Theoretical Study of the Harman- Method for Evaluating the Thermoelectric Performance of Materials and Components at High Temperature

A. Jacquot, M. Jägle, J. König, D.G. Ebling, H. Böttner
Fraunhofer-Institut für Physikalische Messtechnik IPM, department of thermoelectric systems
Heidenhofstraße 8, 79110 Freiburg, Germany
alexandre.jacquot@ipm.fraunhofer.de, Phone: +49 (0)761/8857-459, Fax: +49 (0)761/8857-224

Abstract

Over the past decade IPM did implement various measuring techniques applicable to thin films and massive Materials [1]. The customer-oriented measuring systems combine accuracy, rapidity, and few efforts for the mounting of the sample. Some systems are even fully automated, and some measurements are offered to third parts on a commercial basis. In this paper we want to discuss the Harman method for measuring the thermoelectric properties at high temperatures.

The Harman method [2] is known to enable the direct measurement of the Figure of Merit at or below room temperature. Beside the simplicity to put the method in practice, the thermoelectric properties are measured in the same direction. The second advantage is that a technological Figure of Merit, which does account for the electrical contacting of the thermoelectric material, is accessible without being forced to make the entire thermoelectric device. In this paper a correction factor is derived to take account for the heat loss by radiation at higher temperatures, the contact resistances and the effect of the geometry of the sample. The correction factor is evaluated for various experimental conditions and the key features of an experimental setup for measurements at high temperature are discussed.

The Harman- Method

The Harman- Method has been used more or less exclusively for the measurement of the Figure of Merit of Bi_2Te_3-based materials at room temperature because Ohmic contact can be relatively easily made on this material (10^{-11} Ωm^2) [3] and the radiated heat could be neglected. In this case, the sample arrangement is simple and is shown in the figure 1. The sample, a bar or a rod relatively narrow and long, is soldered to feed lines. The solder cover the whole surface of both ends of the sample, so that the current streamline be parallel to the longitudinal axis of the sample.

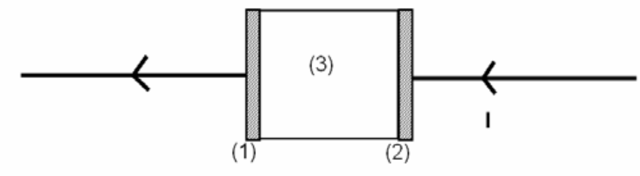

Figure 1: *Arrangement of the sample*

When an electrical current I is flowing in the sample, heat is generated (pumped) at the junctions. In the steady state, this heat will just be equal to the heat flowing in the sample:

$$I\alpha T = K\Delta T \qquad (1)$$

ΔT is the temperature difference along the sample, α is given by:

$$\alpha = \alpha_S - \alpha_M \qquad (2)$$

where α_S and α_M is the Seebeck coefficient of the sample and of the electrodes, respectively.

The equation (2) can be rewritten as a function of the voltage drop V_ρ at the electrodes, the electrical conductivity σ and the thermal conductivity k :

$$\frac{\sigma\alpha}{k}T = \frac{\Delta T}{V_\rho} \qquad (3)$$

Since, $\Delta T = \alpha/V_\alpha$, the equation (3) can be written as a function of a pseudo Figure of Merit Z_{α_M} :

$$Z_{\alpha_M}T = \frac{V_\alpha}{V_\rho} \qquad (4)$$

The sequence of the measurement is as follows:

- Measurement of the voltage drop V_T between the electrodes in the steady state
- Switching off of the current source
- Measurement of the voltage drop V_α just after the turning off of the current source.
- Calculation of V_ρ by subtracting V_α from V_T

Correction factors

At high temperature, the radiated heat has to be taken into account. Furthermore, and independently of the temperature of measurement, the effect of the electrical contact resistance on the measurement should not be overlooked since the Harman- method uses the same wires for the feed line and for the voltage measurements. As a consequence, the voltage V_ρ has to be added to the voltage drop due to the contact resistance V_c:

$$V_{\rho+c} = V_\rho + V_c \qquad (5)$$

We can already take note that the contact resistance, if not taken into account in the data analysis, lead to an underestimation of the Figure of Merit.

