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THERMOELECTRIC MATERIAL CHARACTERIZATION AT 300 K

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SUMMARY

A methodology and measuring equipment have been developed to characterize pieces of thermoelectric material that are used in large scale systems where thousands are required. Equipment that has been designed, built and used, is described that enables the measurement of thermal conductivity k and of the Seebeck Coefficient s

The electrical resistivity r of all pieces is measured and an average value is calculated. Seebeck s and thermal conductivity k are measured on pieces of known electrical resistivity. Experience confirms that, in the electrical resistivity range, a linear correlation is valid between s and r also between k and r.

The s and k values corresponding to the average value of r can be introduced into mathematic models of thermoelectric systems. The performances calculated in this way have been experimentally confirmed.

1. OBJECT

The designer of thermoelectric equipments where pieces of thermoelectric material are associated with each heat exchanger (see Fig. 1) needs to know the thermoelectric properties of the (thermoelectric) material.

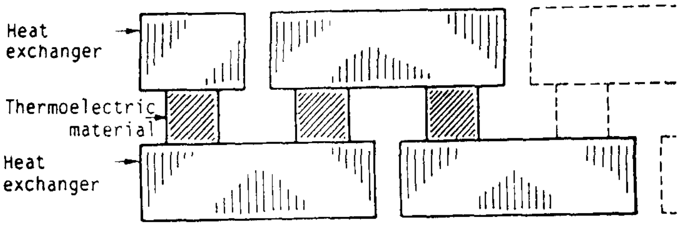

FIG. 1 : Schematic of heat exchangers

The first step consists in developing simple equipment that enable the measurement of the 3 parameters, which have values of the order of those indicated below for doped bismuth telluride.

r : electrical resistivity 10 $\mu\Omega$.m
s : Seebeck coefficient 200 μV/K
K : thermal conductivity 1.5 W/(m.K)

on pieces of thermoelectric material that have the dimensions of those used in systems.

The technique described is valid for pieces such :
- area 0.5 to 2 cm^2
- thickness 0.5 to 10 mm

When the dimensions for area are 1,5 cm^2 and for thickness 1.5 mm,
- the electrical resistivity is obtained by measuring a resistance which is of the order of 100 microohms
- the thermal conductivity consists in measuring a heat flux of the order of 3 watts ($\Delta T = 20$ K).

The resistance R is measured with commercial microohmeters ; the set up procedures are described. The Seebeck coefficient s and thermal conductivity k measurements requires a small unit that creates a ΔT. This equipment is described. For thermal conductivity a standard is also required. With the equipment presented the 3 parameters r, s and k can be measured. Thousands of pieces have been measured for r and hundreds for s and k.

An analysis of results is presented that leads to average values per lot, that can be used to calculate thermoelectric systems.

2 - THERMOELECTRIC MATERIAL : DIMENSIONS - INTERFACES

The dimensions used in this study were :
- thickness always very close to 1.5 mm
- area 1.3 to 1.9 cm^2

The interface influences considerably the measurements. Briefly we indicate results on material with nickel plating, and or with a pretinned surface, and justify why we have chosen to do all our measurements with the material soldered onto nickelplated copper discs.

Dimensions

In the thickness measurement we have included the solder and the nickel plating thickness on the material if there is one.

Thickness can be measured after soldering by using thickness gauges. The horizontal dimensions of the material are obtained using thin sliding callipers.

Interfaces

Pieces of thermoelectric material can be purchased, depending on the manufacturer, nickel plated, pretinned, or with both. Such pieces have been placed between 2 nickel plated copper discs as shown in fig. 2.

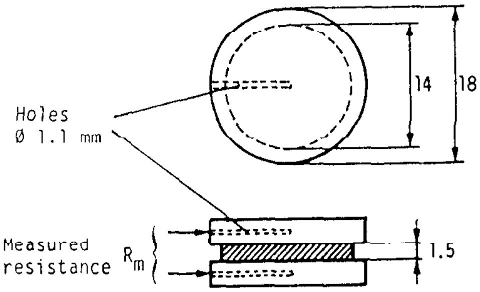

Fig. 2 : Sample

The contact resistance of soldered junction was obtained by soldering together 10 copper discs of 18 mm diameter of known resistivity (9 soldered junctions),and measuring the total resistance. The surface resistance per junction was found to be 0.6 ± 0.2 $\mu\Omega.cm^2$. First the measurements are done with pieces assembled with an electrically conductive lubricant (Elecolit 495), then the same pieces are cleaned and soldered to the copper discs and measurements are repeated.

