nanovoltmeters are fitted within an air-cooled and temperature stable enclosure. The uncertainty for the 2182A under optimal settings and during the standard calibration period is 40 nV.

As a diagnostic evaluation of the instrumentation, Figure 4 plots a representative thermal stability measurement as recorded by all four thermocouples over a period of 750 s measured on a doped silicon material. Individual thermal fluctuation for each thermocouple is below 10 mK and the deviation between each thermocouple temperature is less than 60 mK, which is likely a natural static thermal offset of the lower probe. These data are also plotted in Figure 4 for a thermal stability measurement under high vacuum. The thermal stability is typically between 20 mK and 40 mK at higher temperatures. This is better than the overall furnace stability due to the thermal mass of the probe.

There are many references that describe the challenges of forming Ohmic contacts between metal and semiconductor interfaces.^{24,25} High temperatures limit the use of solders and epoxies. In this embodiment, the method of forming good electrical and thermal interfaces at high temperature on a variety of materials is using controlled pressure contacts. One diagnostic test is to conduct current-voltage (IV) sweeps at each measured temperature. Figure 5 illustrates a representative IV plot for the 2- and 4-probe contacts using a doped silicon sample under isothermal conditions. The r² for these plots are 1 and 0.99996, respectively, indicating Ohmic behavior. The zero current voltage offset is minimal at 0.56 μ V for the 2-probe and 0.13 μ V for the 4-probe. The typical voltage offset is between 0.2 and 5 μ V.

Often low pressure, pure helium gas is used as an intermediary to enhance thermal contact between the thermocouple and the sample. However, there are reports suggesting low pressure gases such as helium and nitrogen may affect the thermal contact and thus the measured Seebeck coefficient value.^{26,27} Without sufficient measurements on standardized reference materials, it is a challenge to determine the optimal gas pressure. Indeed, the evacuation of the sample chamber can significantly affect the Seebeck coefficient value for a material measured under a poor thermal contact. This dependence is illustrated in Figure 6, where the filled circles



FIG. 4. Representative thermal stability measurements as recorded for all four thermocouples over a period of 750 s contacting a doped silicon material.

are the Seebeck coefficients for n-type Bi2Te3 SRM 3451, measured in the 2-probe arrangement with a poor thermal contact. At 300 K the reference value is $-231.16 \ \mu V/K.^{28}$ The data obtained under high vacuum are noticeably lower than those obtained under ambient conditions. Of particular interest, is the voltage vs. temperature difference plot in the inset of Figure 6, shown for the Seebeck coefficient measured at the lowest pressure. A tacit assumption is that a linear voltage vs. temperature difference plot is indicative of an isothermal contact. However, the linear relationship for this data point ($r^2 = 0.99998$) suggests the prudent assumption is that while a nonlinear relationship may imply a poor thermal contact, the corollary is not true: that a linear relationship implies a good thermal contact. Section VI discusses some additional diagnostics to evaluate the thermal interface. Fortunately, the thermal contact can be modified using a thermal interface material. The open circles in Figure 6 are the Seebeck coefficients for the same Bi2Te3 SRM material, measured in the 2-probe arrangement but using graphitic interface foil between the sample and each tungsten probe (Graftech International eGraf HT 1210). The data obtained under high vacuum are identical to those obtained under all pressures measured, including ambient conditions. This interface material is routinely used to enhance the thermal contact and does not increase the contact voltage offset as measured using IV sweeps. In addition, the foil creates a barrier to prevent chemical reaction of the test sample with the tungsten probes. Alternative diffusion barriers include nickel and platinum thin foils. Methods of obtaining isothermal and Ohmic pressure contacts are currently the focus of an ongoing investigation and are beyond the scope of the apparatus description.



FIG. 5. Representative IV plot for the 2- and 4-probe contacts using a doped silicon sample under isothermal conditions. The r^2 for these plots are 1 and 0.99996, respectively. The zero current voltage offset is 0.56 μ V for the 2-probe and 0.13 μ V for the 4-probe.



FIG. 6. Seebeck coefficient values at 300 K for Bi₂Te₃ SRM 3451 measured under a poor thermal contact (filled circles) and the Seebeck coefficient using a graphite-based foil interface (open circles). The inset shows the voltage vs. temperature difference plot for the Seebeck coefficient measured at the lowest pressure (circled).