The Figure of Merit will also be underestimated if the radiated heat is not taken into account, because it will decrease the temperature gradient generated by the Peltier effect, and consequently V_α. The equation (4) should then be corrected with a factor β larger than 1:

$$Z_{\alpha_M}T = \frac{V_\alpha}{V_\rho}\beta \qquad (6)$$

Derivation of the correction factor β

The full derivation of the correction factor β has not been published yet, and is given below. Nevertheless, the starting equation, which just replaces the equation (1) when the radiated heat and the difference of contact resistances between the electrode 1 and the sample and the sample and the electrode 2 are taken into account, can be found in the article of T.C. Harman [4]:

$$I(\alpha_S - \alpha_M)\overline{T} = K_m(T_h - T_c) + K_S(T_h - T_c)\sum_{n=0}^{\infty}\frac{2(L/a)\gamma^2 \coth(\lambda_n L/2)}{(\lambda_n a)[(\lambda_n a)^2 + \gamma^2]} + \pi a^2 h_M (T_h - T_c)/2 + I^2 \Delta R_C/2 \qquad (7)$$

Where T_h and T_c are the temperature of the hot and cold ends of the sample, respectively. The average temperature of the sample is given by:

$$\overline{T} = (T_h - T_c)/2 \qquad (7)$$

K_m and K_S are the thermal conductance of the electrodes and of the sample, L and a are the length and diameter of the sample, respectively. Besides h_M is equal to $4\sigma_R \varepsilon \overline{T}^3$ where σ_R is the Stefan-Bolzmann's constant and ε_M is the emissivity of the electrodes. γ represents ha/κ_S, where $h = 4\sigma_R \varepsilon \overline{T}^3$, ε and κ_S being the emissivity and the thermal conductivity of the sample, respectively. ΔR_c is the difference of contact resistance at the junction electrode/sample and not their absolute value.

λ_n is calculated by solving the following equation:

$$(\lambda_n a)J_1(\lambda_n a) = \gamma J_0(\lambda_n a) \qquad (8)$$

Where J_1 and J_0 are the functions of Bessel.

The specific contact resistance r_c (resistance per unit of area) is introduced in the equation (7) by replacing I with:

$$I = \frac{\pi a^2/\rho L}{1 + 2 r_c/\rho L} V_{\rho + ii} \qquad (9)$$

When the thermal conductivity substitutes for the thermal conductance, it turns out that:

$$K_S = k_s \pi a^2/L \text{ and } K_M = \kappa_M \pi a^2/L \qquad (10)$$

Where L and L_M are the lengths of the sample and of the feed lines, respectively.

After several rearrangements, the equation (7) becomes:

$$\frac{(\alpha_S - \alpha_M)^2}{\rho \kappa_S}\overline{T}\frac{V_{\rho+c}}{V_\alpha} = \left[1 + \frac{2r_c}{\rho L}\right]\left[\frac{V_{\rho+c}^2 \Delta r_C(\alpha_S - \alpha_M)}{2\rho^2 \kappa_S L V_\alpha (1 + r_c/\rho L)} + \frac{\kappa_M b^2 L}{\kappa_S a^2 L_M} + \frac{h_M L}{2\kappa_S} + \sum_{n=0}^{\infty}\frac{2(L/a)\gamma^2 \coth(\lambda_n L/2)}{(\lambda_n a)[(\lambda_n a)^2 + \gamma^2]}\right] = \beta \qquad (11)$$

Method of calculation of β

The equation (7) comes also as:

$$Z\overline{T}\frac{V_{\rho+c}}{V_\alpha} = a_1\left[a_2 V_{\rho+c}^2 + a_3 + a_4 + a_5\right] \qquad (12)$$

a_1 represents the effect of the contact resistance.

a_2 arises from the effect of the difference of the contact resistances.

a_3 account for the heat losses along the feed lines.

a_4 represents the heat radiated by the feedlines.

a_5 represents the heat radiated by the sample.