The resistance values R are given below :

Thermoelec material	Assembled (1) with Ag lubricant	(2) Soldered	Difference (1) - (2) Ag lubricant minus soldered	
	$\mu\Omega$	$\mu\Omega$	$\mu\Omega$	$\mu\Omega$.cm2
pretinned				
N type	220	150	70	50.4
P type	152	115	37	26.6
Ni plated				
N type	384	106	278	211.5
P type	302	108	194	151.5

The last column of above table shows the increase in interface resistivity due to a silver (Ag) lubricant, which confirms the necessity to solder the thermoelectric material to copper discs.

3 - EQUIPMENT DESCRIPTION AND PROCEDURES

The equipment comprises standard commercially available electrical measuring equipment and two small set-up that can be custom made.

Electrical resistivity

The electrical resistance is measured and resistivity r is deduced from :

$$R = r.\frac{e}{S}$$

We are dealing with a thermoelectric material that is highly sensitive to the average temperature T and especially to temperature differials between interfaces. The following resistance temperature relationship has been adopted for bismuth telluride. We have found it to be sufficiently accurate for values of (T - 300) not exceeding ± 10 K.

$$R(T) = R\ (300).[1 + 0.005\ (T - 300)]$$

The ohmeter consists of a constant DC current power supply and of a voltmeter graduated in micro-ohms. Commercial micro-ohmeter use currents between 0.1 and 1 A. R is the real resistance, R_m is the measured resistance as :

$V = R.I + s.\Delta T$ and

$R_m = V/I = R + s.\Delta T/I$

As s is approximately to 200 uV/K, this shows, in the worst case of I = 1 A, that when we are aiming for a precision of 1 %, ΔT must be less than 0.005 K, this is very small. The Joule power $R.I^2$ gives in the material a temperature elévation of about 10^{-4} K per second. This can be neglected. A micro-ohmeter using an AC current eliminates theoretically the Seebeck influence, but our experience is that such meters have only a precision of several percent.
The micro-ohmeter is calibrated with a 100 micro-ohms resistance Ref. Sefelec 124 100.
Each manufacturer has a power supply with a different time constant for the current to reach its nominal value. It can be estimated by measuring on an oscilloscope or on a fast chart recorder that enables one to record 10 Hz. the current versus time through a standard 100 $\mu\Omega$ resistor and through samples previously chosen to have resistances within 10 % of 100 $\mu\Omega$.
A schematic of the holder is given. It was found absolutely necessary to use a four points probe technique and that the current must reach the sample directly at the center.

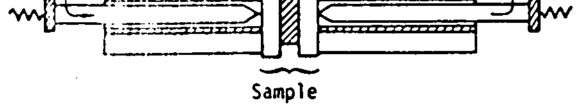

Fig. 3 : Schematic of holder

Seebeck coefficient

Description

To measure the Seebeck coefficient it is necessary to create a ΔT between the two interfaces of the copper disc soldered to the two interfaces of the thermoelectric material. The following apparatus was designed and two prototypes have been built.

A schematic is shown fig. 4 and fig. 5 is a photograph of the unit without its thermal insulating guard.

