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Early and current experimental methods for determining thermal conductivities of metals

Simón Reif-Acherman [*]

School of Chemical Engineering, Universidad del Valle, A.A. 25360 Unicentro, Cali, Colombia

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ABSTRACT

Different experimental techniques were developed and proposed for determining the thermal conductivities of metals in the eighteenth and nineteenth centuries. Each one reflects the ingenious application of a number of physical principles, some of which only emerged in the panorama of the physical sciences of the moment. The production in recent decades of many revolutionary materials with structures that vary on the length scale of several nanometers, with applications in electronic and optoelectronic devices, have driven a natural evolution in the experimental techniques from steady-state to transient methods, involving modern theoretical models, advanced instrumentation, and ingenious practical developments. This article presents a historical-technical account of the whole evolution, highlighting the main advantages and disadvantages of those most important, some of the technological circumstances that prompted the emergence of new techniques, as well as their comparative estimation capabilities.

1. Introduction

Thermal conductivity is a basic property of many materials. Its application ranges from the transfer of heat in solar panels and cooling of computer chips to materials used in building insulation and dentistry, among others. Extreme values of thermal conductivities provide opportunities for specific studies, as it is the case, for example, with materials like diamond, with high thermal conductivity, used for the mounting of superconductors in order to prevent damage from overheating and other applications in thermal management of electronics, or thermoelectric materials, such as skutterudite minerals, poor thermal conductors, with great potentials for uses in small-scale refrigeration and power generation applications.

It is nowadays known that values of thermal conductivity of a given material may vary due to differences in its composition, be affected by moisture or other conditions, change with time and with mean temperature and temperature difference, and depend upon its prior thermal history. Even more special considerations appear with substances exhibiting appreciable inhomogeneities, anisotropies, rigidity, or especially high or low resistance to heat flow. Measurement of these properties becomes then a problem that affects many areas of material science and engineering.

Unlike electrical conductivity, thermal conductivity cannot be measured directly. This particular circumstance has contributed from past time to force the utilization of ingenuous methods for its determination. A substantial number of the currently used methods for the measurement, including those where temperature of the material measured does not change with time, and others where measurement is done during a process of heating up, is derived to a greater or lesser degree of techniques originally developed more than a century ago. Among a great variety of materials in nature, metals, in pure condition or as a component of high-strength alloys, become from then the backbone of industrial development. Their use in nineteenth century was not only limited to boilers and other thermal machines for different purposes, but also involved several other areas, such as the manufacturing of instruments of precision. Studies on heat conduction involving these materials, meanwhile, had become in those times a widely, implicit or explicitly, activity from both, practical and theoretical, viewpoints, covering from heating and cooling steps at different scales of industrial processes, to subjects of increasing interest, such as the, by then, intriguing subject of the temperature of earth's interior and its behavior with time. The studies on the experimental determination of thermal conductivities of metals and alloys, as well as their temperature dependence, aroused the

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[*] Tel.: +57 23392335; fax: +57 23312935.
E-mail address: simon.reif@correounivalle.edu.co

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historical interest of scientists of different nationalities in the nineteenth century and the first decades of the twentieth century, thus also contributing to the understanding of the thermal properties of those materials and to the whole phenomenon of heat conduction in these materials and its difference from those of radiation and convection. The discovery of new materials, mainly from the second part of the twentieth century, meant a challenge in the study of their properties and in the development of ingenious and accurate methods for their experimental determination.

An interesting recent article presents a summarized account of the first contributions to the study of thermal conductivity, as well basic details of some few of the original methods of its measurements in the eighteenth and nineteenth centuries [1]. This article attempts provide an appropriate picture of the evolution of the methods used in the determination of this property, which is, in no way, a full description of all the many developed experimental measurement techniques for metals, and in some cases for solids in general. The picture begins with the classical techniques, presenting a full account of the more relevant facts and details related with the early experimental contributions to the subject and their corresponding responsible persons. A second part shows the general details of the most important current techniques used for determining thermal conductivities of a 'world' of new materials and the main motivations that forced their development.

1.1. The formal beginning of the story

While the idea of thermal conductivity is implied from the seventeenth century in concepts associated with the transfer of heat from one body to another, such as heat itself, temperature, specific and latent heats, and of the flow of heat, it was the French mathematician and physicist Jean Baptiste Joseph Fourier (1768–1830) the first to give, historically speaking, a thoroughly definition of conducting power and to expose a mathematical theory of heat conduction. Both were set forth by him in his *Théorie Analytique de la Chaleur*, published in 1822 [2]. Physicists as his countryman Jean-Baptiste Biot (1774–1862) had preliminarily worked with continuous bodies, separating the treatment of the interior heat transfer and the surface effects. Others such as the also French Guillaume Amontons (1663–1705) and the German Johann Heinrich Lambert (1728–1777) had previously carried out experiments about the variation of temperature of a bar heated at one end, concluding the first that the decreasing of temperature with the distance was linear, and the second logarithmic. Regardless of the correct answer, what was shown was an approximate complete qualitative, although not quantitative, understanding of this particular process of conduction of heat. It was Fourier who first brought order out of the confusion existing about the subject [3].

Beginning in 1802, and alternating different models, Fourier was able to formulate a theory, which was later experimentally confirmed. A Memoir on "the propagation of heat in solids", presented five years later, focused on heat diffusion between discrete masses and exposed some special cases of continuous bodies (bar, ring, sphere, cylinder, rectangular prism, and cube). Partially based on the Newton's law of cooling, it means that the flow of heat between two adjacent molecules is proportional to the difference of their temperatures, Fourier was able to show that temperature T could be expressed for the more general equation of motion for an infinite three-dimensional solid as a function of the corresponding positional coordinates x, y, and z, and time t, according the partial differential equation:

$$\frac{\partial T}{\partial t} = k\left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2}\right) \tag{1}$$

where k is the thermal conductivity depending of the material of the solid. The so-called heat equation, according Fourier, described how heat traveled through materials as a wave, which, no matter how complex it is, could be represented by the addition of many different simple waves, expanded and mostly mathematically represented by geometrical series of sines and cosines.

A heated annulus in two situations, steady and transient states, was the first case to which Fourier not only applied his mathematical theory but also compared the results of his analysis with experimental facts. The equipment described was too simple. The element was a polished iron piece of about 30 cm diameter, held in place by wooden supports, heated by an adjustable burner, and provided with six holes drilled halfway into the ring, four of which holding thermometers. Steady state was achieved when one point in the ring was heated while rest of the ring was allowed to radiate heat freely. Transient state was analyzed meanwhile when the ring was placed halfway into a furnace and then removed to an insulating bath of sand. An initial distribution of uniformly hot around one half, and cold around the other, quickly changed to a semi-uniform state as heat began to flow from hot to cold. According Fourier, the irregular distribution of temperature could be described by frequencies of several component sinusoidal waves around the ring. The initial simple sinusoidal pattern would gradually dampen until the ring was at a uniform temperature. The addition of explicit statements of initial conditions to this and other experiments allowed the corresponding comparison with experimental tests. By combining the mathematical solutions of the models of this annulus with that corresponding to the cooling of a uniformly heated sphere, Fourier was able to determine for first time, more theoretically than experimentally, the thermal conductivity of iron. Regarding earth's temperature behavior, the heat conduction model contributed in passing to verify that the effect of external sources very quickly vanished with earth's depth, and that diffusion of heat from the interior of the earth was an insignificant factor in its surface temperature.

