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REVIEW OF SCIENTIFIC INSTRUMENTS **85**, 095121 (2014)

New experimental methodology, setup and LabView program for accurate absolute thermoelectric power and electrical resistivity measurements between 25 and 1600 K: Application to pure copper, platinum, tungsten, and nickel at very high temperatures

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In this paper we describe an experimental setup designed to measure simultaneously and very accurately the resistivity and the absolute thermoelectric power, also called absolute thermopower or absolute Seebeck coefficient, of solid and liquid conductors/semiconductors over a wide range of temperatures (room temperature to 1600 K in present work). A careful analysis of the existing experimental data allowed us to extend the absolute thermoelectric power scale of platinum to the range 0-1800 K with two new polynomial expressions. The experimental device is controlled by a LabView program. A detailed description of the accurate dynamic measurement methodology is given in this paper. We measure the absolute thermoelectric power and the electrical resistivity and deduce with a good accuracy the thermal conductivity using the relations between the three electronic transport coefficients, going beyond the classical Wiedemann-Franz law. We use this experimental setup and methodology to give new very accurate results for pure copper, platinum, and nickel especially at very high temperatures. But resistivity and absolute thermopower measurement can be more than an objective in itself. Resistivity characterizes the bulk of a material while absolute thermoelectric power characterizes the material at the point where the electrical contact is established with a couple of metallic elements (forming a thermocouple). In a forthcoming paper we will show that the measurement of resistivity and absolute thermoelectric power characterizes advantageously the (change of) phase, probably as well as DSC (if not better), since the change of phases can be easily followed during several hours/days at constant temperature. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4896046]

I. INTRODUCTION

Electronic transport properties (i.e., electrical and thermal conductivities, thermoelectric effects) are important for fundamental understanding of conducting materials and for industrial processes. Electronic transport properties are directly linked to the atomic structure, crystallographic lattice, size and growth of grains, texture, defects, diffusion, formation of intermetallic phases, nucleation, precipitation, aggregation, dislocations, clustering, vacancies, etc. Therefore, electronic transport can be used to characterize changes in the solid, especially phase transformations and their kinetics. At room temperature, the resistivity of common semiconductors is about 10^3-10^9 $\mu\Omega$.cm while that of metallic alloys is between 1 and 200 $\mu\Omega$.cm.[1] Absolute thermoelectric power, absolute Seebeck coefficient, or absolute thermopower are the correct denominations of the property that will be studied. It is absolute in the sense that it is an intrinsic property of a material (physical concept) in opposition to relative thermoelectric power which is the difference of two absolute thermoelectric powers (engineer concept) used in a thermocouple or in a Peltier device. In what follows we will simply use "thermoelectric power" omitting "absolute" since this expression is the most used in the literature. The thermoelectric power of metals is generally in the range between -40 μV/K and $+30$ μV/K,[2] while that of semiconductors (for example, silicon at room temperature[3]) can reach between -1500 and $+1600$ μV/K and even more at lower temperatures. Electronic transport coefficients measurement techniques are described in Rowe's CRC Handbook of thermoelectrics[4] in Secs. 15, 16, and 32. Industrial devices have been developed for measuring semiconductor properties: (ZEM 3 of ULVAC[5] up to 1273 K, IPM-SRX of Fraunhofer[6] up to 900 K, SB100 of MMR technologies[7] (70-730 K), LSR-3 of LINSEIS[8] between -100 and $+1500\,^\circ$C following the furnace), and RZ2001i of Ozawa Science[9]) up to $1000\,^\circ$C, but most of them (except IPM-SRX to our knowledge), use static measurements. These equipments are, in general, sufficiently accurate to measure the high thermoelectric power of semiconductors but fail to measure accurately enough the low resistivities and low thermoelectric power of metals and metallic alloys, the main object of this paper. Some researchers developed laboratory devices to study metallic alloys. These devices operate at cryogenic temperatures,[10–14]

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at moderate temperature (between room temperature and 700 K-1000 K),[15–18] or at high temperatures (up to 1300 K).[19–24] Very few authors worked at higher temperatures. The exception is Vedernikov.[25] Most of the industrial experimental devices[5–9] have been cited in articles concerning semiconductors. A very interesting discussion on nonlinear and contact potential effects on the measured thermoelectric power has been published by Werheit *et al.*[26] When such effects appear, classical thermoelectric power measurement methods may fail, but not our experimental design. An interesting review paper on semi-conducting thermoelectric materials and their use has been published by Snyder and Toberer[27] and contains many references. A very general review of Martin *et al.*[28] devoted to high temperature thermoelectric power metrology has been published some years ago and completes pertinently our list of references. Martin *et al.*[28] described the two classical methods used for measuring thermoelectric power, i.e., the large temperature difference method and the small temperature difference method. Contrarily to all papers cited before, we used another method to measure thermoelectric power which has been first described by Ivory.[29] An experimental setup has been developed in our laboratory to measure resistivity[30] of liquid metals and alloys ranging between room temperature and 1575 K. The measurement of thermoelectric power[31] is based on the non-classical method of Ivory. It was continuously improved in our laboratory.[32–40] This setup was recently adapted to be used to measure the same properties for solid conducting or semi-conducting materials by Gasser *et al.*[41] It is driven by an original LabView program written by Gasser[42] to measure automatically and simultaneously (or separately) the electrical resistivity and the thermoelectric power of a pure element or an alloy as a function of temperature and time. The program enables measurements in the range of temperature for which ASTM EMF versus temperature and temperature versus EMF polynomials exist.[43] It is also necessary that the thermoelectric power of platinum, which is the reference of the thermoelectricity scale, is accurately known. It has been given by Burkov *et al.*[19] and has been improved by us in present work, in an extended range of temperatures (between 25 K and 1600 K). Every couple of metals A/B for which tables like those of NIST exist or have been determined experimentally, i.e., EMF $E_{A/B}$ as a function of temperature and EMF $E_{Pt/A}$ and $E_{Pt/B}$ as a function of temperature, may be used is our LabView program. For high temperatures or for very reactive materials, interesting thermoelectric reference wires are the tungsten and rhenium alloy thermocouple family of type C, D, or G. Their data may be introduced in the program in the tables of the screen called "configuration" which will be described later. It is more difficult to extend the thermoelectric scale to lower or higher temperatures than, respectively, 25 K and 1600 K since we lack accurate references of thermoelectricity. However, this is not impossible and we will give some indications to do it. In present work, our device has been used between room temperature and 1600 K. The LabView program was used to measure accurately resistivity and thermoelectric power as function of temperature for several pure metals to test the program and the experimental device. In this paper we give more accurate results and/or will extend the thermoelectric power and resistivity to a higher and until now unreached temperature range. Absolute thermoelectric power between 0 and 1800 K is also discussed. A second couple of interpolation formula of ATP of platinum, a little less accurate, will be given.