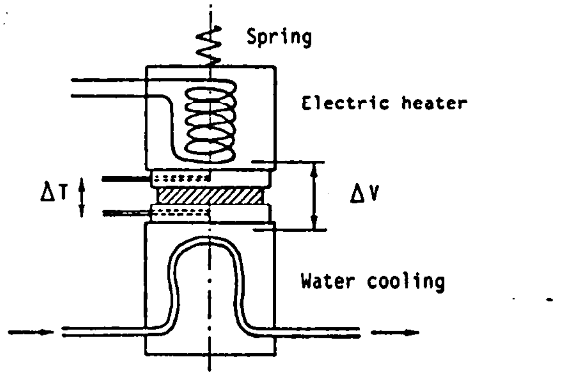

Fig. 4 : Schematic of Seebeck measurement

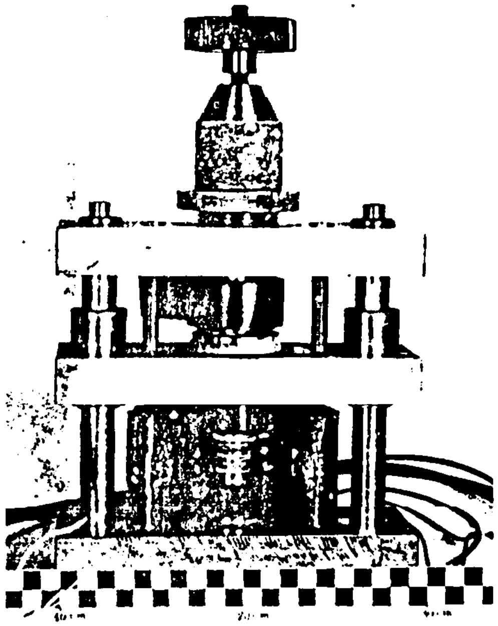

Fig. 5 : Photograph of temperature difference unit

A spring in the head gives a force of 250 to 1000 Newtons on to the interface of diameter 18 mm (area 2.54 cm^2) which corresponds to a pressure of 1 to 4 MPa (10 to 40 atmosphere).
Heat sink compound is put onto both surfaces at each interface (Dow Corning G 340).
A microvoltmeter with a sensitivity of 1 μV (A.O.I.P. VNIM 1) is used for the Δ V measurement and also for the temperature measurements made with copper-constantan thermocouples sealed in stainless steel tubing of 1 mm O.D. Thickness of thermocouples wires is 0.05 mm. The tubing is placed in 1.1. mm holes with heat sink compound.

Procedures and calibration

A sample is placed in the unit with water flowing through the base, the voltage on the electrical heater is ajusted to obtain a ΔT of the order of 15 to 20 K. It takes about 30 minutes for thermal equilibrium to be obtained.

Two slightly different procedures are used depending whether the sample contains or does not contain holes in its copper discs for temperature and voltage measurements.
To obtain values with a precision of ± 1 % it is necessary to drill 2 holes to the center of each copper disc, one for temperature and one for voltage measurements.

A study was done with 20 samples, where the ΔT and ΔV were measured on the sample's copper discs and simultaneously on the copper pieces of the unit in contact via heat sink compound with the sample's discs. It was found that :

$$\frac{\Delta V \text{ measured on unit}}{\Delta V \text{ measured on sample}} = 0.96$$

with a standard deviation $\sigma = 0.015$

The procedure consists in measuring ΔV, T_C and T_H, then inverting the thermocouples, remeasuring the above values and taking the average values. This procedure reduces thermocouple error.

Another procedure consists in measuring ΔT then either T_H or T_C.

By experience one ajusts the temperature so that the average material temperature is close to 27°C (300 K). For the materials used we have always corrected for temperature using the relation :

$$s(T) = s(300).\left[1 + 0.0015\ (T - 300)\right]$$

Thermal conductivity

The temperature difference unit previously described is used for this measurement. A standard is placed below (or above) the sample to be measured as shown in schematic below.

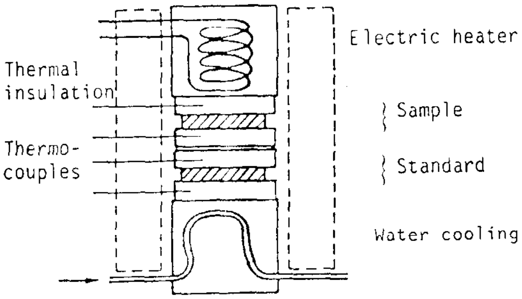

Fig. 6 : Schematic of thermal conductivity measurement

Reference standards

In the following procedure, the overall voltage across the standard and the sample is measured, so it is advantageous to associate the same type (N or P) of material of the standard as that of the sample, otherwise the overall ΔV would be very small.

This ΔV is the sum of the two terms $s.\ \Delta T$ for sample and standard and is a good indicator of the measurement coherence. The thermal conductivity of 2 N type and 2 P type samples, selected to have an average resistivity and Seebeck coefficient, was measured by the Laboratory of Solid State Physics of Professor Jean Paul Issi at the University of Louvain-la-Neuve, Belgium.
The two sets (N and P) of standards are considered to be our primary standards ; one set is kept at the Department of Professor Issi and the other at the Centre de Recherches de Pont-à-Mousson (CR-PAM) a Company in house Research Center. The set kept at the CR-PAM has the following characteristics at 300 K (27°C).

Ref. Nr	Size e * S mm * cm^2	Resist. r $\mu\Omega$.m	Seebeck s μV/K	Thermal conduct. k W/(m.K)
589 N	1.5 * 1.54	10.23	199.7	1.568
590 P	1.5 * 1.54	10.82	200.5	1.470

Secondary standards have been calibrated versus the two primary ones.
A delicate probleme in thermal conductivity measurements is the estimation of heat losses, the geometry we are dealing with where the height (thickness) of the sample is small (1.5 mm). The heat flux through the specimens is large and the lateral heat losses are comparatively small. An estimation of heat losses for such geometry [1] and [2] , leads to a value between 2 and 5 % of heat flux giving the same range of accuracy for the measured value of thermal conductivity.