1.2. Relative conductivities

To the extent that it was recognized that the heat conduction capacity varied from one substance to another, simple techniques were devised to compare the thermal conductivities for two or more metals. An apparatus (Fig. 1, left) designed by the Dutch physician Jan Ingen-Housz (1730–1799), following a suggestion of his friend, the American scientist Benjamin Franklin (1706–1790), consists of a prismatic box containing oil, which can be heated to a high temperature [4]. Bars of the same size and cross-section of the different solids whose thermal conductivities are to be compared are passed at one end through one side of the box into the oil. The surface of each bar is initially coated uniformly with a thin

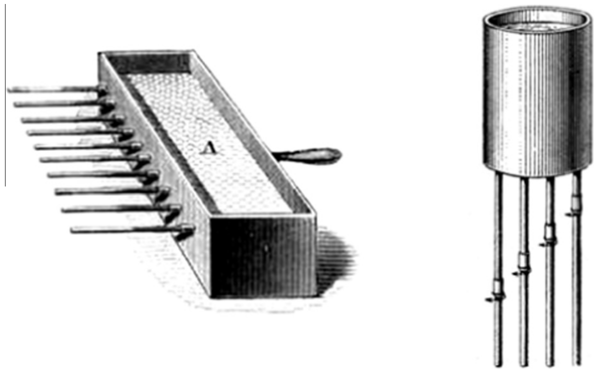

Fig. 1. Ingen-Housz's and Edser's apparatuses.

layer of white film wax. Once the oil is heated and the temperature sustained, heat is conducted along the bars at different rates, which are indicated by the melting of the wax. Once the immersion is enough prolonged and the temperatures of the bars reach a steady state and all the heat which enters them by conduction leaves them by radiation, the different specific heats become of no account, and it is only necessary to measure the distance of each bar along which the wax is melted in order to compare the thermal conductivities of the different substances. Taking into account the equal perimeter of all the bars, thermal conductivities are proportional to the squares of these distances:

$$\frac{k_1}{l_1^2} = \frac{k_2}{l_2^2} = \frac{k_3}{l_3^2} = \cdots \frac{k_n}{l_n^2} \tag{2}$$

In order to overcome the difficulty to decide exactly how far the wax is melted in each bar, the British physicist Edwin Edser (1866–1932) proposed a vertical arrangement of the bars (Fig. 1, right); as the was melted, a pointed index was able to fall and the different lengths of wax melted was subsequently given at any instant by the corresponding positions of the indexes [5].

An improved arrangement based on this model was proposed in 1821 by the French physicist César Mansuète Despretz (1789–1863) [6]. The apparatus (Fig. 2) allowed the comparison of the conducting powers of several solids by forming them into similar long bars. One end was turned and dipped into a bath of molten metal that gave a constant source of heat. Thermometers were inserted into small cavities in the bar, at equal distances apart, being the cavities filled up with mercury. By subtracting the general temperature of the room from the temperature indicated by each thermometer, it is possible plot out a curve that described the results of the experiments and that Despretz expressed in form of a law: while the distances along the rod being in arithmetical progression, the measured excesses of temperature decrease in geometrical progression. It was later shown that this law did not admit general application. It mainly prevailed for very good conductors, such as gold, platinum, silver and copper, only approximate true for iron, zinc, lead and thin, and did not apply to non-metallic substances.

Taking the conducting power of gold as 1000, Despretz was able to construct a table of conductivities (see Table 1):

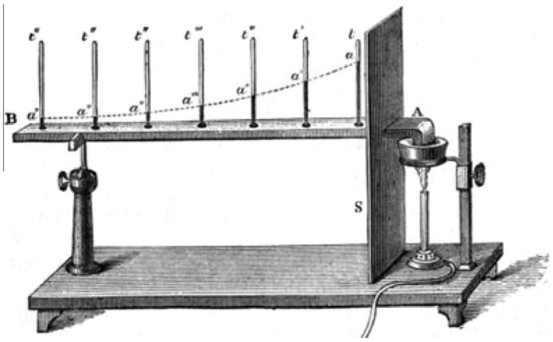

Fig. 2. Despretz's apparatus.

Table 1
Thermal conductivities reported by Despretz.

Platinum	981	Tin	304
Silver	973	Lead	179
Copper	897	Marble	23
Iron	374	Porcelain	12
Zinc	363	Brick earth	11

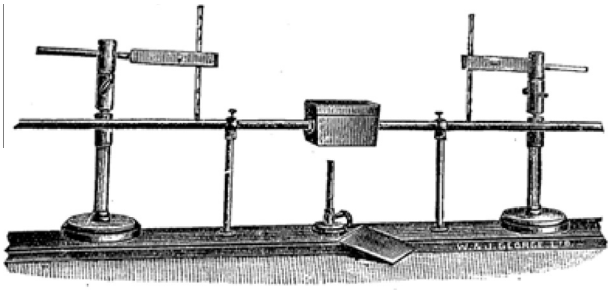

Fig. 3. Glazebrook's apparatus.

A similar experiment for only two metals, proposed by the English physicist Richard Tetley Glazebrook –later Sir- (1854–1935) compared distances for equal temperatures [7]. The apparatus (Fig. 3) consists of two bars, originally of cooper and iron, from 1 to 2 m long, respectively, and provided with small holes at distances of 10 cm apart, each hole being just large enough to contain the bulb of a thermometer. One end of each bar is fixed inside an iron vessel which contains melted lead. Vessel's heating by a heat source was controlled by a gas regulator in order to keep the temperature constant. The fact that temperature falls much more rapidly along the iron that along the cooper bar is easily observed when temperatures are read once the steady condition is reached. The observation about which points in one bar have the same temperatures of some selected points in the other, and the subsequent measurements of the corresponding distances, allowed the proportionality compliance raised in the equation presented above.

Two important facts could decisively alter the results of the recently described method. First of them dealt with the surface of the bars involved. As the heat transfer involved, besides conduction, convection and radiation, it was necessary that the bars whose conductivities are to be compared should have the same emissivity, fact that only could be achieved, at least approximately, by coating them with some material. The lampblack used by Despretz in order to correct this difficulty increased however so much the convection heat transfer coefficient that the temperature-drop along the bar became inconveniently large. The use of other coating materials such as varnish, or even better, white paper pasted on, and the alternative implementation of the bar's electroplating proposed by other experimenters [8] not only secured uniformity of surfaces but also solved in some degree the mentioned problem of convection. Second fact had to do with the holes where the thermometers were sunk in the bars, which, in the case where the widths of those cavities were not small compared with the diameter of the bars, would introduce discontinuities in the material, and subsequently would alter both, the flow of heat and the distribution of temperature.

More than two decades later, the Norwegian physicist Lorentz Christian Langberg (1810–1857) tried to correct the above second mentioned fact by introducing bismuth-antimony thermocouples instead of the thermometers used by Despretz, being the junction applied against the bar [9]. Current intensities were determined by the heating of the weld. The promising modification failed, however, mainly due to Langberg neglected making the same closeness of contact with the thermocouple in all cases and because of the increasing sensitivity of the experiments to some accidental causes such as air currents due to the use of wires instead of bars. Two German physicists, Gustav Heinrich Wiedemann (1826–1899) and Rudolf Franz, employed an improved version of the same method by adopting many precautions neglected by Langberg. The main sources of error removed in these new series of experiments were the returning to work with bars, this time electroplated and with exactly equal dimensions -about half a meter

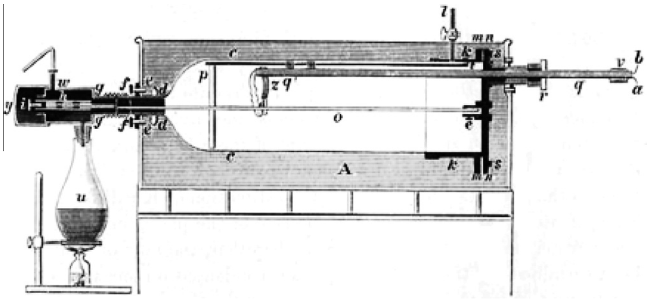

Fig. 4. Wiedemann and Franz's apparatus.

long, 6 mm of diameter, and three equidistant points for temperature's determination-, and by the calibration of the thermocouple done by direct experiments made by heating, within the apparatus itself, a hollow tube of steel filled with mercury and containing a thermometer [10] (Fig. 4).

Each bar under examination (*o* in the figure) was then fixed horizontally in the center of an air-tight glass vessel, which allowed doing the experiments both in vacuum and in air. The vessel was immersed in a water-bath A whose temperature could be determined and kept constant. The end of the bar was heated by steam through *w*, being the temperature thus kept approximately constant at 100 °C. Temperatures at various points along the bar were then determined by means of the thermoelectric junction, which was of small dimensions in order to not abstract too much heat. Results found by Wiedemann and Franz differed significantly from those of Despretz, as it is shown in Table 2, where thermal conductivity of silver was assigned with 100.