In Sec. II we describe our new experimental setup. The measurement procedure is presented and described in Sec. III. The absolute scale of thermoelectricity is extended and commented in Sec. IV. The LabView program is presented in Sec. V. The experimental results are presented and discussed in Sec. VI. The conclusion shows the importance of electronics transport measurement to characterize phase transition and their kinetics.

II. DESCRIPTION OF THE HIGH TEMPERATURE MEASUREMENT SETUP

The general description of the experimental setup is described in Fig. 1. The main elements are a computer on which the executable of the LabView program has been installed. This computer controls the measurements and the data acquisitions which are stored in four text files to be used later. Simultaneously, the resistivity and the thermoelectric power are plotted on graphs, either as a function of temperature or of time. It allows following the experiment in real time. In parallel, a PID temperature controller is used to

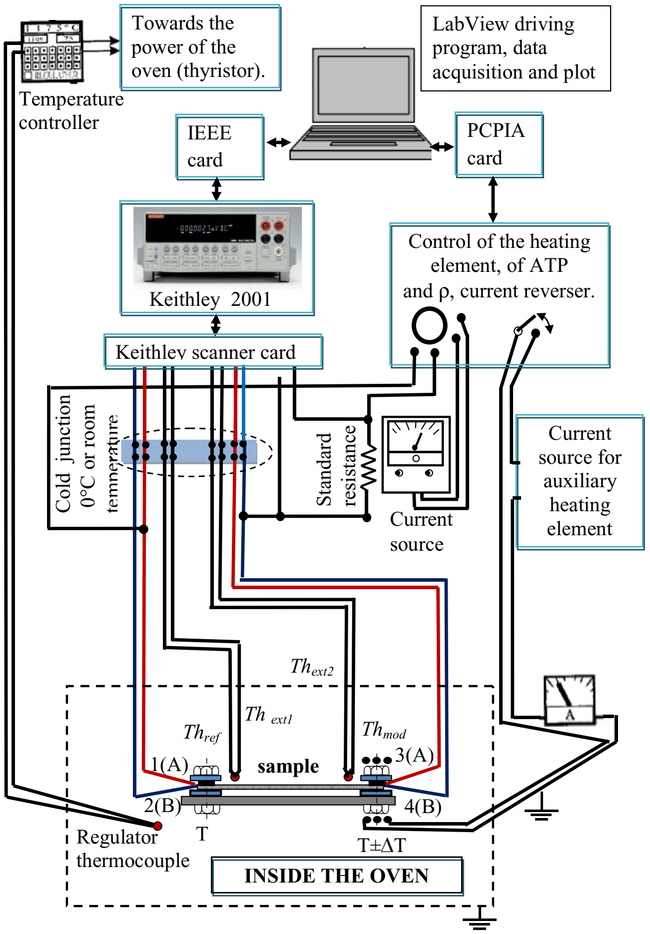


FIG. 1. Description of the experimental setup for simultaneous determination of thermoelectric power and electrical resistivity.

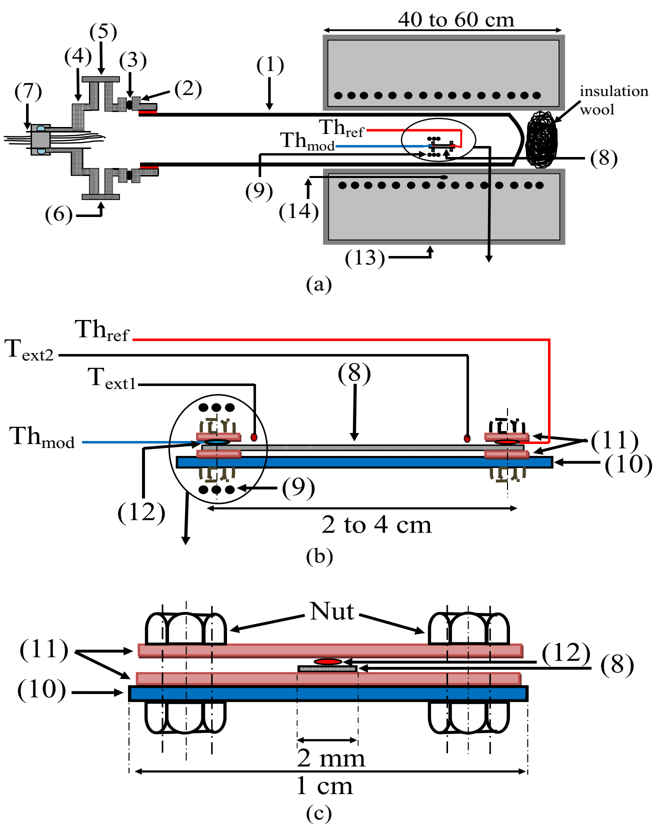


FIG. 2. (a) Measuring device introduced in a fused silica tube put into a furnace. (b) Sample fixation: longitudinal cutting presenting the whole sample. (c) Sample fixation: details of the contact with the two reference wires forming a thermocouple. Side cutting.

program the temperature of the furnace as a function of time. Measurements are made with a Keithley 2001 multimeter and its 10 channel scanner card. A current source is connected in series with a standard resistance (to measure the current) and the sample resistance. In order to avoid parasitic thermoelectric EMFs, the direction of the current is inverted when measuring the resistivity. A second current source, with alternative or direct current, is used to feed an auxiliary heater used to create a variable temperature gradient. The sample is putted in a quartz tube under vacuum or neutral atmosphere (argon) itself placed in the furnace. The general measurement setup is shown in Fig. 2(a). It is composed of a closed quartz tube (1) (or ceramic tube at higher temperatures) with a stainless steel flange (2) connected through a toric joint (3) to a 4 way vacuum cross (4). This latter is provided with necessary outputs for vacuum (5), pressure (6), and electrical connections (7). The sealing of the output (7), between wires of the electrical connections and the multi-holes ceramic pearl, is provided with epoxy resin. The sample (8) is in the middle of the furnace (13). At one end of the sample an auxiliary heater (9) creates the variable temperature gradient to measure the thermoelectric power. The main heating is provided by a horizontal furnace (13). The thermocouple (14) is linked to a temperature thermocouple controller PID"JUMO dTRON 304". The sample (circled in Fig. 2(a)) is represented in more detail in Fig. 2(b). We use four thermocouples (of K type in our measurements), two of them, Th_{mod} (modulated temperature) and Th_{ref} (reference temperature), are in physical contact with the sample and are used to measure temperature, resistivity, and thermoelectric power. The two other thermocouples T_{ext1}, T_{ext2} (Fig. 2(b)) are placed along the sample (8) to follow independently its temperature gradient. For resistivity, the sample is supplied by an independent current source. A ceramic sample holder (10) ensures the mechanical rigidity of the device. Samples can be rods, wires, ribbons, or sheets. The connections can be adapted to the shape of the sample. Figure 2(b) represents the device used with ribbons. The details of the contact with the sample (circled on Fig. 2(b)) are represented in more detail in Fig. 2(c). Two stainless steel flat parts with two holes (11) allow pressing electrodes on the sample by screwing. The thermocouple junctions obtained as balls (12) after welding are flattened to discs to increase the contact surface and improve the quality of clamping.