Procedure

A standard and a sample are placed one above the other in the temperature differential unit. Four thermocouples T1, T2, T3 and T4 are placed in the 4 holes in the copper discs, numbered D1 to D4. Heat sink compound is used at each interface.

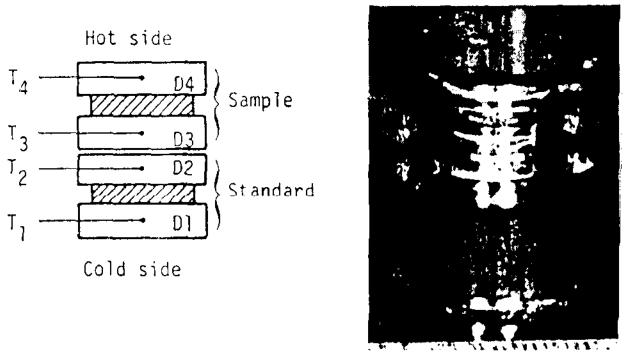

Fig. 7 : Thermocouples referencing

A procedure with thermocouples T1 to T4 is used more frequently that one with two temperature thermocouples and two differential temperature thermocouples.
With 4 temperature thermocouples, each checked in an oil bath to have an accuracy better than 0.1 K, the procedure to reduce inaccuracies due to the differences in lateral heat losses between the upper and the lower piece end to slight differences in thermocouples characteristics, consists in making 4 sets of measurements as indicated in the table below : 2 sets with the sample above the standard and 2 sets with the sample below the standard.

The 4 sets correspond to the thermocouples located in a given disc. In the table below, the second column is the location :

Piece	Location	Disc N°	Thermocouples	
			1st set	2nd set
Sample (b)	Upper piece	D 4 D 3	T 4 T 3 ΔT_b= T4-T3	T 1 T 2 ΔT_b= T1-T2
Standard (a)	Lower piece	D 2 D 1	T 2 T 1 ΔT_a= T2-T1	T 3 T 4 ΔT_a= T3-T4
			3rd set	4th set
Standard (a)	Upper piece	D 2 D 1	T 2 T 1 ΔT_a= T2-T1	T 3 T 4 ΔT_a= T3-T4
Sample (b)	Sample	D 4 D 3	T 4 T 3 ΔT_b= T4-T3	T 1 T 2 ΔT_b= T1-T2

The average of the 4 values of ΔT_b across the sample ΔT_{av} (Spl) and the average of the 4 values of ΔT_a, across the standard ΔT_{av} (Std) are calculated. The thermal conductivity of the sample is obtained from :

$$k(Spl) = \frac{e(Spl)}{e(Std)} \cdot \frac{S(Std)}{S(Spl)} \cdot \frac{\Delta Tav(Std)}{\Delta Tav(Spl)} \cdot k(Std)$$

An example of values is given below, where a microvoltmeter is used to measure the signal from thermocouple, the cold junctions are in an ice bath.

Piece	Location	Thermocouples					
		Nr	T°C	ΔT	Nr	T°C	ΔT
Sample (b)	Upper	T4	39.50	12.52	T1	39.71	12.76
		T3	26.98		T2	26.95	
	Lower	T4	27.39	11.16	T1	27.37	11.15
		T3	16.23		T2	16.22	
Standard (a)	Upper	T2	37.98	10.37	T3	37.93	10.34
		T1	27.61		T4	27.59	
	Lower	T2	26.76	10.88	T3	26.61	11.11
		T1	15.88		T4	15.50	

Piece	ΔTav	Tav
Sample (b)	11.90	27.55
Standard (a)	10.68	26.98

The temperatures are given to 0.01 for calculation purpose. The temperature correction (Taverage near 300 K) is less than 0.001 as the precision of the standard is ± 3 %. This is negligible.

$$k(Standard) = 1.568 \ W/(m.K)$$

$$\frac{e(Spl)}{e(Std)} = 1 \quad \frac{S(Std)}{S(Spl)} = 0.994 \quad \frac{\Delta Tav(Std)}{\Delta Tav\ (Spl)} = 0.897$$

therefore : k(Sample) = 1.387 W/(m.K))

4 - SAMPLING and MEASUREMENTS

The first method that comes to mind is to measure on all the pieces of a batch the resistivities, Seebeck coefficients and thermal conductivities, then calculate the mean values and standard deviations. An exemple is given below based on 10 N and 10 P samples.