The additional observation of the electrical conductivities of those metals whose thermal conductivities Wiedemann and Franz measured led them to conclude that both properties were not only of the same order, but that they were so sensible in the same proportion that the ratio of the thermal to the electric conductivity was approximately the same for all metals. The generalization of this law, almost two decades later extended by the Danish mathematician and physicist Ludvig Valentin Lorenz by suggesting that the ratio was additionally proportional to the absolute temperature [11], was the subject of many subsequent investigations, being confirmed by some and denied by others. The use of this relation for most metals allowed, however, a prediction of their thermal conductivities with an accuracy of about 5–10%, once the values of the corresponding easiest property to be measured, electrical conductivity, were known [12].

Despretz's general method was not without its drawbacks. Its preferential applicability to very good conductor materials, such as silver, gold, and copper, together with its requirement of very difficult to obtain large quantities of each metal with higher standards of purity, and its inapplicability to compounds such as amalgams because the employment of mercury in the holes of the bars, were all factors to be corrected in order to identify a sufficiently accurate method of overall coverage. The English chemists Frederick Crace-Calvert (1819–1873) and Richard Johnson proposed a different series of experiments for determining the relative facilities of conduction [13]. Their more sophisticated apparatus (Fig. 5) was composed of a deal box A with a cover, painted white externally and internally, inside of which there were located two vulcanized India-rubber square vessels B and C, of determined, although different, capacities. Inner vessels were also painted white, surrounded with wadding, and provided of a deal board D between them in order to still further prevent any radiation of heat. A square bar of the metal G whose conductivity is to be determined is positioned at definite distances from the bottom of vessels B and C, and in a such way that specified parts of it are in each one of the vessels, other covered by the sides of the boxes through which it passes, and a remaining definite portion, H, covered with a piece of vulcanized India-rubber tubing. Once the vessels were put in water and their temperatures equalized, they are carefully placed in the wooden box, surrounded with wadding, and some quantity of water at the temperature of the room, poured into the vessel C. Experiments began when a fixed quantity of water at some higher determined temperature is injected to vessel B. Taking into account that the apparatus provided the necessary dispositions for that this latter vessel remained at steady state, the rise of temperature in vessel C, measured by a very sensitive thermometer (and not by the above mentioned thermo-electrical process proposed by Langberg and later by Wiedemann and Franz), introduced through one of the holes, must have been entirely due to the heat conducted by the square bar of metal G used.

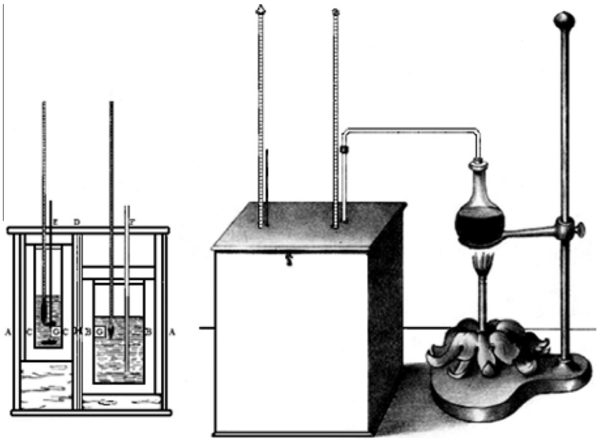

Fig. 5. Crace-Calvert and Johnson's apparatus.

It is clear that it was not the absolute quantity of heat communicated to the bar in vessel B which was determined in vessel C, but the relative facility of conduction by the various metals used in the bars, all circumstances being the same. According the authors, their method enabled them "to determine with accuracy the conducting power of all the ordinary metals, and of seventy of their alloys and thirty of their amalgams", with "such consistent results, that we have not only been able to determine the influence exercised on the conducting power of metals by the addition of 1% or 2% of another metal, but also to appreciate the difference of

Table 2
Thermal conductivities reported by Wiedemann and Franz.

Copper	73.6	Iron	11.9
Gold	53.2	Steel	11.6
Brass	23.1	Lead	8.5
Zinc	19.0	Platinum	8.4
Tin	14,5	Bismuth	1.8

Table 3
Thermal conductivities reported by Crace-Calvert and Johnson.

Silver (1000/1000)	1000	Malleable iron	436
Gold (1000/1000)	981	Tin	422
Gold (991/1000)	840	Steel	397
Copper (rolled)	845	Platinum	380
Copper (cast)	811	Sodium	365
Mercury	677	Cast iron	359
Aluminum	665	Lead	287
Zinc (rolled)	641	Antimony (cast hor.)	215
Zinc (cast)	628	Antimony (cast ver.)	192
Cadmium	577	Bismuth	61

conductibility of two alloys made of the same metals, and only differing by a few percentage in the relative proportions of the metals composing them". Nevertheless, the method does not seem to have transcended or have been used in later works. Table 3 lists the values reported by Crace-Calvert and Johnson for the metals they used with thermal conductivity arbitrarily designed by 1000.

Comparative steady-state measurement techniques in which a specimen is joined directly to, or sandwiched between one or two different reference materials, and surrounded by a heated guard cylinder, are still used to evaluate thermal conductivities in the range 0.15–150 W/m · K and at temperatures between 100 and 1300 K. Principles of the different existing variations are similar, it means the establishment of a temperature gradient along the test stack, by which it is assured or maximized longitudinal heat flow by adjustment of either the temperature gradient in, or the isothermal temperature of, the guard cylinder.

With far less complications in the corresponding configurations and significant less time consuming in operation than most absolute methods, the general versatile and flexible comparative techniques are recommended not only to be used with metallic and other highly conducting materials where long, thin, rod-type specimens are necessary, but also other engineering homogenous, heterogeneous, and composite solid materials such as ceramics, polymers, and refractories, among others, especially where the samples are too small or with something unusual shapes to accept heater and the heat sink designs required by the absolute methods. Reliable measurements, usually obtained when the thermal conductivity of the reference material is similar than that of the measured material, are in an order approximately 2% lower than those obtained by traditional absolute methods [14].

1.3. Absolute conductivities – plate method

The Fourier's fundamental differential equation, by which it is stated the direct proportionality between the small amount of heat dq crossing a surface A and the rate of decrease of temperature in the direction of flow of heat dT/dx, was early used for the quantitative determination of k, once certain indirect techniques for the determination of q were established. The most, seemingly, simple process was proposed by the French physicist Jean Claude Eugène Péclet (1793–1857), and included a vase of cylindrical shape and uniform thickness, whose inner and outer surfaces were exposed to a vapor stream at 100 °C, and ice at 0 °C, respectively. Thickness was small enough to consider that the whole body was kept at uniform temperature in any time. The amount of heat transferred from inside to outside was then indirectly measured by the quantity of melting ice. The experiments were, however, not successful. Péclet found practically the same value for k for every material he tried. It was obvious to him that the experimental errors were mainly due to the presence of layers of stagnant water in both sides of the cylinder, which affected the heat transfer process, and subsequently the temperatures of its both faces. Water is a bad conductor and the presence of even a thin film of 1 mm of still water has a temperature gradient through it. Péclet took then great precautions to secure efficient stirring, thus improving considerably the results [15]. Fig. 6 shows the improved design. The new apparatus was composed of two cylindrical tin vases arranged one within the other (the interspace filled with a thermally insulating substance such as carding cotton), with the plate whose conductivity was looked for to be determined closing the inner vase, and was provided with by a complicated rotating mechanism able to renew 1600 times per minute the liquid in contact with the sides of the plate. Taking into the account the new source of error provided by the heat produced by the rotating apparatus at such velocities, Péclet was able to determine the thermal conductivities of plates of metals such as copper, lead, tin, zinc, and cast iron with error margins reaching up to twenty percent regarding the later usually accepted values.

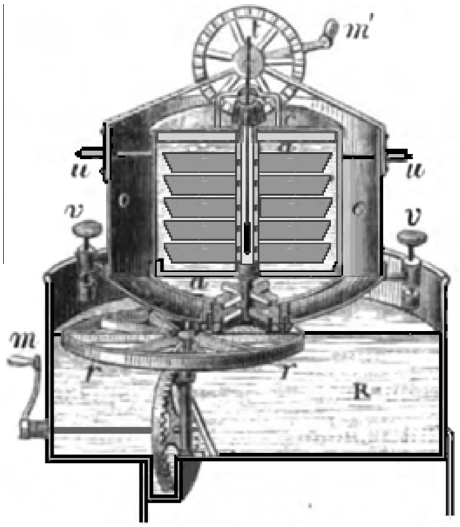

Fig. 6. Péclet's apparatus.