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VI. EXPERIMENTAL METHODOLOGY AND PROTOCOLS

There are two primary techniques used to measure the relative Seebeck coefficient: the integral and the differential. In the integral method (or large ΔT), one end of the specimen is maintained at a fixed temperature T_1 while the opposite end is varied through $T_2 = T_1 + \Delta T$, the temperature range of interest.¹ An analytic approximation is applied to the entire data set $V_{ab}(T_1,T_2)$, then differentiated with respect to T_2 . The integral method approximates TE operating conditions and can often minimize the influence of voltage offsets due to the large thermal gradients and subsequently larger voltage signals. However, it is difficult to maintain a constant T_1 throughout the large ΔT at high temperatures, requiring additional corrections. It is therefore most useful for longer samples, wires, metallic ribbons, and semimetals.

To this end, we implement the more preferred differential method, in which a small thermal gradient is applied to the sample at an average temperature of interest T_o. The Seebeck coefficient can then be obtained by the ratio of the electric potential and the temperature difference using Eq. (1), provided $\Delta T/T_o \ll 1$, and $\Delta S/S \ll 1$, when $V \propto T_o$. In a typical measurement, the temperature difference is between 0.001 T_o and 0.02 T_o. Differential methods can be categorized into three conditions according to the behavior of the thermal gradient: steady-state (dc), quasi-steady-state (qdc), and transient (ac), with respect to the observation time scale, i.e., the time interval required to measure one voltage channel.¹ This apparatus measures the Seebeck coefficient in both dc and qdc conditions. Under steady-state conditions, the Seebeck coefficient is often calculated from the linear fit of multiple electric potential/temperature difference data points to avoid the assumption that the experimental data are collinear with the ordinate (V = 0, ΔT = 0), effectively eliminating any extraneous voltage offset ($\approx 1 \ \mu V$ -100 μV). Note: the current source used for resistivity measurement must be set in a high impedance mode, typically using an internal relay, during Seebeck coefficient measurement to avoid an offset voltage formed by trickle current.

To overcome the time burden required to stabilize multiple steady-state ΔTs , the qdc condition employs an increasing heat flux and/or and dynamic ΔT where the voltage and temperature difference are continuously recorded. Typical gradient heating rates in this apparatus are between 5 mK/s and 50 mK/s with data recorded at 2 s, 5 s, or 20 s intervals (adjustable). This condition also provides an opportunity to evaluate the thermal interface quality. A discrepancy between the Seebeck coefficient data obtained under different heat pulses may be indicative of a poor thermal interface. Figure 7 compares voltage vs. temperature difference plots obtained under three different heat pulses: 2 mK/s, 8 mK/s, and -3 mK/s but with similar average sample temperatures (compound average). These data were recorded for a temperature difference between 0.5 K and 1.5 K. The Seebeck coefficients for all three data sets agree within 0.5 μ V/K (the apparatus reproducibility), including the value obtained under a negative heat pulse. The absence of thermal hysteresis in the Seebeck coefficient is a reliable indication of an isothermal contact inter-



FIG. 7. Comparison of voltage vs. temperature difference plots obtained under three different heat pulses: 2 mK/s, 8 mK/s, and -3 mK/s with similar average sample temperatures T_{avg}. These data were recorded for a temperature difference between 0.5 K and 1.5 K. The Seebeck coefficients for all three data sets agree within 0.5 μ V/K (the apparatus reproducibility).

face. It is therefore prudent to perform these diagnostic tests periodically throughout the measurement cycle.

Some experimental implementations under the qdc condition incorporate only one voltmeter and a voltage channel switcher, and thereby stagger the acquisition of the ΔV , T₂, and T₁ parameters. As a result, the thermal drift between each parameter acquisition introduces error in the measured Seebeck coefficient by distorting the temperature-voltage correspondence. Consequently, the character of the distortion is dependent on the parameter acquisition sequence. In this embodiment, the three nanovoltmeters (two dedicated to the T₂ and T₁ thermocouples (2- or 4-probe) and the third to measure the thermoelectric voltage) measure each parameter simultaneously to avoid staggered acquisition errors. This is accomplished programmatically using a general purpose interface bus trigger.