		Resistivity r	Seebeck coeff. s	Thermal conductivit. k
		$\mu\Omega$.m	µV/K	W/(m.K)
N type	mean σ	11.054 0.731	205.39 4.87	1.533 0.034
P type	mean σ	11.415 0.487	199.91 2.49	1.420 0.021

This procedure requires the same number of resistance measurements, thermal conductivity measurements (with dimensions), and Seebeck measurements.
Another method is developed that reduces considerably the number of Seebeck and thermal conductivity measurement for a given number of electrical resistivity measurements and it is compared with the first method.

The methodology is dictated by the objective of reducing the time required to evaluate a given lot of material that generally in our case consists, at least, of several hundred pieces.

Depending on the degree of automation and preparation the time required for each type of measurement varies considerably, but in the case of normal laboratory measurements, the following times are a good basis for comparaison :

- resistance : 20 seconds to one minute
- Seebeck : 4 minutes
- Thermal conductivity : 20 minutes

We call a batch a large number of pieces for which we need average characteristics. Depending on the size of the batch and the degree of precision required the number of pieces selected randomly to make up a lot is chosen. In the cases that we deal with, the number of pieces per lot varies for each type of material from about 10 to several hundreds
The procedure is composed of 3 parts that are described further on :

- resistance measurement of all pieces of the batch
- selection of a limited number of pieces from the batch to make the lot (generally 10 to 15)
- measurement of Seebeck coefficient and thermal conductivity of all pieces of the lot.

Electrical Resistivity :

Generally for a given batch the dimensions are measured only on the lot of 10 to 15 pieces chosen to cover the range of resistances, the average dimensions are used to calculate resistivity from electrical resistance.
A frequency distribution curve for resistance is plotted in fig. 8 for N as well for P type material. As average dimensions have been obtained from measurements on 10 to 15 pieces, the electrical resistivity scale can be places on an axis parallel to resistance scale axis. The average values R_{av} and r_{av} and the standard deviation σ are given.

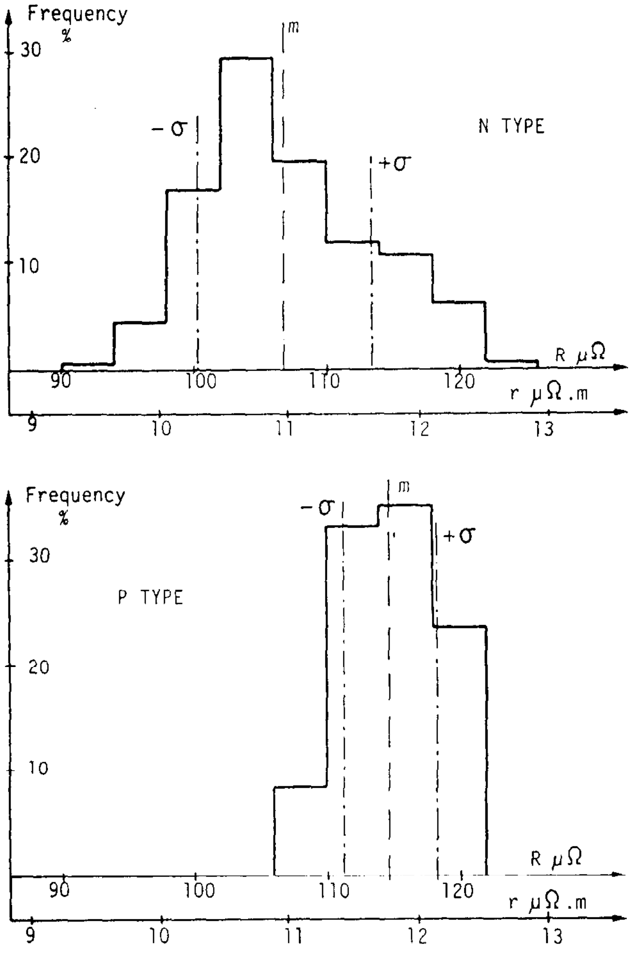

Fig. 8 : Frequency distribution of resistivity of N type and P type pollycristalline material.

Experience led us to correlate Seebeck and thermal conductivity to electrical resistivity. The correlation between Seebeck and thermal conductivity is less interesting.