A more usable method, also based in the experimental realization of the theoretical conditions implied in the fundamental formula of Fourier, was proposed in 1895 by James H. Gray. He experimented with small rods of about 6 cm long and 3 mm in diameter, fastened on the one end to a copper hot-water bath and on the other to a copper sphere of about 5.5 cm diameter [16]. Fig. 7 shows a perspective drawing and a sectional view of the apparatus containing the axis of the wire, W, to be tested. A thermometer inserted in a small hole in the sphere measured its rise of temperature, which, knowing its heat capacity, the rate of heat could be calculated and the conductivity determined. The chief advantage of the method was the requirement of only a few grams of each metal to be studied, instead the comparatively large amounts utilized in the other techniques, fact that became it useful with even the rarest and most expensive metals. With trials lasting between two and three hours, Gray was able to determine the thermal conductivities of metals such as silver, copper, gold and platinum. Regardless the temperature dependence, Gray's values showed errors not exceeding 3.0% for the three first metals, and about 6.0% for platinum with respect to current data at ambient temperature.

Edwin Herbert Hall (1855–1938), the North-American physicist discoverer of the Hall Effect, momentarily revived the use of the method in 1895 by working on its main difficulty and source of

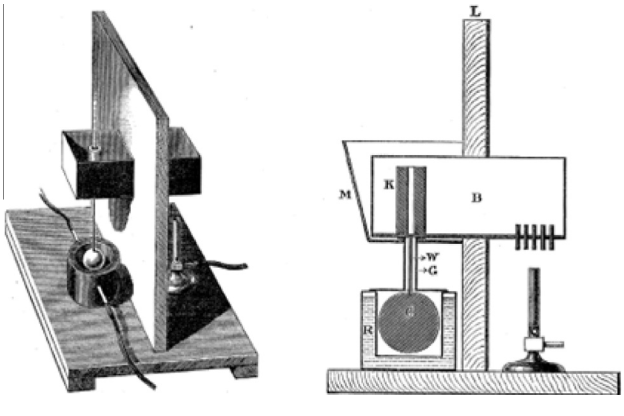

Fig. 7. Gray's apparatus.

error: the accurate determination of the temperature difference of the two faces of the plates. The ingenuous implemented improvement consisted of making the two faces of the thin metal plate the junction of a thermo-electric element [17]. The method made use of a disc of iron about 10 cm in diameter and 2 cm thick. Each side of it was coated with an electrolytic deposit of copper about 0.05 cm thick. The difference of temperature existing between the two surfaces of the disc was indicated by the thermo-electromotive force resulted from a differential thermocouple formed by thin copper wires electrolytically attached to the coatings (about 1 °C, corresponding to 10 μV). Two separate flows of water, with temperature differences of eight to ten degrees between them, were made to flow across each face of the disc. The heat coming through the disc was given by the measured rate of flow of one stream of water and its change of temperature between entering and leaving the vessel containing the disc. Probable radiation could to be neglected by surrounding the whole apparatus by a water jacket having a temperature near to that of the disc. Although later employment of thicker discs and thicker layers of coating improved uniformity of temperature over each face of the disc and made simpler the calculation of the mean difference of temperature between the two faces, values obtained by Hall became barely acceptable for pure iron, and too high for cast iron.

1.4. The guard-ring method

The only helpful way to obtain accurate results with the plate method was to take temperatures in the metal itself and not outside it. A way to do that is when the plane faces were vertical, and small vertical holes could be drilled in the plate, one near each face. Temperatures of the metallic plate could be thus taken by using either small thermometers or some thermo-electric method. With the temperatures of the two faces of a plate of known thickness determined, the only remaining quantity required for the determination of k was the amount of heat flowing through the plate. Fig. 8 represents a basic outline of an experiment conducted on this principle. In it, ABCD is the plate under examination, forming the faces AB and CD the ends of chambers filled with steam and ice, respectively. Amounts of steam condensed, or instead ice melted per second, are the simplest ways to get a measure of the quantity of heat flowing.

This method was successfully applied to the determination of the thermal conductivity of mercury by the French Professor of Physics, Alphonse Berget (1860–1934), and later extended to other metals [18]. The apparatus (Fig. 9) included a cylindrical column of mercury AB, contained in a glass tube, which was surrounded by another column of mercury, the latter acting as a guard-ring and preventing loss of heat by lateral radiation. This assembly can be thus considered equivalent to a part of an infinite wall, with the two faces at two constant temperatures and with a linear distribution of temperature along the column if the conductivity was supposed constant. Temperatures were measured at four different heights with the help of a thermopile formed by thermoelectric junctions inserted in the side of the vessel and the mercury itself. The mercury guard-ring rested on a sheet-iron plate, which in turn rested on the ice surrounding the bulb of a Bunsen's ice calorimeter into which the column AB protruded. This calorimeter was the instrument used by Berget for indirectly gage, with higher precision, the heat flowing at measuring the increase in volume of the surrounding ice-water solution caused by the melting of the ice. Mercury was heated at the top of the apparatus by steam introduced by tubes, as shown in the figure.

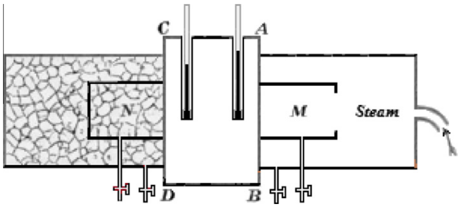

Fig. 8. Basic scheme of the guard-ring method.

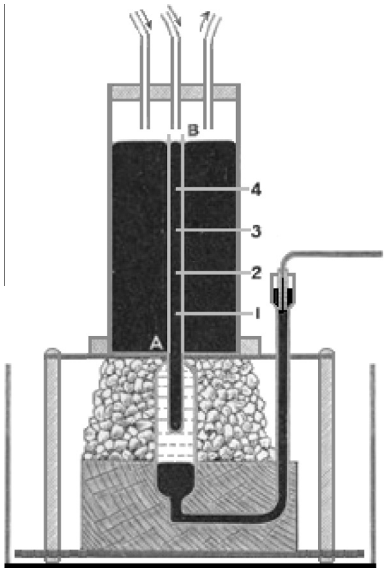

Fig. 9. Berget's apparatus.

Berget's mean value found for mercury was less than 1% higher than the currently one known at 25 °C. Application of the method to other metals, such as copper, brass, and iron, led to higher absolute errors (8.9%, 9.6%, and 16.9%, respectively).

1.5. Steady-state heat flow along a bar

Experiments begun in 1837 by the Scottish physicist and glaciologist James David Forbes (1809–1868) on the thermometric effect of the whole solar heat which fell in a year on the surface of the globe, how much of it was transmitted to the interior and how much dissipated at the surface, what depth did the influence of the seasons extend, and in what manner was that influence modified at different depths and with different soils [19] led years later to the earliest successful numerical determination of the absolute conductivity of a metal. Forbes had an important background in issues related with heat transfer. In 1833 he had already pointed out an original analogy between the conducting powers of metals for heat and for electricity, by which he stated that the order for both properties was the same; that is that those metals which had the lowest electric resistance, also conducted heat best [20]. Additionally, he had shown that these properties were almost proportional to one another.