III. MEASUREMENT PROCEDURE

The resistivity measurements have been realized by passing a DC current (I equal or less than 50 mA in present work) through the sample, placed in series with a stable standard resistor R_{stand} (AOIP of 0.1 Ω at 20 °C). The current is deduced from the voltage measured on the standard resistance. The quality of the measurements is improved by the insertion of a current inverter circuit to eliminate thermoelectric EMFs. The voltages are measured by using either a Keithley 2000, 2001, or 2700 multimeter with its scanner card with a relative accuracy better than 0.05%. The electrodes are in contact with the sample (and must not react with it). They are used to measure resistivity, temperatures, thermoelectric power, and temperature gradient. The resistivity of the sample ρ_{samp} is given by the following equation:

$$\rho_{samp} = (U_{samp}/U_{stand}) \cdot (R_{stand}/C), \tag{1}$$

where U_{samp} and U_{stand} are, respectively, the voltages at the sample and at the standard resistance. The integral $C = \int_0^L dl/s(l)$, where L is the length, s(l) is the section at position l, and dl is the element of length, is called sample constant. It characterizes the geometry of the sample whatever it is. If its temperature dependence is not known, no more expansion occurring at the phase changes, the resistivity reported below is an "apparent resistivity". It must be corrected from the expansion to become the real physical resistivity. The method of determination of the thermoelectric power used has been first proposed by Ivory.[29] A small temperature difference ($\Delta T(t)$) varies with time t.[29,31–33,39,40,44] The voltages V_{12} (t) correspond to Th_{ref} and V_{34} (t) to Th_{mod}. They allow temperature measurements. The voltages V_{13} (t) and V_{24} (t) between the electrodes of the same kind are used for thermoelectric power measurements and are recorded while varying the temperature gradient with time. They are used in Eq. (2) for the calculation of the slope p defined below:

$$S_{samp}(T_m) = [S_{A/B}(T_m)/(p-1)] + S_A(T_m), \tag{2}$$

where $S_{A/B}$ and S_A are, respectively, the thermoelectric power of the couple A/B and of the element A. The slope p is equal to that of $\Delta V_{24}(t)/\Delta V_{13}(t)$; $\Delta V_{24}(t)$ and $\Delta V_{13}(t)$ being the (small) variations of the voltages between identical wires. T_m is the average temperature on the sample. Ideally, there is an initial temperature gradient along the sample, Th_{mod} being lower than Th_{ref}. The auxiliary heater (9) of Fig. 2(b) brings Th_{mod} at a temperature above Th_{ref} (in general, symmetrically). Typical measurements begin at $Th_{mod} = Th_{ref} - 2\,^\circ C$ and end at $Th_{mod} = Th_{ref} + 2\,^\circ C$. Before starting the experiment, a compromise is needed for choosing two important parameters: the heating rate and the current required for resistivity measurements. We use, in general, a heating rate of around 0.5 °C/min when we measure thermoelectric power. It is not recommended to measure thermoelectric power for higher heating rates than 1 °C/min since one thermoelectric power measurement needs between 2 and 10 min following the accuracy desired. At constant temperature it is recommended to measure resistivity alone, since thermoelectric power measurements induce small temperature oscillations. For resistivity measurements, we use the highest current which does not heat the sample by Joule effect. If the current is too high, the effect on the measured value of resistivity is immediate and is a good indicator of self heating. Once the sample is placed in the quartz tube, we apply successively and several times vacuum then argon pressure in order to be sure to have a clean atmosphere over the sample. The pure argon pressure inside the quartz tube is maintained at a pressure slightly higher than the atmospheric one during the whole experiment.

IV. ABSOLUTE SCALE OF THERMOELECTRICITY

In every laboratory, one is able to make a measurement of the EMF $E_{A/B}$ delivered by a thermocouple A/B and to deduce by derivation the difference of thermoelectric power between the two elements of the thermocouple. However, neither the thermoelectric power of an element $S_A = dE_A/dT$ nor the absolute Peltier coefficient Π_A are accessible experimentally. It is necessary to use the second Kelvin law linking the thermoelectric power to the integral of the Thomson coefficient between 0 K and the considered temperature. Thomson coefficient is the only thermoelectric property of a single element (pure metal or alloy) which is measurable. The first coherent scale of thermoelectricity has been established by Cusack and Kendall[45] by compiling available thermoelectric powers for different metals (pure copper, silver, gold, platinum, palladium, tungsten, and molybdenum) between 100 K and 2400 K. Today the "new" absolute scale of thermoelectricity used is that deduced by Roberts[46–48] from his own and more accurate Thomson coefficient measurements of lead (0 to 350 K[46]), lead (273 to 550 K[47]), copper, gold, platinum (273 to 900 K[47]), platinum (273 to 1600 K[48]), and tungsten (273 to 1800 K).[48] There is no unique reference metal in the whole range of temperature. Moore and Graves[49] gave smoothed values of platinum between 25 K and 1200 K, partly measured by them, partly taken from the bibliography. At low temperatures, measurements are made relatively to lead and the reference of absolute thermoelectric power is that measured by Christian *et al.*[50] in 1958 and is included in Cusack's scale.[45] Burkov[19] corrected Moore and Graves's values for lead between 100 and 273 K from the difference between the thermoelectric power of Roberts[46] and that of Christian *et al.*[50] We extended Burkov method to 25 K. So it is now possible to have an absolute thermoelectric power of platinum between 25 K and 1600 K. These values have been included in our LabView program. However, it is still possible to extend the "new thermoelectric scale of Roberts" by comparing the thermoelectric power of tungsten of Cusack[45] due to Lander[51] (+17.41 μV/K at 1800 K) to that of Roberts (+19.15 μV/K) and to correct from the same difference the Lander thermoelectric power of platinum at 1800 °C. The platinum thermoelectric power of Roberts must be algebraically 1.74 μV/K higher than that of Lander,[51] thus the thermoelectric power of platinum would be −26.92 μV/K at 1800 K in a "corrected" Roberts scale. It is the best which can be done, however, it is necessary to recall that Cusack's scale is not homogenous like Roberts one. The extension of the thermoelectric power of platinum to temperatures lower than 25 K is also possible. The missing values can be found in Appendix A of Bentley's book.[2] We can select the values above 5 K and up to 20 K (0.2 μV/K at 5 K; 0.9 at 10 K; 2.4 at 20 K). These values are taken from the curves presented in Fig. 3 of Kuhn *et al.* paper[52] and from Figs. 2 and 4 of Lee *et al.* paper.[53] A careful analysis of their curves on graph 2 and 4 give us slightly more accurate values (+0.25 μV/K at 5 K, +0.84 μV/K at 10 K, +1.67 μV/K at 15 K, and +2.44 μV/K at 20 K) and of course the thermopower of platinum is zero at zero Kelvin. They are compatible with the values reported by Bentley which have been given with one decimal less. However, the reference scale of thermoelectricity is not clearly given in their papers. It probably does not matter for such small values. The results are consistent with those of Roberts at 300 K and with the corrected ones of Moore between 100 and 300 K. However, a difference reaching 0.25 μV/K is observed between 30 and 100 K.