The factor of correction β can be calculated easily, if the geometry of the sample and electrodes, the material properties, the temperature gradient and the contact resistances are known. In this case a_1, a_2, a_3, a_4, a_5 and V_α can be evaluated as well as $V_{\rho+c}$, $V_{\rho+c}$ being the solution of a second order polynomial:

$$V_{\rho+c} = \frac{a_6/(a_1 a_2) \pm \sqrt{\Delta}}{2} \qquad (13)$$

where

$$\Delta = a_6^2/(a_1^2 a_2^2) - 4(a_3 + a_4 + a_5)/a_2 \qquad (14)$$

It is worth noticing that there can be two values of β when the contact resistances on both side of the sample are not the same.

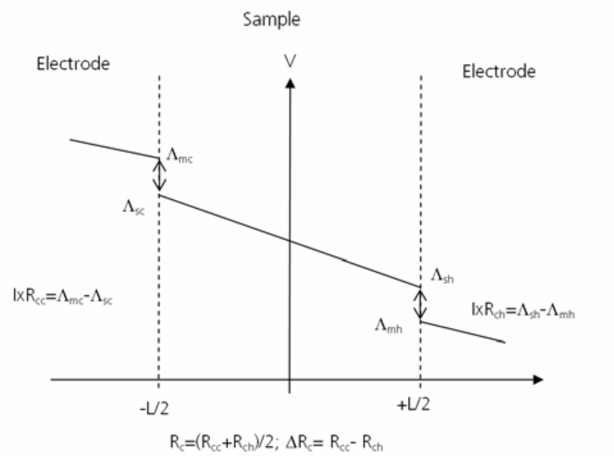

Figure 2: *Model for the electrical contact resistances*

Effect of the sample geometry and emissivity on β

The correction factor β as well as $a_x, x = 1..5$ has been calculated with the following data:

Table 1a: *Data use for the results presented in the table 1b.*

$\overline{T}$ [K]: 900 K	ρ [W .m]: 20e-6	L_M [m]: 10e-2
T_h [K]: 902	r_c [W .m^2]: 0	b [m]: 5e-4
T_c [K]: 898	a [m]: 5e-3	Δr_c [W .m^2]: 0
κ_S [W.m^{-1}.K^{-1}]: 2	κ_M [W.m^{-1}.K^{-1}]: 20	
α_S [V.K^{-1}]: 200e-6	α_M [V.K^{-1}]: 20e-6	

The results are shown in the table 1 for various emissivity and length of the sample. It can be seen that the sample must be significantly shorter than 1 cm for the heat loss by radiation be reasonable low. The calculation has been done with a value of the emissivity of 0,5 and temperature of 900 K. If it is not the case, the heat radiated will dramatically impact the measurement of the Figure of Merit. For example, the figure of merit will be underestimated by about 41% if the sample is 2 cm long and if its emissivity is 0,5. If we are looking at the other factors that can affect the measurement, the heat radiated is by far the most important at high temperature, if the electrical contact resistance are neglected.