Working with a modified method and apparatus regarding those of Despretz, Forbes devoted from 1841 to find absolute results for the conductivity of iron bar by determining the heat flow through it, in which a longitudinal gradient of temperature was maintained. Experiments were carried out in two parts. For the first one, he used a bar AB (see Fig. 10) of as pure iron as it was possible to get, 8 feet along by 1¼ inch square section, mounted on two pivots, so as to be free to radiate in all directions [21]. One end of the bar was raised to, and maintained at, a definite high temperature by being fixed into a crucible containing molten lead or solder, which were kept at as uniform temperature, their melting point, as possible by means of a gas regulator. Beyond

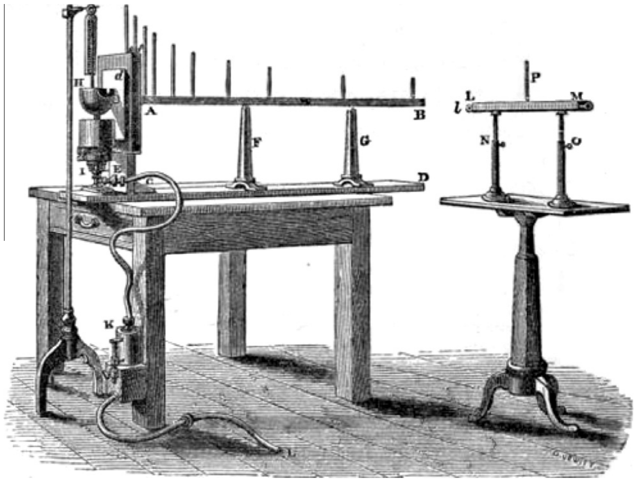

Fig. 10. Forbes's apparatus.

the point of immersion, the bar was defended by screens from the source of heat, thus ensuring that heating beyond A was done by nothing else than conduction. The length of the bar was such that the temperature of the farther end was not sensibly raised during the experiment. A temperature curve was obtained by means of ten thermometers placed in small holes (0.28 inch diameter) drilled in the bar, with readings made six to eight hours after the application of heat began, it means when the bar reached a steady state. While the holes near B were filled with mercury, those near A used instead a fusible metal in a semifluid state, in order to avoid amounts of heat dissipated by convection due to observed differences of temperature between the surface and the central part of the hole when mercury was also utilized. Precautions for accuracy were such that while the holes near B were filled with mercury, those near A used instead a fusible metal in a semifluid state, in order to avoid amounts of heat dissipated by convection due to observed differences of temperature between the surface and the central part of the hole when mercury was also utilized.

The determination of the amount of heat lost by convection and radiation per minute, per unit of length, at each temperature within the range employed, which became the main improvement in the method proposed by Forbes, was made by means of a second bar, LM in the figure, placed near to the first, of the same material and of equal cross section, but of much smaller length (20 inch), also provided with an inserted thermometer and an amalgam around it. Starting afresh, this short bar was heated as uniformly as possible, once for all, to a high temperature and then allowed to cool in the air. Temperatures were then read at exactly equal intervals of time till the bar had practically acquired the temperature of environment.

With the help of the two bars, which Forbes called 'static' and 'dynamical', respectively, he obtained the thermal conductivity of wrought iron for a number of temperatures between 0 and 200 °C, but his values, with approximations of about 20% regarding actually accepted figures, were quickly considered obsolete due to the constancy in the heat specific of the metal he assumed in the corresponding calculations, among other sources of error. Although health problems prevented Forbes from applying the method to any substance but iron, Forbes's results became the first of any real value to the absolute measurement of thermal conductivity. From a conceptual standpoint, the most prominent aspect in the method is that it seeks to determine the conductivity in terms of its definition instead of through the usual solution of Fourier's equation, which, as it is known, is supported on the hypothesis of a constant thermal conductivity and on Newton's law of cooling.

Forbes's experiments were repeated by the Scottish physicist Peter Guthrie Tait (1831–1901) with the same bar, and later extended to others of copper and different metals, in order to determine in what manner the thermal conductivity varied with temperature, and confirm if the variations of electric and thermal conductivities obeyed the same laws [22].

Electrical methods for the measurement of the thermal conductivity of a bar were used in 1900, maybe by first time, by the German physicist Friedrich Wilhelm Georg Kohlrausch (1840–1910). In a simple procedure heat was supplied by passing a constant electric current through a bar whose ends were kept at constant temperatures by contacts with large baths [23]. A steady flow was maintained from the center to the ends, and a certain distribution of temperature was then established throughout the bar, which depended on the thermal and electrical conductivities of the metal, the strength of the electrical current applied, and the heat loss, if any, from the surface of the bar. The temperature was measured at three points along the bar by means of thermocouples inserted in holes. By preventing as possible all these heat loss, Kohlrausch was able to mathematically obtain the following solution to the differential equations for thermal and electric equilibrium:

$$\frac{k}{\sigma} = \frac{1}{2}\left[\frac{(\Phi_1-\Phi_2)(\Phi_2-\Phi_3)(\Phi_3-\Phi_1)}{t_1(\Phi_2-\Phi_3)+t_2(\Phi_3-\Phi_1)+t_3(\Phi_1-\Phi_2)}\right] \tag{3}$$

where σ and Φ represent electrical conductivity and electrical potential, respectively.

The same year, Wilhelm Jaeger, Head of the Scientific Section of the Electrical laboratory at the Physikalisch-Technische Reichsanstalt (PTR) at Berlin, carried out, together one assistant his, Hermann Diesselhorst, the Kohlrausch's method into practice, with a very extensive investigation on thirteen metals (aluminum, bismuth, cadmium, copper, gold, iron, lead, manganese, nickel. palladium, platinum, silver, zinc) and three alloys (brass, constantan, and steel) in the range between 18 and 100 °C [24]. Cylindrical bars of the different metals, 25 cm long and usually about 2 cm diameter, with their ends fitted into copper blocks screwed into large water-baths, were used in the experiments (Fig. 11). The bars were surrounded by a jacket kept at a constant temperature by steam or water circulating outside it, being the space between the bar and the jacket filled with wadding. The certain amount of heat loss through the wadding was estimated by varying the temperature of the jacket. The thermal conductivities were deduced after the obtaining of the ratio of the thermal to the electrical conductivity by means of the above showed equation and a separate easy experiment for the latter property. The values obtained of thermal conductivities showed an increase of the property with temperature for aluminum, gold, manganese, palladium, platinum, constantan, and brass; and a decrease for the other materials studied.

The method of Jaeger and Diesselhorst was later also used for measuring conductivities of some metals at very low temperatures. The development of methods in this range in the last quarter of the nineteenth century and first decades of the twentieth century promoted the investigation of behavior of solids, metallic and non-metallic, at those new conditions, because of the high practical significance that implied the application of the advantageous properties of some specific materials in the industry. Also German physicist Walther Meissner (1882–1974), doctoral student under Max Planck (1858–1947) and coworker of Jeager at PTR, used the method for extensive measurements of thermal and electrical conductivities of copper, platinum, and lithium down to near the temperature of liquid hydrogen, in the range between 20 and 373 K [25].

Some observed experimental difficulties in the application of bar method to high temperatures were partially solved in an inge-

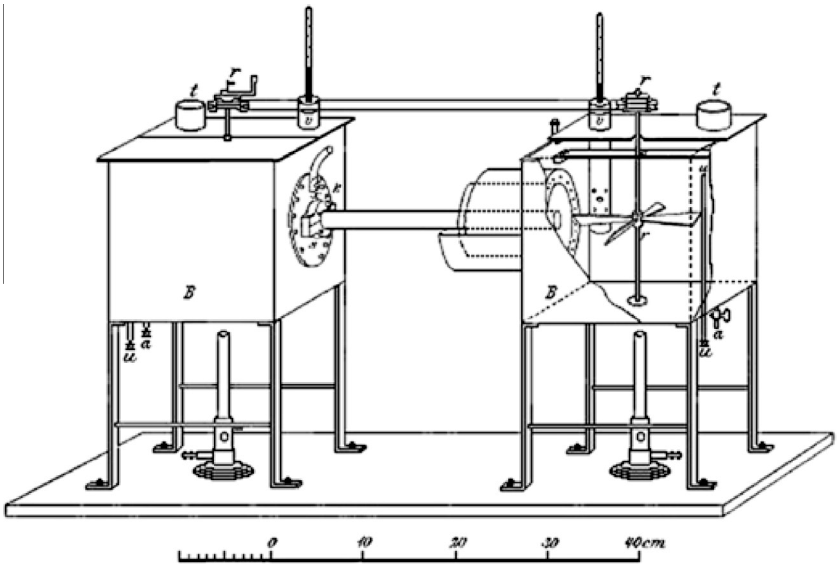

Fig. 11. Jaeger's and Diesselhorst's apparatus.

nious way as a part of his doctorate studies by the later Dean of college of Letters and Science at the University of Idaho, Martin Fuller Angell (1878–1930), by dealing with a radial, instead of a longitudinal, gradient of temperature in a bar of metal heated by an electrical current [26]. The bars used in the experiment were about 15 cm long and 1.2 cm diameter (Fig. 12). An inner hole, 0.168 cm in diameter, was bored through the rod, and made larger at the ends and to within 1.5 cm of the center in order to increase the resistance on each side of the central portion, make greater the heat generated toward the ends, and increase the portion of the bar without longitudinal gradient. In this way, experiments carried out at 1000 °C, for example, showed variation of less than 0.1% in temperature over 1 cm length in the center. Finally, the rod was symmetrically enclosed in a large water-cooled jacket J, from which air was previously exhausted, in order to eliminate possibilities of oxidation.