A. Our thermoelectric power reference

The reference thermoelectric power of pure platinum between 25 K and 1600 K obtained as described above has been introduced in our program. We used the same methodology than Burkov *et al.*[19] to correct Moore's data.[49] Burkov[19] gave an equation valid in the whole temperature range 100-1300 K. To obtain a better accuracy, we split it into two expressions, one between 25 K and 273 K (similar to Burkov's expression but with our new numerical values), the other under a polynomial form between 273 K and 1600 K. The two expressions give the same value at 273 K to within 0.001 μV/K. Our formula between 25 K and 273 K is

$$\begin{aligned} S_{Pt}(T) = {}& 0.2393\,T\,[\exp(-T/74.00) - 0.06255 \\ & + 0.2017/(1 + (T/84.35)^{**}4)] - 1.704. \end{aligned} \tag{3}$$

The temperature T is in Kelvin. The differences with the corrected thermoelectric power given by Moore *et al.*[49] are lower than 0.05 μV/K. For the temperatures between 0 and 1327 °C we fitted on Roberts values[48] by a degree 9 polynomial. The expression of the thermoelectric power of platinum as function of temperature (in Celsius) is

$$\begin{aligned} S_{Pt}(T_c) = {} & (-4.03751 + T_c^*(-0.03509 + T_c^*(0.0000906124 \\ & + T_c^*(-0.000000350184 + T_c^*(0.00000000110523 \\ & + T_c^*(-0.00000000000228982 + T_c^*(2.87318E \\ & - 15 + T_c^*(-2.10535E - 18 + T_c^*(8.30378E \\ & - 22 + T_c^*(-1.36296E - 25)))))))))). \end{aligned} \tag{4}$$

The difference with the experimental values is reduced to a maximum value of 0.015 μV/K at the place of 0.20 μV/K in Burkov *et al.*'s paper and the scale is extended to 1327 °C.

Formulas (3) and (4) ensure that the numerical error on the formula is totally negligible compared to the experimental errors. Between 25 K and 273 K we used corrected values of platinum in order to be consistent with Roberts[46] values of lead. Between 273 K and 1600 K we used directly the "new" and more accurate thermoelectric power scale of Roberts.[48]

We are also able to propose two scales between 0 and 273K on one side and 273 to 1800 K on the other side. In this range Burkov's formula was not able to reproduce correctly the experimental values. We simply used two polynomial expressions fitted on the values discussed above. The temperatures are in Kelvin:

$$S_{Pt} = \sum_0^9 B_{(i)} T^i . \tag{5}$$

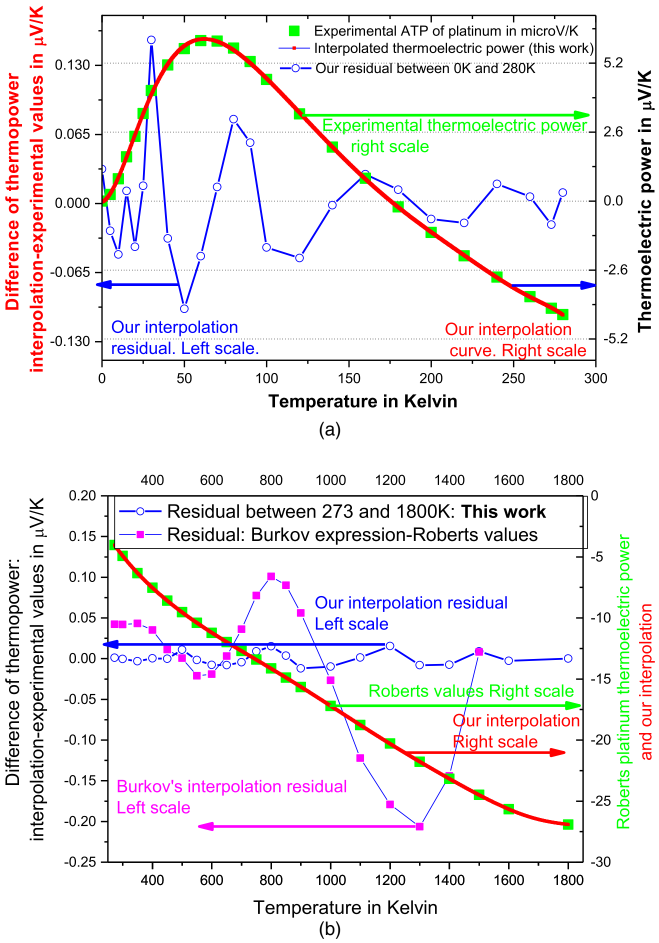
(a) Between 0 K and 273 K

$$B_{(0)} = -0.03244;\ B_{(1)} = 0.01909;\ B_{(2)}=0.0099;$$
$$B_{(3)} = -2.98338 \times 10^{-4};\ B_{(4)} = 4.07308 \times 10^{-6};$$
$$B_{(5)} = -3.25039 \times 10^{-8};\ B_{(6)} = 1.60666 \times 10^{-10};$$
$$B_{(7)} = -4.84368 \times 10^{-13};\ B_{(8)} = 8.15709 \times 10^{-16};$$
$$B_{(9)} = -5.87742 \times 10^{-19}.$$

(b) Between 273 and 1800 K

$$B_{(0)} = 22.1561; B_{(1)} = -0.23328; B_{(2)} = 9.7007 \times 10^{-4};$$
$$B_{(3)} = -2.68107 \times 10^{-6};\ B_{(4)} = 4.80917 \times 10^{-9};$$
$$B_{(5)} = -5.60664 \times 10^{-12};\ B_{(6)} = 4.18456 \times 10^{-15};$$
$$B_{(7)} = -1.92118 \times 10^{-18};\ B_{(8)} = 4.93085 \times 10^{-22};$$
$$B_{(9)} = -5.40695 \times 10^{-26}.$$

We represent in Fig 3(a) the thermopower of platinum of Moore *et al.*;[49] between 25 K and 273 K corrected from the difference between Cusack's and Roberts scale and added the values of Lee *et al.*[53] and the value at 0 K. The residual is plotted on the left scale and is between −0.10 and +0.15 μV/K. In Fig 3(b) we plotted the Roberts values with the corrected platinum value at 1800 K and compared to our interpolation curve. On left scale we plotted our residual curve which varies between −0.01 and +0.01 μV/K. The fit is excellent. In Fig. 3(b), we also compare Burkov's and our difference with the tabulated values of Roberts. Dividing the temperature scale into two regions allows us to fit very accurately the thermopower of platinum.