Seebeck Coefficient and Thermal Conductivity :

A lot of 10 to 15 pieces of each type (N and P) can be chosen randomly or by some criteria. The size of the lot and the selection should depend on the standard deviations that have been measured for the resistivities of prior batches from the same supplier.
The table below is a comparaison between average resistivity of each batch of 217 N and 217 P pieces and a lot of 10 N and 10 P pieces chosen randomly.

	N type		P type	
	r aver. μΩ.m	σ %	r aver. μΩ.m	σ %
Batch:217 pieces	10.998	6.1	11.796	3.0
Lot : 10 pieces	10.748	7.6	11.976	3.2
Ratio : Lot / Batch	0.977	1.157	1.015	1.080

Table 1 : Lot chosen randomly

Table 1 shows that the average resistivity values are off by 1 or 2 percent when only pieces in a random lot are used.
In table 2, the pieces from the same batch are chosen to cover in a regular way the complete span of resistivities. This is an example of N type polycristalline material from Melcor.

Sample n°	Resistivity r	Seebeck coefficient	Thermal conductivity k
Units	μΩ.m	μV/K	W(m.K)
1	10.88	202.57	1.629
2	10.26	201.52	1.626
3	10.52	204.87	1.604
4	10.68	203.12	1.584
5	11.05	209.32	1.573
6	11.17	208.07	1.584
7	11.41	211.34	1.557
8	11.90	213.72	1.563
9	12.35	215.88	1.527
10	12.80	215.98	1.516
mean	11.222	208.64	1.576
σ	0.901	5.50	0.038

Table 2 : Lot selected to cover range of resistivity

From table 2, we see that the average resistivity of the selected lot is not better than that of table 1, but the object of this type of selection is to improve the precision (X^2) of the correlations between r, s and k that are given in the next paragraph.

Correlations between parameters

Simple linear correlations are sought between the 3 parameters r, s and k. There are 3 combinations :
s versus r ; k versus r and s versus k.
Examples of the 3 correlations are given below corresponding to the selected lot presented above.

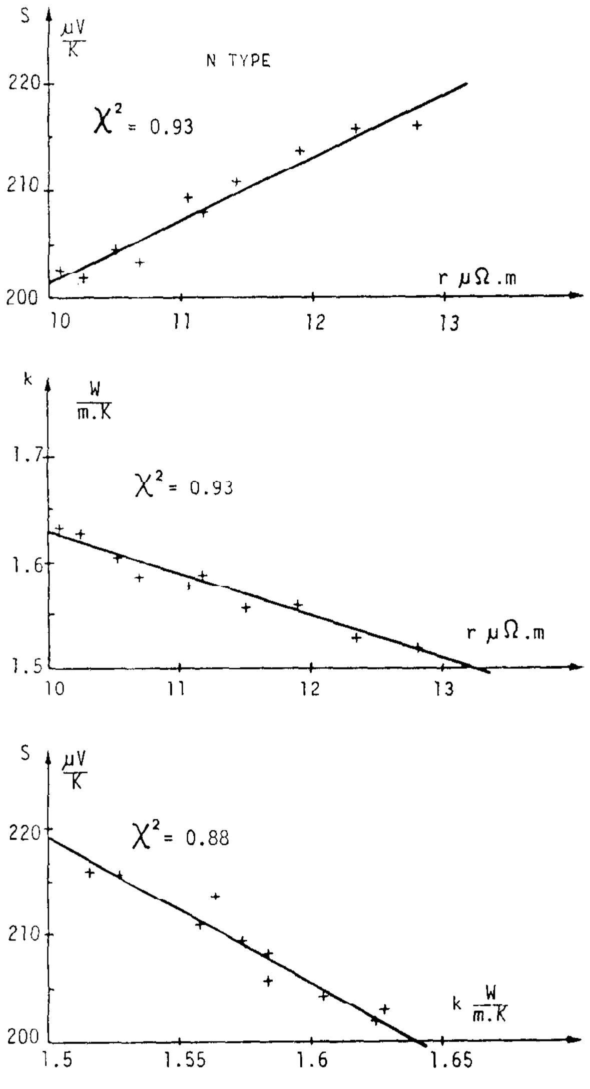

Fig. 9 : Correlations between r, s and k

The values of X^2 above 0.8 indicate that there is a valid correlation. The two first correlations are chosen because the resistivity r is the variable and all the pieces of the batch are measured for r so the average r_{av} and the standard deviation σ are known.