One method to explore the effect of voltage/temperature correspondence distortion under the qdc condition is to program the 3 nanovoltmeters to simultaneously acquire the data repeated in rapid succession, then combine the successive thermoelectric voltage and hot and cold thermocouple readings that represent a specific time delay. In this manner, it is straightforward to mimic the acquisition that would occur using only one nanovoltmeter and a switching card while also retaining the data obtained by simultaneous acquisition. This process ensures both the thermal heating rate and the average sample temperature are identical since the data used are from one measurement cycle. The optimal accuracy for the 2182A nanovoltmeters is obtained for a number of power line cycles setting of 5. This corresponds to an aperture (analog to digital conversion) time of 83.3 ms, and a total measurement time of 2.3 s. As a demonstration of staggered acquisition error, Figure 8 shows the experimental results of a Seebeck coefficient measurement on a doped silicon material under simultaneous acquisition (filled circles), compared with the Seebeck coefficients under a 2.3 s staggered acquisition for a V:T₂:T₁ sequence (open squares) and the inverse $T_1:T_2:V$ sequence



FIG. 8. Experimental results of a Seebeck coefficient measurement on a doped silicon material under simultaneous acquisition (filled circles), compared with the Seebeck coefficients under a 2.3 s staggered acquisition for a V:T₂:T₁ sequence (open squares) and the inverse T₁:T₂:V sequence (open triangles). The Seebeck coefficient for the simultaneous acquisition is $-224.26 \ \mu$ V/K, compared with $-209.21 \ \mu$ V/K (V:T₂:T₁) and $-240.35 \ \mu$ V/K (T₁:T₂:V).

(open triangles). The Seebeck coefficient for the simultaneous acquisition is $-224.26 \ \mu V/K$, compared with $-209.21 \ \mu V/K$ (V:T₂:T₁) and $-240.35 \ \mu V/K$ (T₁:T₂:V). This represents a 7% error for an average heating rate of 28 mK/s. If additional voltage instrumentation is not available, averaging the Seebeck coefficient obtained for one sequence and its inverse yields a value of $-224.78 \ \mu V/K$, similar to that obtained under simultaneous acquisition.

As one evaluation of the accuracy of the apparatus, Figure 9 plots the Seebeck coefficient measured on the n-type Bi_2Te_3 NIST SRM 3451 (filled circles), a low temperature Seebeck coefficient standard reference material in the temperature range 10 K–390 K. These data were measured using the qdc technique (see inset in Figure 9) for a 2-probe arrangement as suggested in the SRM supporting information. The



FIG. 9. The Seebeck coefficient measured on the n-type Bi₂Te₃ NIST SRM 3451 (filled circles) shown in comparison with the NIST certified reference data (unfilled circles). The dotted line is the parametric fit provided in Ref. 28 for comparing intermediate values. The dashed lines represent the uncertainty band for the NIST certified values.



FIG. 10. The experimental Seebeck coefficients (filled circles) measured on a p-type $Si_{80}Ge_{20}$ bulk alloy material used in RTGs for deep space power generation. These data are plotted in comparison to digitally extracted reference data from Ref. 29 (open circles). The lines are guides for the eye only. The error bars represent the type B instrumentation uncertainty of 0.9%.

measured data are shown in comparison with the NIST certified reference data (unfilled circles). The dotted line is the parametric fit provided in Ref. 28 for comparing intermediate values. The dashed lines represent the uncertainty band for the NIST certified values. The relative error between the experimental Seebeck coefficients and the NIST certified data indicate an accuracy of $\approx 0.5\%$ in the measured temperature range.

As an additional evaluation at higher temperature, Figure 10 shows the experimental Seebeck coefficients (filled circles) measured on a p-type Si₈₀Ge₂₀ bulk alloy material used in radioisotope thermoelectric generators (RTGs) for deep space power generation. These data are plotted in comparison to digitally extracted reference data from Ref. 29 (open circles). The lines are guides for the eye only. These data were measured using the qdc condition in the 2-probe arrangement and show excellent agreement with the reference data. As an additional diagnostic, we compared the Seebeck coefficient near 700 K measured using an increasing thermal gradient and a decreasing thermal gradient to test for hysteresis. The Seebeck coefficient measured for an increasing gradient is 192.84 μ V/K at an average sample temperature of 710.24 K, and measured for a decreasing gradient is 192.39 μ V/K at an average sample temperature of 710.25 K. We currently estimate the type B instrumentation uncertainty for the Seebeck coefficient at 0.9% (expanded uncertainty, with coverage factor k = 2 for a 95% confidence level). A more robust uncertainty budget, including type A uncertainty, is being developed as part of ongoing methodology and probe arrangement comparison studies using this apparatus. These studies will be used to determine optimal Seebeck coefficient measurement protocols in a forthcoming publication.

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