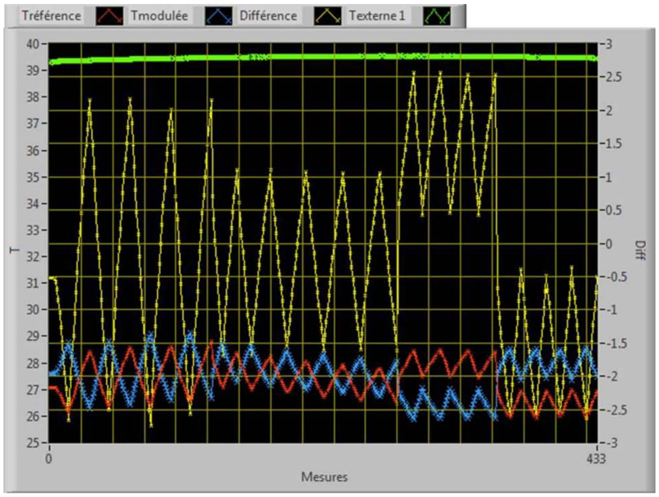
(a)
(b)

FIG. 3. (a) Absolute thermoelectric power of pure platinum between 0 and 273 K and our interpolation formula (right scale): Difference of thermoelectric power between measurements of Moore[49] in Cusack's scale corrected from the difference between Cusack and Roberts scale and our interpolation formula (left scale). (b) Absolute thermoelectric power of pure platinum between 273 K and 1800 K (right scale): Difference of thermoelectric power between measurements of Roberts[48] (determined from direct measurement of the Thomson coefficient) and our interpolation formula (left scale).

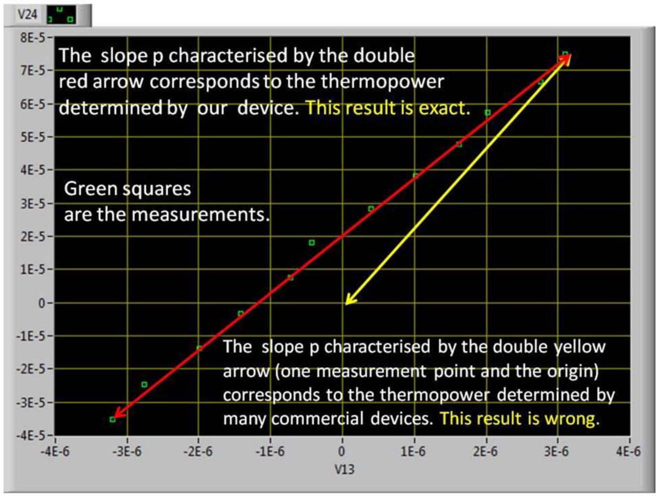
V. LABVIEW PROGRAM

All measurements are recorded in four files in text format for further processing, two for resistivity and two for thermoelectric power. The LabView program needs first to be parameterized. Three screens can be selected. In a first screen called configuration we need to choose the general parameters: the kind of Keithley multimeter used (K2000, K2001, or K2700), the kind of measurements: resistivity alone, thermoelectric power alone, or simultaneous measurements of resistivity and thermoelectric power. Other parameters, specific to the voltmeter (GPIB address, resolution, range, offset compensation, filters, etc.) can also be chosen. We have also to introduce the geometrical constant C necessary to get the resistivity from the sample resistance measurement. For measuring thermoelectric power, we have to choose the interval of temperature ΔT around the reference temperature. It is generally set to $-2\,^{\circ}$C to $+2\,^{\circ}$C but it can also be asymmetrical: for example, ($\mathrm{Th_{mod}} - \mathrm{Th_{ref}}$) can be varied between $+3\,^{\circ}$C and $+7\,^{\circ}$C. This is of great interest to make measurements near the room temperature. The thermoelectric power measurements can be done by selecting one of the eight thermocouples for which polynomials exist in NIST[43] tables (B, E, J, K, R, S, T and N). Two different kinds of identical thermocouples can be used, those which are in contact with the sample ($\mathrm{Th_{mod}}$ and $\mathrm{Th_{ref}}$) and the "external" thermocouples ($\mathrm{T_{ext1}}$ and $\mathrm{T_{ext2}}$). The parameters of the chosen thermocouples to calculate, under a polynomial form, the temperature from the EMF A/B, the thermoelectric power of the couple A/B, and the thermoelectric power of the reference wire relative to platinum at temperature T are tabulated under different polynomials following the temperature range. They are not reported here and can be found in the ASTM book.[43] The program selects automatically the most accurate polynomial to calculate temperature and thermoelectric power.

On a second screen called "resistivity," the ten last measurements appear in a table. Measurements concerning the resistivity are represented on a plot either as a function of temperature or as a function of time. The scale can be chosen and changed during the experiment. For resistivity measurements, the geometric sample constant C depends on the measurement accuracy of the dimensions (width, length, and thickness). Sometimes the geometric constant of the sample is difficult to measure accurately (typical accuracy is 5%-20%). To characterize phase changes only, it is possible to make relative measurements. The "relative resistivity" can arbitrarily be set to 1 at room temperature at the beginning of the experiment. An alternative is to first determine independently the resistivity at room temperature (on a larger sample, for example, for which the dimensions can be more accurately measured). Then, at room temperature, we set the geometrical constant C of the (smaller) sample (which will be used for high temperature measurements) to a value in order to get exactly the same resistivity as that determined more accurately at room temperature.



(a)



The slope p characterised by the double red arrow corresponds to the thermopower determined by our device. This result is exact.

Green squares are the measurements.

The slope p characterised by the double yellow arrow (one measurement point and the origin) corresponds to the thermopower determined by many commercial devices. This result is wrong.

(b)

FIG. 4. (a) LabView program, front panel 3: Temperatures (left scale) and difference of temperature (right scale yellow dots and curve). (b) LabView program, front panel 3bis: V_{24}(t) versus V_{13}(t) (to determine the slope p).