5 - APPLICATION TO MODELING

Large thermoelectric systems require hundreds or thousands of pieces of thermoelectric material. Complete characterisation of all pieces is not feasible economically.

An example of how the authors use the above method is given in the graph below :

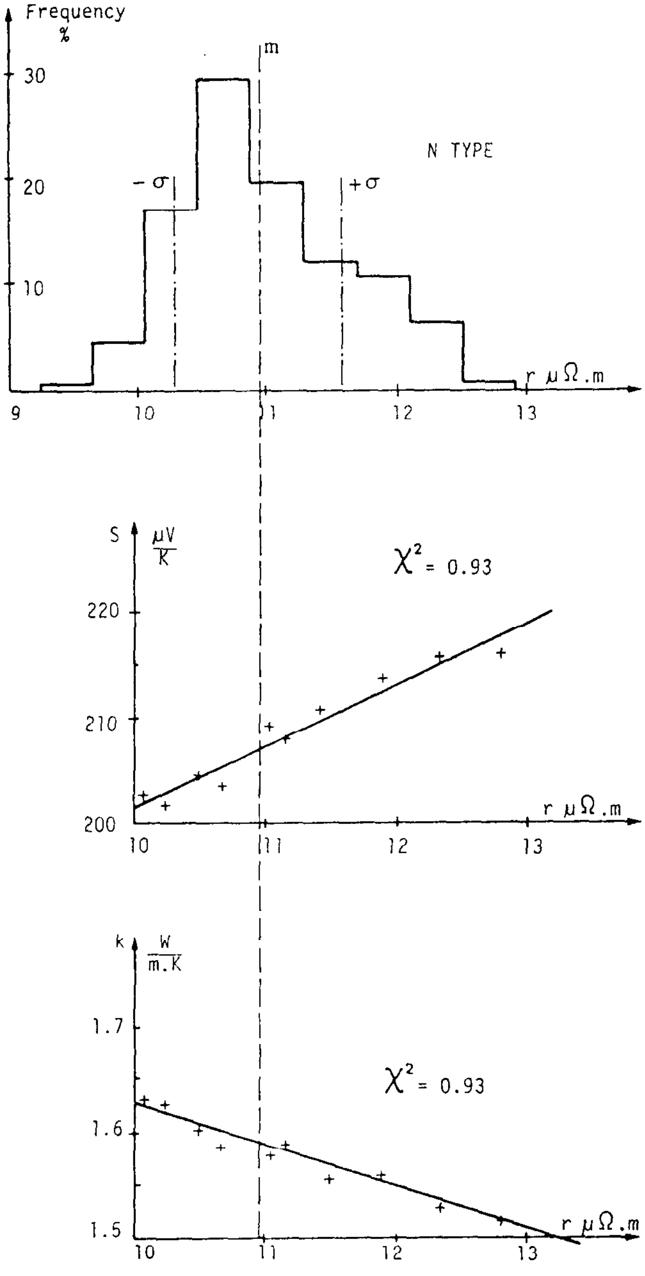

Fig. 10 : Average modeling characteristics determination for N Type material

This example corresponds to an N type material and the P Type material is shown in fig. 11. These materials are purchased from Melcor of Trenton N.J.