The temperatures were measured by two thermocouples CC of platinum and platinum–rhodium wire, taking special care with that of the surface. On the other hand, a welding transformer capable of furnishing 1700 amperes alternating at a voltage of 2.5 volts was used to supply the energy required. In its simplest way, the thermal conductivity for a bar of radius r_1 was thus obtained by

$$k = \frac{EIr_1^2}{4(t_2 - t_1)} \tag{4}$$

if the current density was assumed constant over the cross section, or by

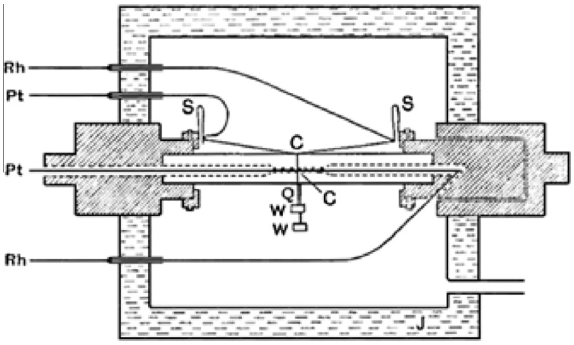

Fig. 12. Schematic assembly of Angell's apparatus.

$$k = \frac{EI}{2(t_2 - t_1)}\left[\frac{r_1^2 - r_2^2}{2} - r_2^2 \log\frac{r_1}{r_2}\right] \tag{5}$$

for the most general case, when the experiment was carried out with a hollow cylinder, where E represented the fall of potential along one centimeter, I the current density, r_1 and r_2 the radios inside and outside the cylinder, and t_1 and t_2 the temperatures at the axis and circumference, respectively.

The experiments allowed Angell to determine the thermal conductivities of aluminum between 100 and 600 °C, and of nickel between 300 and 1200 °C. The results at those high temperatures showed an increase in the conductivity of the former in the full range and a decrease for nickel, significant up to 700 °C, and more slowly up to 1200 °C.

It was working on the temperature dependence of heat conductivity that the British professor of physics, Charles H. Lees, improved the bar method in order, initially, to make it suitable for bad conductors. After having used an experimental technique based on an assembly of disks in series for the measurement of the thermal conductivities of materials such as glass, sulfur, ebonite, wood and cork, among others [27], Lees devoted to the study of this property for a number of metals and alloys over a range of temperature from −180 °C to 30 °C, using a modification of the original Forbes's method. In the apparatus (see Fig. 13) R was a bar of metal, 7 or 87 cm long and 0.5 cm diameter, whose lower end was fitted into a copper disc D, which formed the bottom of a cylinder T closed at the top [28]. The bar was provided with a heating coil C of platinoid wire and two platinum resistance thermometers A and B separated by a known distance *l*. The whole apparatus was wound with a second heating coil *p* of the same resistance as C, and another coil P, which allowing the temperature of the apparatus to be increased if desired. The wire frame in which the copper cylinder was placed, rested on the bottom of a thermos vessel V, in which the apparatus could be cooled.

The heat passing in the bar from A to B was calculated through an appropriate measurement of the difference in temperature between these points. The experiments in order to get it started at the liquid air temperature. The current was then first switched on to C until a difference of resistance equivalent to about 5 °C was obtained between A and B, and, subsequently on to *p*, thereby attempting that the heat supply rate to the apparatus as a whole was constant throughout the experiment. The heating was

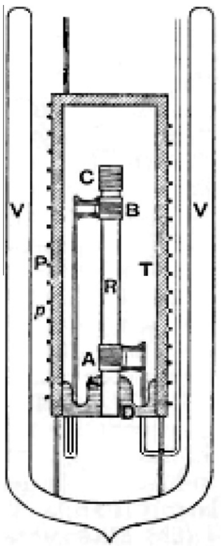

Fig. 13. Lees's apparatus.

continued until the readings of the resistances A and B were constant, after which the temperatures at A and B were measured. The differences between these temperatures when the heating current flowed round C, less the mean difference in temperature (before and after) when the current was flowing through *p*, gives the difference in temperature which would be produced if the heating current were continued in C and the surrounding tube T kept at a constant temperature. Thermal conductivity could then be found directly. Fig. 14 shows the smooth curves of the behavior of thermal conductivity with temperature for nine metals and six known alloys, drawn as nearly as possible through the points given by the experimental observations. The dotted lines to the right in the graph were added by Lees in order to provide a comparison with some of the values found by Jaeger and Diesselhorst.

Forbes's method was never completely forgotten, and publications introducing modifications in order to eliminate sources of systematic errors incorporated in the original technique occasionally appear reported in the literature [29]. A last modification to the bar method deserved to be mentioned from educative viewpoint. It corresponds to the work devised by the British George Frederick Charles Searle (1864–1954) for his teaching of experimental physics at Peterhouse College, Cambridge. The method, based on the continuous-flow calorimetry, differed from Peclet's original method by the substitution of a tube for a plate [30]. The equipment is quite simple (Fig. 15) and consisted of a solid bar of the metal under study, about 5 cm diameter and 20 cm length, fitted at one end to a circular chamber A through which steam flows. A coil of thin copper tubing B through which circulated cold water was soldered to the bar near the other end. The ends of this tubing were connected to copper cups. The full bar, with its fittings, were surrounded by thick layers of felt in order to prevent significant loss of heat, packed in a wooden box, made in two halves (only one is shown in the figure).

The amount of heat received by the water from the bar was easily determined by finding the weight of water flowing in a given time, and reading the difference in the temperatures between its input and output. The temperature gradient down the bar once the steady-state was reached was determined by the difference between the readings of the thermometers T_1 and T_2 placed in the copper tubes brazed into the bar at a known distance apart. Thermal conductivity was then obtained by dividing the rate of flow per square centimeter by the temperature gradient. The method was specifically devised for copper, but should to apply equally good with whatever other metal of high conductivity, with which the heat conducted along the bar is far very large compared with that which passed from one end of the bar to the other by conduction through the felt covering and that which escaped altogether from the bar. Mean results of about 377 W/m · K obtained for copper, differed in only 2.3% from the nowadays currently accepted value of 385.7 W/m · K.

The relative simplicity in the specimen preparation (usually of cylindrical shape) and the location of thermocouples are two of the reasons by which axial (or longitudinal) and radial methods are still currently used for some fast measurements of thermal conductivities. Their use is usually recommended for metals, steels, and other metallic alloys with conductivity ranges between 10 and 500 W/m · K and an approximate temperature range of 90–1300 K. An expected uncertainty of 0.5–2.0% in the measurements could be further improved if its main disadvantage specially at high temperatures, the heat losses existing in the experiments, is at least partially solved. For measurements at cryogenic

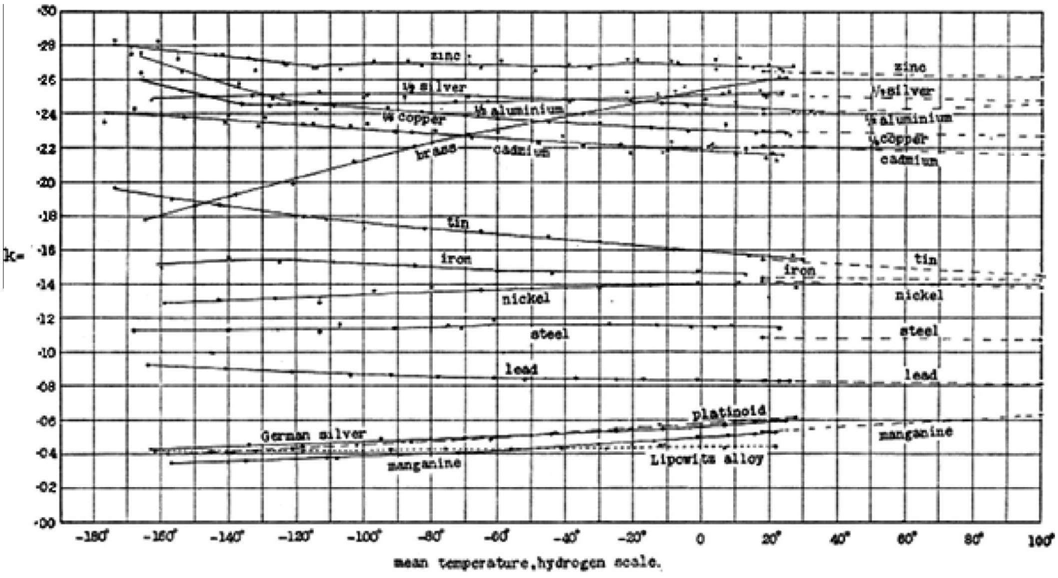

Fig. 14. Curves of variation of thermal conductivity with temperature according to Lees of thermal conductivities *k* of pure metals and alloys with temperature.

