

# Thermoelectric measurements



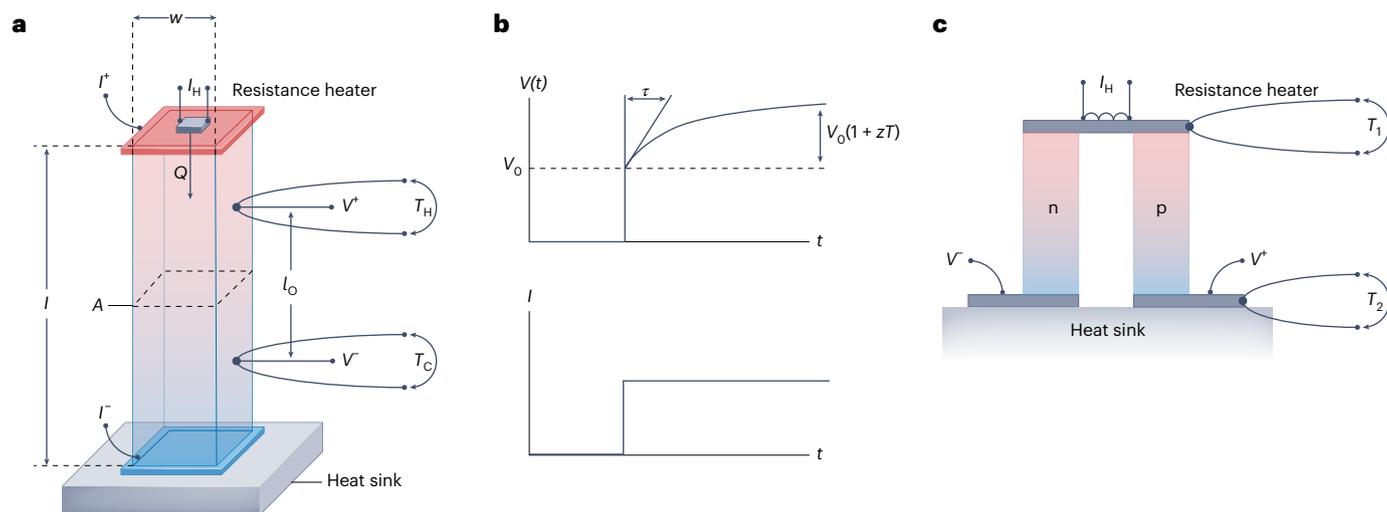
Joseph Heremans and Joshua Martin discuss the reproducibility of thermoelectric measurements and conclude that the uncertainty on the figure of merit  $zT$  is of the order of 15–20%.

**T**hermoelectric (TE) technology converts heat into electrical power in thermoelectric generators (TEGs) and uses electrical energy to pump heat in thermoelectric coolers (TECs)<sup>1</sup>. For a given temperature difference and load, the efficiency of TEGs and TECs is a function of the Carnot efficiency and the thermoelectric figure of merit  $zT = S^2T/\rho\kappa$ , where  $S$  is the Seebeck coefficient,  $\rho$  is the electrical resistivity,  $T$  is the absolute temperature and  $\kappa$  is the total thermal conductivity.  $zT$  measures the amount of thermodynamic irreversible losses in the conversion process. There are two ways to measure  $zT$ : (1) calculate it from measurements of  $S$ ,  $\rho$  and  $\kappa$  (ref. 1), or (2) measure it directly. Because the power output of TEGs and TECs scales with material volume, we concentrate on measurements of bulk samples.

The resistivity  $\rho$  is measured using four contacts placed on a sample as shown in Fig. 1a. The resistivity  $\rho = (V/I)(A/l_0)$ , where  $V = V^+ - V^-$  is the averaged bipolar voltage,  $I$  is the averaged  $\pm$  current through the sample, and  $A$  and  $l_0$  are the average cross-sectional

area of the sample and the distance between the centres of the two voltage contacts, respectively. In principle,  $\rho$  is defined in an isothermal environment, but often the sample is mounted on a heat sink (Fig. 1a). Both Joule heating and Peltier heating or cooling can affect results. Joule heating can be avoided by using small currents and bipolar measurements. Peltier cooling creates a temperature difference across a sample (Fig. 1a), which generates a Seebeck voltage that adds to  $V$ . The time-dependent voltage is shown in Fig. 1b: the voltage immediately after the current is applied is  $V(t) = V_0$ , but after a time  $\tau$  the voltage reading is  $V(t \gg \tau) = V_0(1 + zT)$ . Typically,  $\tau = l^2/D (\approx 1 \text{ s})$ , where  $D = \kappa/C$  is the thermal diffusivity,  $C$  is the isobaric volumetric specific heat and  $l$  is the length of the sample. Although noise and temperature errors affect  $\rho$ , the largest uncertainty arises from measuring  $A$  and  $l_0$ .  $A$  is measured to within  $\approx 0.5\text{--}1.0\%$ .  $l_0$  is measured between the centre of the voltage contacts with an uncertainty dominated by the ratio of contact diameter to  $l_0$ , often quite large ( $\geq 10\%$ ) on small samples.