On a third screen we represent on a table the ten last measurements of thermoelectric power. On a graph (Fig. 4(a)) we plot (left scale) temperatures as a function of the number of measurement iterations (blue: $\mathrm{T_{mod}}$, red: $\mathrm{T_{ref}}$, and green: $\mathrm{T_{ext1}}$). On the right scale of the graph we represent the difference of temperature Diff $= \mathrm{T_{ref}} - \mathrm{T_{mod}}$ (yellow dots and large zigzag curve on the graph). As can be observed on this example, we first measure between -2.5 and $+2\,^{\circ}$C then we skipped to the interval -1.5 and $+1\,^{\circ}$C, then to $+.5$ and $+2.5\,^{\circ}$C, and finally -2.5 and $-0.5\,^{\circ}$C. Each increase and decrease of the difference of temperature (yellow curve left graph) generates one point on the graph where the thermoelectric power is plotted as a function of temperature or of time (not represented). We are thus able to make measurements in different quadrants and so to overcome the problems of nonlinearity and of Schottky voltage at the junction discussed by Werheit *et al.*[26] To be sure that the sample is placed in the most adequate position of the furnace, we also measure and plot the difference of temperature $\mathrm{T_{ext1}} - \mathrm{T_{ext2}}$ (not represented). We can move the furnace relatively to the quartz tube to adjust the "natural" temperature gradient along the sample. We can also visualize the curve V_{24} (t) as a function of V_{13} (t) whose slope p enters into Eq. (2). A typical measurement is plotted in Fig. 4(b). As can be observed, the linear curve does not pass through zero (0.0, 0.0). In general, the classical measurement method (the thermoelectric power being defined by ΔV/ΔT) is done by taking one point (one ΔV and one ΔT) and by postulating that at $\Delta T = 0$, $\Delta V = 0$. Evidently this is wrong, especially at high temperatures. Ivory's dynamical method[29] overcomes this difficulty and gives a correct thermoelectric power even if the two thermocouples $\mathrm{Th_{mod}}$ and $\mathrm{Th_{ref}}$ are not exactly identical. In the LabView program, we are also able to choose the quadrant and the range in which the measurements have to be done. In general, thermoelectric power measurements are made at constant temperature. This is not the case in our measurements. We have shown that if the increase of temperature is sufficiently slow (0.5-1.0 deg/min for metallic alloys), we can measure continuously the thermoelectric power. The "reference temperature" increases linearly with time while the "modulated temperature" oscillates around the ramp of the "reference temperature".

VI. RESULTS AND DISCUSSION

We will now proceed in two steps. First, we want to check the accuracy of the thermoelectric power measurements and the self consistency relatively to thermoelectric "standards" especially for thermoelectric power. Our measurements are based on a thermoelectric scale where copper, platinum, and tungsten play an important role. We also present our new resistivity measurements which are not linked to a reference scale as for thermoelectric power. Second, we will make measurements to extend the measurement range and present new accurate results in very severe environment (temperatures up to 1600 K) in the new thermoelectric scale.

Resistivity is a bulk property when the thermoelectric power characterizes the material at the contact with the reference element. We used platinum (Johnson Matthey) and copper (Jumo) high purity wires (99.99%), while the purity of the Johnson Matthey nickel rod is 99.999%. To obtain the resistivity we must exactly know the shape of the material and this is the most important source of error especially when the sample is small. To overcome this difficulty we make a preliminary measurement by the four probe technique on a larger sample, near room temperature at a regulated temperature, variable between 15 and 40 °C. We used a 2500 mm long and 0.5 mm diameter copper wire, an 1100 mm long and 0.2 mm diameter platinum wire, and a 130 mm long and 5 mm diameter nickel ingot. Dimension measurements are repeated and we used a mean value of about 20 measurements. The accuracy on the diameter is 1 μm; the accuracy of the length is 1 mm for copper and platinum wire and 0.05 mm for the nickel ingot (between potential electrodes). The overall accuracy on the resistivity is better than 1%. Once an accurate resistivity is determined near room temperature, we make measurements at high temperature with a smaller sample. At the beginning of the experiment, the geometric constant is introduced in the LabView program in order to get exactly the same resistivity as the large sample at room temperature. At 300 K we obtained a resistivity of 1.710 $\mu\Omega\cdot$cm for copper, 11.06 $\mu\Omega\cdot$cm for platinum, and 7.355 $\mu\Omega\cdot$cm for nickel. These values are 0.4% below the value of the CRC Handbook of Physics and Chemistry[1] for copper, 1.7% above for platinum, and 2.1% above for nickel. Concerning platinum we are 1% above Burkov.[19] We are also 1.3% higher than Laubitz *et al.*[54] for copper and 1.4% for platinum (at 273 K).

To obtain the absolute thermoelectric power we must make a measurement and then subtract the thermoelectric power of the reference element in contact with the sample. We must also choose a scale of thermoelectricity. The knowledge of an accurate reference thermoelectric power is necessary. The purity of the metal and of its crystallographic state may also have an influence on the result.

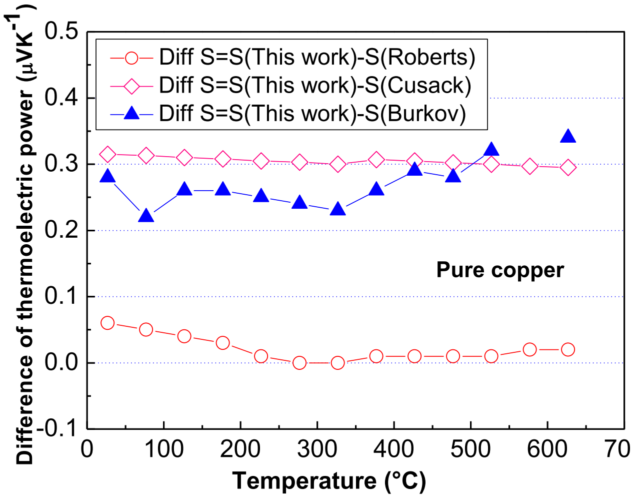


FIG. 5. Pure copper: Difference of thermoelectric power between this work and, respectively, Burkov[19] (—▲—), Cusack[45] (—◇—), and Roberts[47] (—○—).

A. Absolute thermoelectric power

We first compare our measurements with the bibliography, on our samples, with our experimental design, and with our scale of thermoelectricity introduced in the LabView program. As indicated before, we selected the "new" scale of thermoelectricity of Roberts.[46–48] We used, as reference wires, the K type thermocouple except for tungsten where we used an S thermocouple. For temperature above 273 K, the thermoelectric power of four metals has been determined. The first one is copper. We plot in Fig. 5 the difference between thermoelectric power of Roberts,[47] Cusack,[45] and Burkov[19] and our one. The scale of thermoelectricity used by the different authors may also be different. We are at a maximum of 0.06 μV/K of the Roberts value which can be considered as an excellent result, it is probably the best accuracy that an experimentalist can obtain at high temperatures with a now quasi-industrial experimental design. This is coherent since our scale of thermoelectricity is the same. The only difference is the sample. The difference is larger with Cusack[45] and Burkov[19] values. Our results are nearly 0.3 μV/K below theirs. However, Cusack's values are based on his older thermoelectric power scale while Roberts thermoelectric power values are directly linked to his new scale of thermoelectricity deduced after 10 years work on Thomson coefficient measurements for lead (1977, 1981), copper (1981), platinum (1981, 1985), and tungsten (1985). All thermoelectricity tables and NIST polynomials are based on the Roberts scale. They have been introduced in the LabView program. Thus, it is fully consistent that our results fit better with Roberts's values and Fig. 5 is representative of the scale of thermoelectricity chosen and of the high quality of our measurements. We reported in Fig. 6 the thermoelectric power of copper together with Roberts's values.[47] It is clear that we get excellent results. We did the same with platinum (Fig. 7) which is the best calibrating material for this apparatus. As mentioned before, we used Roberts's data[48] of pure platinum to calculate our reference of thermoelectricity. Therefore, platinum thermoelectric power measurements enable a direct comparison