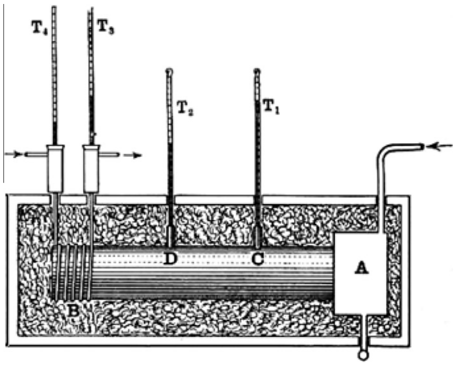

Fig. 15. Searle's apparatus.

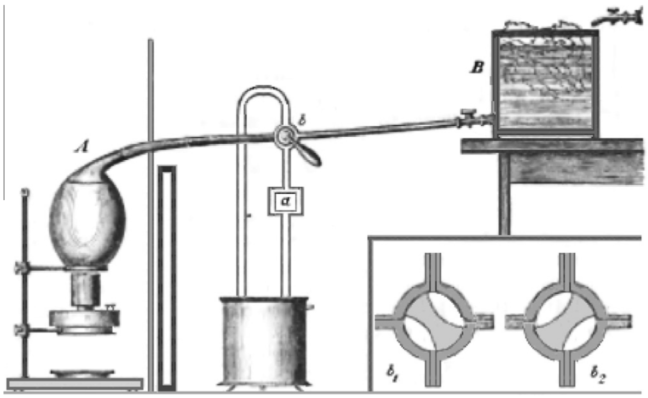

Fig. 16. Ångström's apparatus.

temperatures radiant losses does not constitute a serious problem, guard heaters and thermal insulation are usually not necessary, and even the conventional described longitudinal heat flow method could be considered as satisfactory. The situation is different at higher temperatures, although heat losses including those occurring by radiation from the surface of the specimen over the long path length, and even in radial direction, by convection currents around the sample, and by heat conduction through the connection leads, could be kept at a reasonable level especially for the radial heat flow method by different ways. Examples of these ways include suitable insulation between the parts or operation in a vacuum environment to limit heat transfer between the specimen and the surroundings. A general disadvantage of these methods is the long time taken to reach the required equilibrium, while significant sources of error are associated with the failure to establish equilibrium and the accuracy of measurements of temperature, sample dimensions and thermocouple spacing.

Recent studies using an improved test apparatus based on the measurement principle of the longitudinal steady-state heat flow metal have allowed a new optimum possibility for the determining in a working cryogenic temperature range (5–80 K) of the thermal conductivities of the superconductor tapes used in current high temperature superconductor leads, such as those made by tapes of Bi-2223 coalesced into a stack sheathed by a silver alloy [31].

1.6. Periodic heat flux technique

In 1861, the Swedish physicist Anders Jonas Ångström (1814–1874) proposed a novel, for the time, experimental technique for the determination of the thermal conductivity of iron and copper [32]. He had quite clear weaknesses of the available methods. On one side the aforementioned difficulty to accurately measure the temperatures of the surfaces in contact with water vapor in the Peclet's method, and on the other the impossibility of definitively removing the influence of the radiating power of the surfaces of the magnitudes of thermal conductivity determined in the different modifications of the bar method made necessary the proposal of a new method to obviate these drawbacks. Unlike the previous methods, which required a steady state of temperature and a consequent steady flow of heat, in the Ångström's dynamic method one end of a long bar of small and arbitrary, but uniform, cross-section was subjected to a periodic change of temperature, being alternately heated and cooled for equal time intervals, while the other end was left at the temperature of the surrounding medium. Fig. 16 shows the basic assembly, where the position of the cock *b* indicates when the bar, whose section is identified as *a*, is surrounded by a current of vapor from the boiler *A*, or by other of cold water from the vessel *B*. The temperature at points along the bar fluctuate periodically, and, on account of the surface radiation and convection, the thermal waves traveling then down the length of the rod are attenuated, both losing amplitude and experiencing a phase shift. After a few cycles, a steady-periodic state independent of the initial distribution is reached, being the fluctuations in temperature measured as a function of time at two selected points along the bar by means of thermometers, thermocouples, or other type of sensor. Temperatures become a periodic function of the same frequency as that of the heat input, and a comparison of their waves led, by a clear mathematical treatment that Ångström accompanied to his experimental procedure, to the determination of the thermal conductivity value for the metal by a simple formula independent of the nature of the bar's surface, nowadays written as

$$k = \frac{c\rho l^2}{2\theta \ln\left(\frac{A_c}{A_f}\right)} \tag{6}$$

where c and ρ are the specific heat and density of the material, respectively, l the distance between the temperature sensors, θ the time delay directly measured between the two waves, and A_c and A_f the amplitudes of the temperature waves measured at the close and the far sensor, respectively.

Ångström's first experiments were made with square bars 570 mm long and 23.75 mm side, with perforations of cavities 2.25 mm in diameter at intervals of 50 mm, which contained the bulbs of thermometers provided with convenient scales. The periodic time was twenty-four minutes, twelve for heating and twenty for cooling. The temperatures for the two selected points were observed for each minute during one or more of these periods, and the values found for the conductivity of copper and iron at the mean temperature of 50 °C were 381 and 68.2 W/m · K, respectively. A subsequent more careful series of experiments with bars 1178 mm long and 35 mm thick, provided with thermometers at intervals of 200 mm, and a heating apparatus so modified that different temperatures could be obtained, gave the following correlations in actual units for the same metals [33],

$$\text{For copper}: \quad k = 0.982333(1 - 0.001519\ T) \tag{7}$$

$$\text{For iron}: \quad k = 0.198783(1 - 0.00214\ T) \tag{8}$$

which, for a temperature of 25 °C for example led to values only differing 1.35% and 1.53% of the currently accepted values for those metals at the same temperature.

It was clear from the beginning that Ångström's method was applicable with elements whose dimensions allowed them to be considered virtually semi-infinite; it meant with that the heat flow was substantially parallel to the sample axis and the neglecting the reflection of temperature waves at the end of the specimen opposite to the thermal source. Neither this, no other assumptions implicit in the method, such as the independency of the temperature in the range studied of the thermal conductivity, specific heat and surface conductance, and the constancy of the temperature of the edge of the sample remote from the heater, were, or they are, actually fulfilled. Similar circumstance happened with the assumption that the surface loss was directly proportional to the excess of temperature over the surrounding air, which, even for the moderate ranges employed in the method, was not nearly correct.

The Angstrom's method was rediscovered and modified since beginnings of the twentieth century to the extent that modern laboratory instrumentation made more effective the generation and subsequent monitoring of the temperature waves. One such variation of the experimental arrangement, historically significant, was proposed by two British, the physicist Hugh Longbourne Callendar (1863–1930) and the civil engineer John Thomas Nicolson (1860–1913), as part of their joint study in the summer of 1895 on the efficiency of steam engines, and, specifically, on the rate of condensation of steam when in contact with metal surfaces at various pressures and temperatures [34]. A basic scheme of the apparatus they devised is shown in Fig. 17. Using periods of 60, 90, and 120 min, steam pressure was varied in the heater so as to produce approximately simple harmonic oscillations. The value they found for cast iron was $0.1144\,(1 - 0.00006\,T)$ is in close agreement with other obtained by more modern methods.