The Seebeck coefficient is also commonly measured using the mount<sup>2</sup> shown in Fig. 1a. A heat flux  $Q$  is applied to the sample to generate a small  $\Delta T = T_H - T_C (\ll T)$ , where  $T_H$  and  $T_C$  are the hot and cold thermocouple temperature, respectively.  $S$  is given by  $S = V/\Delta T$ , where  $V$  is the Seebeck voltage. Although  $S$  is insensitive to geometrical errors, there are three sources of uncertainty: uncertainty on  $V$  and  $\Delta T$ , and the voltage and temperature must be measured at the same time and location on the sample. Because Seebeck voltages are small, residual voltages that appear when  $\Delta T = 0$  must be subtracted. A collection of stabilized electric potential/temperature difference data points  $\{(V, \Delta T)\}$  are measured under steady-state conditions and with increasing values of  $Q$ ;  $S$  is calculated as the slope of the unconstrained linear fit to the data. The measurement of  $\Delta T$  requires that probes and sample surface are in good thermal contact. The thermal contact resistance between sample and probes is inversely proportional to interface thermal conductance and square of contact radius. The probes also perturb the



**Fig. 1 | Thermoelectric measurements.** **a**, Mount for measurements of resistivity  $\rho$ , Seebeck coefficient  $S$  and static heater-and-sink measurements of the thermal conductivity  $\kappa$ .  $A$  is the average cross-sectional area,  $l$  is the length of the sample and  $w$  is its thickness,  $l_0$  is the distance between the centres of the two voltage contacts. **b**, Time dependence of the measured d.c. voltage  $V(t)$

(top) following a current ( $I$ ) pulse (bottom). This can perturb electrical resistivity measurements or be used in the Harman method to directly determine  $zT$ .

**c**, Thermocouple mount to directly determine the  $zT$  of an unknown material (the n- or the p-leg of the thermocouple). The unknown material is paired with a complementary material (the p- or the n-leg, respectively) of known  $zT$ .

surface temperature, creating errors up to  $\approx 14\%$  in  $S$  at 900 K; this is reduced by using small-diameter and low-thermal-conductivity probes, radiation shielding and measuring under vacuum. Experiment and modelling both demonstrate that these errors are asymmetric and dependent on contact relative locations<sup>3</sup>. A time delay in measuring  $V$ ,  $T_H$  and  $T_C$  distorts  $V/\Delta T$ , introducing an error that can exceed 10% but is minimal in steady state. If the measurement locations of  $V$ ,  $T_H$  and  $T_C$  are not identical, for example, when using differential thermocouples, the uncertainty in  $S$  can be similar to their displacement percent<sup>3</sup>.

Common techniques to measure thermal properties include longitudinal steady-state (measuring  $\kappa$ ), laser flash ( $D$ ), transient plane source ( $\kappa$ ,  $D$ ,  $C$ ), or differential scanning calorimetry (which measures  $C$ )<sup>2,4</sup>. At  $T \leq 300$  K,  $\kappa$  is typically measured using static heater-and-sink techniques (Fig. 1a):  $\kappa = (Q/\Delta T)(l_0/A)$ , where  $Q$  is the power produced by a resistive heater. The measurement proceeds like that for  $S$ , with  $\kappa$  derived from the slope of a linear regression through a series of  $\{(Q, \Delta T)\}$  points taken after  $\Delta T$  stabilizes, that is, at a time longer than  $\tau$  (some commercial instruments use a transient method). The geometry uncertainty is the same as for  $\rho$ . The sources of uncertainty on  $\Delta T$  are the same as for  $S$ . The main error source is due to thermal losses where the heat does not go fully through the sample. Thermal radiation loss is negligible at  $T < 150$  K. At  $T > 200$  K, it scales as  $T^4$  following the Stefan–Boltzmann law.

At  $T \geq 300$  K,  $D$  is measured using laser flash analysis. With a reference specimen,  $C$  and thus  $\kappa = DC$  can be calculated.  $C$  can also be measured using differential scanning calorimetry, or estimated from the Dulong–Petit law, which must always be checked for consistency. Uncertainty in  $D$  is relatively small and reported directly and reliably using commercial instrumentation. The uncertainty in  $C$  can be larger in samples of high atomic number (most TE materials), or near phase transitions, where laser flash and differential scanning calorimetry techniques greatly underestimate  $D$  and  $C$  if enthalpy changes in the phase transition are ignored. The latter results in underestimations of  $\kappa$  and overestimations of  $zT$ .