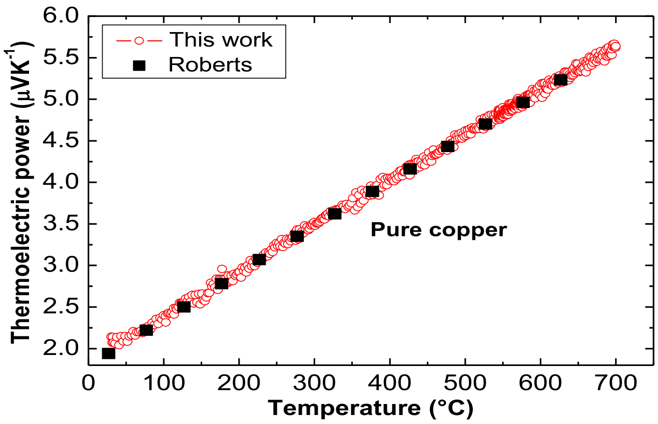


FIG. 6. Thermoelectric power of pure copper as a function of temperature. This work (—○—) compared to the Roberts one[47] (■).

with Roberts's values. The curve of Fig. 7 is also in very good agreement with Roberts's results. The remaining difference is due to the fact that Roberts used platinum 67 while the wire used in this test is pure platinum wire from an S thermocouple. In Fig. 8 we represent our measurements of the thermoelectric power of tungsten also measured by Roberts.[48] To do these measurements we used S thermocouples. Here again our results are in very good agreement with Roberts, the only point which is different is that at 1327 °C which is 0.36 μV/K below Roberts point. In Fig. 9 we represent the thermoelectric power of pure nickel. It has been extensively studied at low temperatures. Our results are in excellent agreement with Burkov[19] at all temperatures measured by them and with Ponnambalam[15] but only between 300 and 700 °C. Our results disagree with those obtained with IPM-SRX appearing in different documents downloadable on Fraunhofer site.[55] The only measurement values at high temperature[25,56] have been measured up to 1200 °C. These measurements are based on the old Cusack-Kendall[45] thermoelectric scale. The ferromagnetic transition is well observed by a change of the sign of the temperature dependence of thermoelectric power (Fig. 9 inset) at exactly 360 °C.

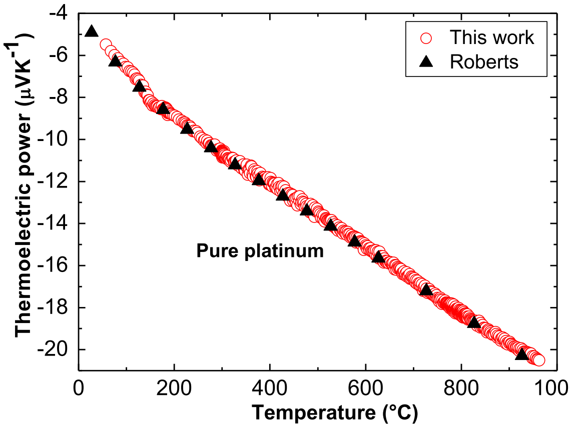


FIG. 7. Thermoelectric power of pure platinum as a function of temperature. This work (○) compared to the Roberts one[48] (▲).

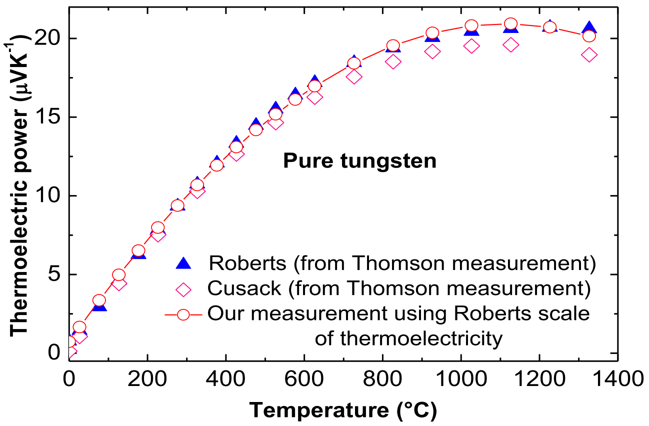


FIG. 8. Thermoelectric power of pure tungsten as a function of temperature. This work (—○—) compared to that of Roberts[48] (▲) and Cusack[45] values (◇).

B. Electrical resistivity

The resistivity has first been determined at room temperature (see above) with a good accuracy. Smaller samples are put in our high temperature design and are then measured simultaneously with thermoelectric power.

1. *Copper*

The resistivity of copper is reported in Fig. 10. We also reported results of the literature: those of CRC handbook[1] and of Schuster *et al.*[57] who retreated the old Matula's data.[58] We corrected our raw measurements from the expansion by using Powell and Tye[59] expansion measurements. Our results are lower than the bibliography[57] at high temperatures. The maximum difference is observed at 800 °C and reaches −4%.

2. *Platinum*

Our results are represented in Fig. 11 together with other authors[19,28,59,60] up to 1000 °C. We did not find measurements at higher temperature except one "non-contact" method

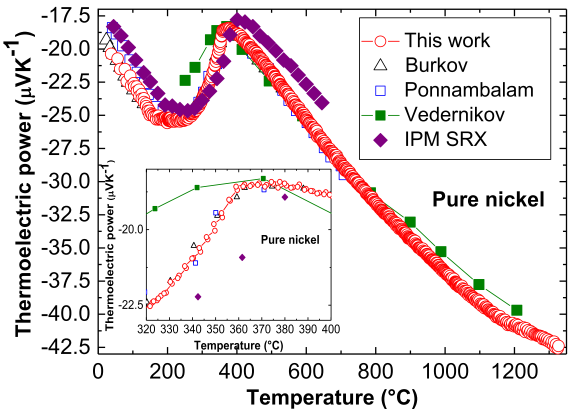


FIG. 9. Thermoelectric power of pure nickel as a function of temperature: This work (—○—) compared to that of Burkov[19] (△), Ponnambalam[15] (□), Vedernikov[25] (—■—), and IPM SRX[55] (◆). Inset: Thermoelectric power of pure nickel as a function of temperature. Expanded scale between 300 °C and 450 °C. The Curie temperature appears clearly.