Table 1b: *Effect of the sample geometry and emissivity on* β*. The data used for the calculation are reported in the Table 1a.*

$L_S \setminus \varepsilon$	0	0,5	1
0,2 cm	$V_{\rho+c}$ =9,989e-4 β=1,002 $a_1(r_C,..)$=1 $a_2(\Delta r_c,..)$=0 $a_3(\kappa_M,..)$=2e-3 $a_4(h_M,..)$=0 $a_5(\varepsilon,..)$=1,000	$V_{\rho+c}$ =1,036e-3 β=1,049 $a_1(r_C,..)$=1 $a_2(\Delta r_c,..)$=0 $a_3(\kappa_M,..)$=2e-3 $a_4(h_M,..)$=4,1e-2 $a_5(\varepsilon,..)$=1,005	$V_{\rho+c}$ =1,081e-3 β=1,095 $a_1(r_C,..)$=1 $a_2(\Delta r_c,..)$=0 $a_3(\kappa_M,..)$=2e-3 $a_4(h_M,..)$=8,3e-2 $a_5(\varepsilon,..)$=1,011
1 cm	$V_{\rho+c}$ =9,896e-4 β=1,002 $a_1(r_C,..)$=1 $a_2(\Delta r_c,..)$=0 $a_3(\kappa_M,..)$=2e-3 $a_4(h_M,..)$=0 $a_5(\varepsilon,..)$=1,000	$V_{\rho+c}$ =1,330e-3 β=1,347 $a_1(r_C,..)$=1 $a_2(\Delta r_c,..)$=0 $a_3(\kappa_M,..)$=1e-2 $a_4(h_M,..)$=2.07e-1 $a_5(\varepsilon,..)$=1,130	$V_{\rho+c}$ =1,650e-3 β=1,347 $a_1(r_C,..)$=1 $a_2(\Delta r_c,..)$=0 $a_3(\kappa_M,..)$=1e-2 $a_4(h_M,..)$=4,13e-1 $a_5(\varepsilon,..)$=1,248
2 cm	$V_{\rho+c}$ =1,007e-3 β=1,020 $a_1(r_C,..)$=1 $a_2(\Delta r_c,..)$=0 $a_3(\kappa_M,..)$=2e-2 $a_4(h_M,..)$=0	$V_{\rho+c}$ =1,892e-3 β=1,915 $a_1(r_C,..)$=1 $a_2(\Delta r_c,..)$=0 $a_3(\kappa_M,..)$=2e-2 $a_4(h_M,..)$=4,13e-1	$V_{\rho+c}$ =2,6770-3 β=2,710 $a_1(r_C,..)$=1 $a_2(\Delta r_c,..)$=0 $a_3(\kappa_M,..)$=2e-2 $a_4(h_M,..)$=8,27e-1

Effect of the electrical contact resistances

The correction factor β as well as $a_x, x = 1..5$ has been calculated with the following data:

Table 2a: *Data use for the results presented in the table 2b.*

$\overline{T}$ [K]: 900 K	ρ [W .m]: 20e-6	L_M [m]: 10e-2
T_h [K]: 902	$\varepsilon = \varepsilon_M$ =0	b [m]: 5e-4
T_c [K]: 898	a [m]: 5e-3	L_S [m]: 1e-2
κ_S [W.m^{-1}.K^{-1}]: 2	κ_M [W.m^{-1}.K^{-1}]: 20	
α_S [V.K^{-1}]: 200e-6	α_M [V.K^{-1}]: 20e-6	

The emissivity has been set to 0 and the length of the sample is 1 cm. It can bee seen that in this particular case, the contact resistance have to be lower than 1x10^8 Ohm.m^2 to not affect the correction factor more than 10%. Surprisingly, it does seem that the difference of contact resistance at the two ends of the sample, does not drastically affect the measurement. This is perhaps misleading and not true, because when Harman did introduce Δr_c, he only consider the thermal heating due to contact resistances and not it effect on the measured voltages. The physical origin of the second solution of the equation (12) is a consequence of a dissymmetrical heating of the sample at the junctions, which in the worst case can completely offset the Peltier effect.