$zT$  and its uncertainty can be calculated from  $\rho$ ,  $S$  and  $\kappa$ , noting that geometrical uncertainties cancel out if  $\kappa$  is obtained from the static heater-and-sink method and the thermometers are located at the same point as the voltage contacts. A reasonableness check is to verify that  $zT < S^2/L_0$ , assuming that the Wiedemann–Franz relation holds with

$L_0 = 2.4 \times 10^{-8} \text{ V}^2 \text{ K}^{-2}$  (or a justification is given if this does not hold). Adding a direct measurement of  $zT$  makes for a more convincing argument if consistent with measurements of  $zT$  from materials properties within  $\approx 20\%$ . There are three methods.

One is the Harman method (Fig. 1b). A current pulse is applied to a sample mounted either in free space or on a heat sink, and voltage is recorded over a time longer than several  $\tau$ . The immediate voltage response is  $V_0$ , the steady-state ( $t \gg \tau$ ) one is  $V_0(1 + zT)$ , and  $zT$  is derived from these equations. The uncertainty is of the order of 20%, and larger for  $zT \ll 1$ , given the difficulty in identifying the inflection point of the  $V(t)$  curve near  $t = 0$ .

The two alternative methods require the construction of a thermocouple made from the material under study (n- or p-type) and a complementary similar material (now p- or n-type) of known  $zT$  but opposite polarity (Fig. 1c). The thermocouple is instrumented with thermometers on its two ends ( $T_1$  and  $T_2$ ) and is mounted in vacuum with one end attached to a heat sink, and the other with a resistive heater.

One of these alternative methods, appropriate for TEC materials ( $T_1 < T_2$ ), is to determine the maximum temperature difference  $\Delta T_{\text{MAX}}$  of the thermocouple used in the Peltier cooling mode. The current is varied while  $\Delta T = T_2 - T_1$  is measured, until  $\Delta T_{\text{MAX}}$  is reached. The equation  $\Delta T_{\text{MAX}} = (zT_{\text{AVG}})(T_1/2)$  is then used to determine  $zT_{\text{AVG}}$ , which is the average between the  $zT$  of both n- and p-type materials, from which the unknown  $zT$  of the material is derived.

The other alternative method is to run the thermocouple as a TEG ( $T_1 > T_2$ ), putting a known amount of Joule heat  $Q$  into the heater and connecting the thermocouple to an electrical load of resistance  $R$  (not shown), across which the voltage  $V_{\text{OUT}} = V_+ - V_-$  is measured. The TEG's thermal efficiency  $\eta = V_{\text{OUT}}^2/RQ$  and Carnot efficiency  $\eta_c = 1 - (T_2/T_1)$  are measured;  $\eta/\eta_c$  is a function of  $R$ ,  $T_1$ ,  $T_2$  and  $zT_{\text{AVG}}$  that is solved for  $zT_{\text{AVG}}$  (ref. 1). Heat losses and electrical and thermal contact resistance losses are included in the measurements of  $zT$  in the last two methods and result in an underestimation of  $zT$ .

Several interlaboratory studies have identified variability in TE measurements<sup>5</sup>. For example, the National Institute of Standards and Technology (NIST) led a comparison of 12 international laboratories for the measurement of  $S$  between 2 K and 390 K for n-type  $\text{Bi}_2\text{Te}_3$  with an interlaboratory coefficient of variation (standard deviation divided by consensus mean) of  $\approx \pm 4\%$ . Another study in

2015, by Institut de Chimie et des Matériaux Paris-Est compared the TE figure of merit for the skutterudite  $\text{Co}_{0.97}\text{Ni}_{0.03}\text{Sb}_3$  from 300 K to 700 K. The temperature-averaged relative standard uncertainties (at confidence level 68%) were 6%, 8%, 11% and 19% for  $S$ ,  $\rho$ ,  $\kappa$  and  $zT$ , respectively.

A limited number of certified reference material standards are commercially available for TE transport properties<sup>5</sup>. Standard reference material (SRM) 3451 (n-type  $\text{Bi}_2\text{Te}_3$ ) and SRM 3452 (p-type  $\text{Si}_{80}\text{Ge}_{20}$ ) provide reference values for  $S$  and  $\rho$  that together span the temperature range from 10 K to 900 K. Reference material (RM) 8420 (electrolytic iron) provides  $\rho$  and  $\kappa$  values between 2 K and 1,000 K. A reference material is available from the National Physical Laboratory (NPL) 2109 (Inconel 600) for  $\kappa$  in the range of  $14 \text{ W m}^{-1} \text{ K}^{-1}$  to  $22 \text{ W m}^{-1} \text{ K}^{-1}$  covering temperatures between 100 °C and 500 °C.

Researchers are advised to conduct measurements and express uncertainty according to the procedures and terminology definitions contained in the Guide to the Expression of Uncertainty in Measurement (GUM) and NIST Technical Note 1900<sup>5</sup>. Error is a measured quantity value minus a reference quantity value, whereas uncertainty characterizes the dispersion of the quantity values being attributed to a measurand. Any measurement is technically incomplete if researchers fail to provide either a statement of the measurement uncertainty or uncertainty bars for measured quantities, preventing reproducibility of their results.

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## Competing interests

The authors declare no competing interests.