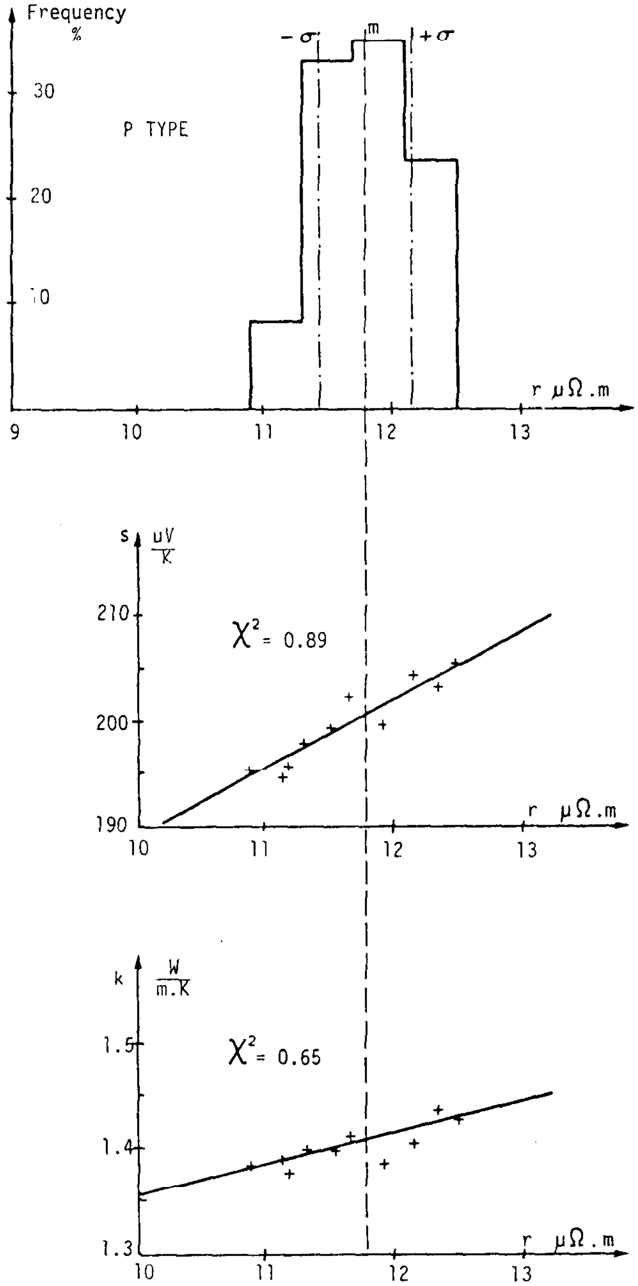

Fig. 11 : Average modeling characteristics determination for P Type material

The shape of the resistivity distribution depends first of all on the manufacturing. Sintered materials have small standard deviations of 1 to 2 %. Polycristalline materials show greater values. We have encountered from the latter standard deviations for batches from one ingot that vary from 2 to 6 % for N type and 3 to 4 % for P type.

Examination of the graphs s = f(r) and k = g(r) gives average values for s and k at average resistivity r_{av}. It is interesting to see how the coefficient of merit Z varies as a function of r ; it is shown in fig. 12.

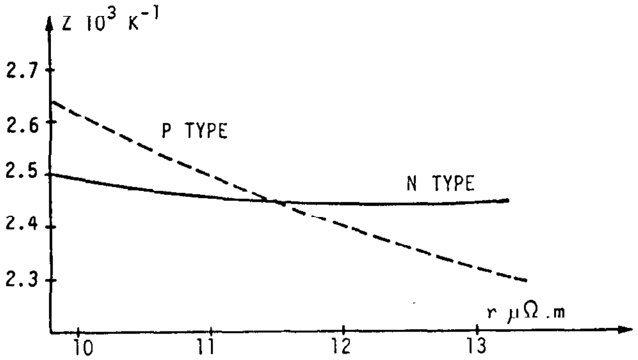

Fig. 12 : Coefficient of merit Z as a function of resistivity r for N and P Type polycristalline material

The average values have been put into thermal mathematical models of large systems, that have been checked experimentally. The calculated and measured performances are within ± 2 %. An example is given below concerning a water-water system with 480 thermoelements (240 N + 240 P type) of the dimensions : area : 1.5 cm^2 - thickness : 1.5 mm. Comparison between experimental values and computed values with the average modeling characteristics is shown in the following table :

	Experimental	Computed
Current A	198.9	198.9 given
Voltage V	12.83	12.95
Frigorific power W	2 056	2 065
Calorific power W	4 649	4 639
Coefficient of performances	0.806	0.802

6 - CONCLUSIONS

A methodology has been described to evaluate the thermoelectric characteristics of a large number of pieces of thermoelectric material such as those used in large scale systems. An apparatus to measure thermal conductivity by comparaison with a standard, and to measure Seebeck coefficient is presented. The frequency distribution of electrical resistivities of all pieces of a batch gives an average value for each type of material (N and P). A small number of pieces are selected to cover the resistance range and their Seebeck and thermal conductivity measurements are plotted versus electrical resistivity. For the small range of resistivities linear correlations are satisfactory, and lead to values of Seebeck and thermal conductivity that are successfully used in thermal modeling.

LIST OF SYMBOLS

Symbol	Units	Designation
e	m	thickness of thermoelectric material
k	W/(m.K)	thermal conductivity
r	Ω.m	electrical resistivity
R	Ω	*electrical resistance*
s	V/K	Seebeck coefficient
S	m^2	area of thermoelectric material
T	K	absolute Temperature
ΔT	K	temperature difference
ΔV	V	voltage difference
		<u>Indices</u>
av	-	average
m	-	*measured*
a	-	standard
b	-	sample

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