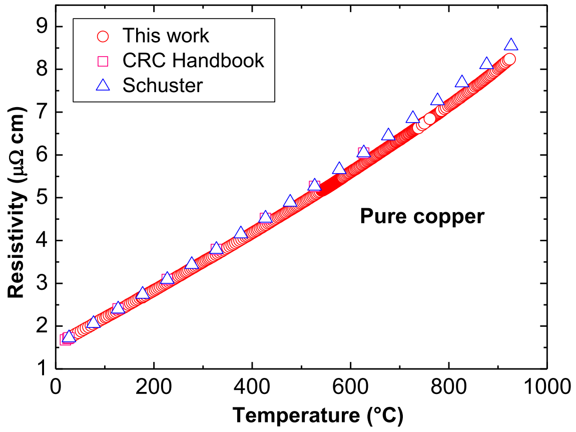


FIG. 10. The resistivity of pure copper as a function of temperature: This work (○) compared with the CRC Handbook values[1] (□) and with Schuster values[57] (△).

from 200 to 2600 °C (liquid and solid)[60] by a one shot pulse heating, the whole experiment being made during less than 30 μs. These results are extraordinarily accurate for such kind of measurement.

3. Nickel

We illustrate in Fig. 12 the new resistivity measurements of pure nickel from room temperature to 1330 °C compared to other results. Measurements are in a relative good agreement with those of literature (Burkov and Laubitz). On the resistivity, the difference is of about 4% with Ponnambalam. As Wilthan[60] for platinum, Cezairlian *et al.*[61] use a short pulse of current of less than 1 s. They give experimental results between 1300 and 1700 K which are reported in Fig. 12. Wolfenden *et al.*[62] indicate that nickel has a Curie temperature at 633 K (360 °C). This ferromagnetic transition appears also clearly by a knee in resistivity versus temperature curve at this temperature (Fig. 12 inset).

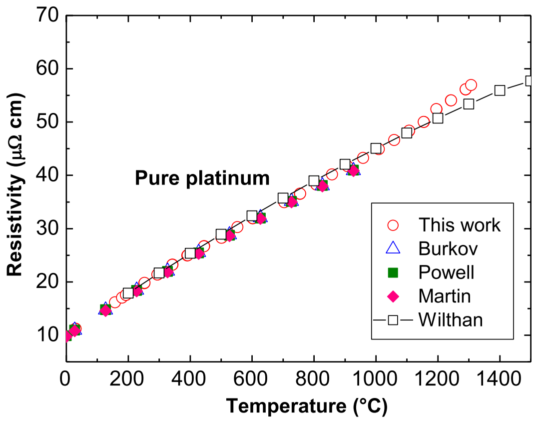


FIG. 11. The resistivity of pure platinum as a function of temperature: This work (○) compared with the results of Burkov[19] (△), Powell[59] (■), Martin[28] (◆), and Wilthan[60] (–□–).

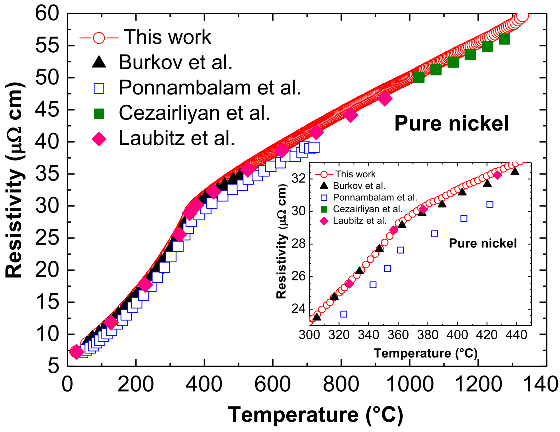


FIG. 12. The resistivity of pure nickel as a function of temperature: This work (–○–) compared with the results of Burkov[19] (▲), Ponnambalam[15] (□), Cezairliyan[61] (■), and Laubitz[54] (◆). Inset: Resistivity of pure nickel as a function of temperature between 300 and 450 °C. The Curie temperature appears clearly.

C. Thermal conductivity

The electrons conduct as well heat than electricity. Thus, thermal conductivity λ is linked to electrical resistivity ρ and to thermoelectric power S by the general relation: $\lambda = (L_0\text{-}S^2)T/\rho$ where L_0 is the "Sommerfeld value" of the Lorenz number. The Wiedemann Franz law which links the electrical to the thermal conductivity is well known and is simply the approximation of this general relation when the thermoelectric power S is neglected. This is not possible with noble and transition metals. This has been extensively discussed by Giordanengo *et al.*[63] We calculated the thermal conductivity from our resistivity and thermoelectric power measurements. The results are very good for platinum (at 3% of the CRC handbook and at 6% from Powell *et al.*[59] values, a little less for nickel and copper). We represent in Fig. 13 our thermal conductivity compared to the values of the literature. As can be seen, our results are in an overall satisfactory agreement

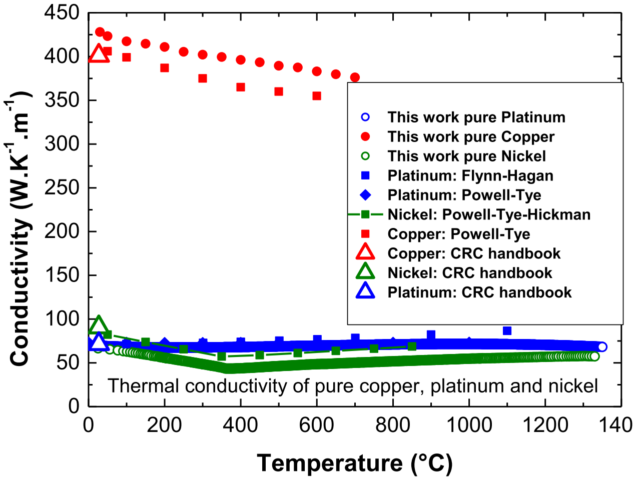


FIG. 13. Thermal conductivity of pure platinum, copper, and nickel as a function of temperature. Our results (circles) are compared with those of CRC Handbook[1] (triangles), Powell-Tye[59] (◆) and (■, red), Flynn-Hagan[64] (■, blue), and Powell-Tye-Hickman[65] (–■–, green).

with the literature[64–71] if one takes into account a more important dispersion of the experimental results than for resistivity and thermoelectric power.

VII. CONCLUSION

The methodology, the experimental device, and the LabView program used gave very good results for an either positive or negative, an either low or high value of the thermoelectric power (pure silicon wafers have been measured at room temperature). Measurements are also in very good agreement with the standards of Roberts's papers[46–48] who defined the thermoelectric power scale. They are consistent with earlier measurements at low and medium temperatures. Measurements of resistivity are very precise and reproducible provided that the resistivity has been accurately measured before at room temperature. The program and the device are very flexible. They allow measurements of a large variety of shapes of conducting samples and of various materials from the most conducting metal to intrinsic semiconductor. But the electronic transport properties are not only interesting in themselves; they are also a very sensitive tool to characterize the change of phase of conductive materials and of their kinetics as observed with the Curie temperature of nickel. This will be the aim of part 2 of this paper.

ACKNOWLEDGMENT

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