Table 2b: *Effect of the sample geometry and emissivity on β. The data used for the calculation are reported in the Table 2a*

$r_c \setminus \Delta r_c$	0 [Ohm.m^2]	1x10^{-8} [Ohm.m^2]	1x10^{-7} [Ohm.m^2]
1x10^{-9} [Ohm.m^2]	$V_{\rho+c}$=1,007e-3 β=1,0201 $a_1(r_C,..)$=1,01 $a_2(\Delta r_c,..)$=0 $a_3(\kappa_M,..)$=1e-2 $a_4(h_M,..)$=0 $a_5(\varepsilon,..)$=1		
1x10^{-8} [Ohm.m^2]	$V_{\rho+c}$=1,097e-3 β=1,111 $a_1(r_C,..)$=1,1 $a_2(\Delta r_c,..)$=0 $a_3(\kappa_M,..)$=1e-2 $a_4(h_M,..)$=0 $a_5(\varepsilon,..)$=1	$V_{\rho+c}$=1,0975e-3 ($V_{\rho+c}$=6,47) * β=1,111 (β=6,5e3) $a_1(r_C,..)$=1,1 $a_2(\Delta r_c,..)$=1,71e-4 ($a_2(\Delta r_c,..)$=5,9e3) $a_3(\kappa_M,..)$=1e-2 $a_4(h_M,..)$=0 $a_5(\varepsilon,..)$=1	
1x10^{-7} [Ohm.m^2]	$V_{\rho+c}$=1,995e-3 β=2,020 $a_1(r_C,..)$=2 $a_2(\Delta r_c,..)$=0 $a_3(\kappa_M,..)$=1e-2 $a_4(h_M,..)$=0	$V_{\rho+c}$=1,995e-3 ($V_{\rho+c}$=6,46) * β=2,0206 (β=6,5e3) $a_1(r_C,..)$=2 $a_2(\Delta r_c,..)$=3,11e-4 ($a_2(\Delta r_c,..)$=3,3e3) $a_3(\kappa_M,..)$=1e-2 $a_4(h_M,..)$=0	$V_{\rho+c}$=1,995e-3 ($V_{\rho+c}$=6,46) * β=2,026 (β=6,5e3) $a_1(r_C,..)$=2 $a_2(\Delta r_c,..)$=3,12e-3 ($a_2(\Delta r_c,..)$=3,3e3) $a_3(\kappa_M,..)$=1e-2 $a_4(h_M,..)$=0

Key features of an experimental setup for measurement at high temperatures.

The heat loss by radiation has to be minimized. It is therefore important that the environment temperature be the same that the sample temperature. The location of temperature sensors, as close as possible from the sample, will be important as well. The coating of the sample with a thin material (few nm) having a low emissivity may also be decisive. The electrical contacts have to be Ohmic. The Harman method is therefore only applicable on particular materials, where the technology to get ohmic contacts exists. The application of the Harman method to the measurement of a particular material may also serve to the industry as an indicator of the maturity of the technology related to the material.

Conclusions

The assertion of Harman that his method could be easily at 1000K was perhaps exaggerated because the sample has to be very short. It is not sure that the optimal geometry that minimizes the heat losses will be suitable to accurately measure the electrical response of the sample. It is nevertheless not excluded that the efforts undertaken to extend this measurement method at high temperature finally pay off at last.

Acknowledgments

The authors would like to thank the chemical company BASF for its financial support.

References

1. Jacquot, A. *et al*, "Measuring methods applicable to thermoelectric Materials: Fraunhofer-IPM capabilities", *25th International Conference on Thermoelectrics,* Vienna, Austria, August 2006, pp. 184-188.
2. Harman, T.C., "Special techniques for Measurement of Thermoelectric Properties", *J. Appl. Phys.*, Vol. 29 (1958), pp. 1373-1374.
3. Stockholm, J.G., "Modern thermoelectric cooling technology", *9th International Conference on Thermoelectrics,* Pasadena, USA, August 1990, pp. 90-108.
4. Harman, T.C. *et al*, "Measurement of the thermal conductivity by utilization of the Peltier effect", *J. Appl. Phys.*, Vol. 30, No.9 (1959), pp. 1351-1359.