The apparatus of other more sophisticated method, proposed in 1915 by the professor of electric engineering at the University of Cornell, R.W. King, and which hold certain resemblance with that of Angstrom, is shown in Fig. 18 [35]. One end of a wire A, 25–50 cm length and 2.5 mm diameter, of the metal whose thermal conductivity was to be determined projected into a heating coil H, from which flowed a periodic current following a sine law. Two thermocouples T, T, each one connected to a short period galvanometer, were attached at equal number of points in the wire. A counter EMF in each thermocouple circuit could be adjusted to balance the thermocouple EMF at its mean value. Velocities of propagation of the waves were given by the lag between the movements of the two galvanometers. A mathematical treatment of the model enabled the author to calculate the thermal conductivity by

$$k = \frac{c\rho}{4\pi}\left(\frac{t_1^2 t_2^2 v_1^2 v_2^2 (v_1^2 - v_2^2)}{t_2^2 v_2^2 - t_1^2 v_1^2}\right)^{1/2} \tag{9}$$

where v_1 and v_2 are the velocities found for waves for two periods t_1 and t_2, and c and ρ the specific heat and the density of the metal, respectively. Results of experiments carried out with waves of periods of 2 and 5 min led to values of k at 35 °C for copper and tin, the only metals for which accurate measurements were made, of 380.37 and 65.06 W/m · K, respectively, 4.9% and 2.9% far from values currently accepted.

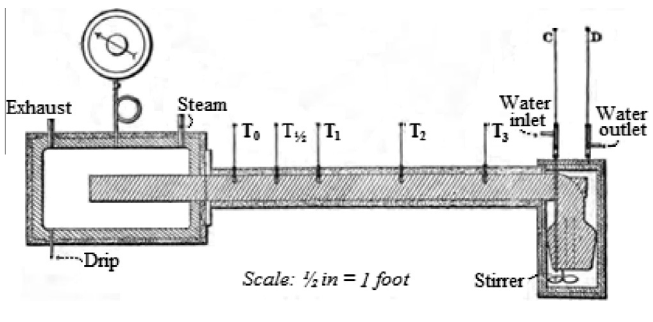

Fig. 17. Callendar' and Nicolson's apparatus.

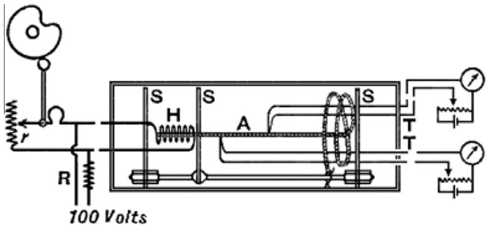

Fig. 18. King's assembly.

2. The Guarded-hot-plate technique

The arrival of the twentieth century brought far-reaching changes in the production of new technological goods, which positively influenced the development of studies in many different areas, including heat transfer. The advent of the mechanical refrigerator in the late 1920's and early 1930's, for example, as well as its different subsequent everyday applications, such as an economic way of producing ice for cooling or the air conditioning of public buildings, marked the beginning of an increasingly wide interest and activity in thermal conductivity measurements on low-conductivity materials for thermal insulation, which was followed by an also great interest in similar measurements on insulating brick and refractories used in industrial applications at high and low temperatures. Developments of and improvements in measurement techniques followed, however, much more slowly. Most of the analytical and experimental work regarding steady-state techniques was related with a new one, the guarded-hot-plate, at or near room temperature [36].

Devised in 1912 by the German Richard Poensgen in his laboratory of the Royal Technical High School in Munich as an improvement of the older methods of Péclet and Lees [37], the method very quickly became not only the most used worldwide technique over the decades, but also, what it is most important, the primary absolute method for the determination of design heat transmission data for homogeneous insulation materials in form of flat slabs. The principle is simple and is based on the steady state heat transfer between a warm and a cold plate (Fig. 19). A flat, electrically heated metering section surrounded on all lateral sides by a guard heater section controlled through differential thermocouples, supplies the planar heat source introduced over the hot face of the specimens, or the material being investigated. The specimens, or material to be tested are often rather large, and The ranges of 0.001–1.0 W/m · K and 90–520 K for thermal conductivity and temperature, respectively, have been considered optimum for uses in materials utilized in the construction of large-scale refrigeration structures and, in general, building materials. Subsequent versions of the original apparatus was standardized by ASTM International in 1945, and designated as the Test Method C 177 [38]. In its most conventional measurement configuration, the apparatus is a symmetrical arrangement where an electrically heated copper plate is sandwiched between two similar specimens, being the assembly surrounded by two flat water-cooled cold plates. Under ideal considerations, the large dimension of the specimens ensured not only a one-dimensional heat flow through a pair of specimens by reducing, regarding the unguarded disc method of Lees, undesired lateral heat flows to negligible proportions, but also allowed more reliable measurements to be undertaken on thicker materials.

3. 1940–1980: New materials, new needs, new techniques

Developments in warfare and electronics became the complex focus at work in many sectors of academia, industry and government in this period. The evident increasing need for knowing very

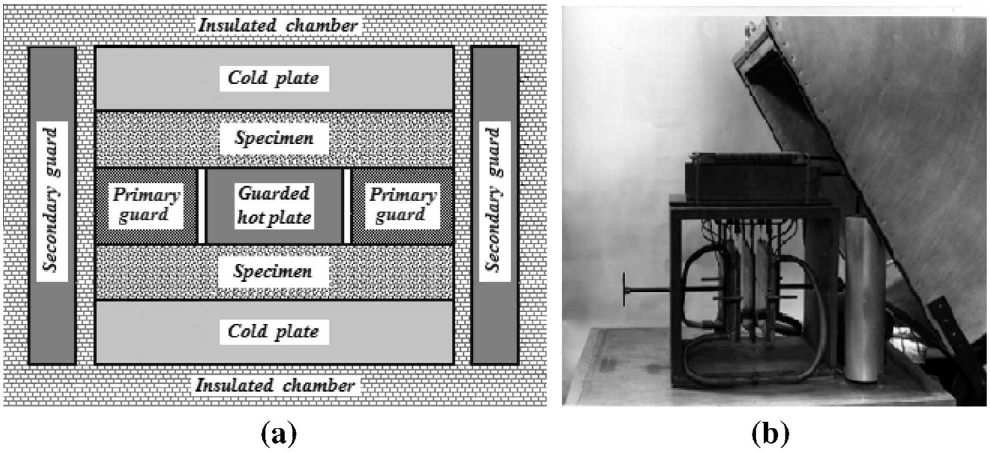

Fig. 19. Guarded-hot-plate technique (a) schematic diagram (b) apparatus built at NIST by M. van Dusen (1929). [*Reprinted courtesy of the National Institute of Standards and Technology, U.S. Department of Commerce. Not copyrightable in the United States.*]

accurate thermal conductivities of metals and alloys in the late 1930's and early 1940's no longer responded to purely academic concerns. No war was so profoundly affected and dominated by science and technology than World War II. New weapons produced by industry become, more than ever, an indispensable resource for the warfare. New materials and new uses for old materials appeared. The mobilization effort for war production of modern weapons required an expansion of industrial facilities not only in the armament industries, but also in basic industries as well. A greater quantity and variety of metals were needed among the different especially important materials required. Aluminum, chrome, copper, iron, nickel, tin, tungsten, and uranium, among others, were important due to their demand in aircraft, naval vessels, tanks, cannons, and other war-oriented industries. High-strength aluminum alloys, for example, contributed to higher, farther, and safer airplanes flights. High-strength duralumin sheets and slabs served as the main material for airplane covering, while complex-preformed blocks produced from them were used to make component parts of airplane engines, propellers, the chassis, and the fuselage frame. Aluminum–manganese alloys were used for welding fuel tanks, while steel and other alloys including metals like cobalt, chrome and tungsten, among others, were also required for major weapon systems. Nimonic, a family of nickel-based high-temperature superalloys, to cite other example, was patented in England and began to be used in the new decade for high-temperature service in jet-engines. Tinplate, a steel sheet coated with tin, was increasingly used for containers; and a 9% nickel steel alloy was designed for cryogenic service because the improvement this metal made on the toughness of ferritic steels (high chromium, magnetic stainless steels with low carbon content). The coming to light of not only one by one aluminum alloys, after the war, for uses in different means of transportation and everyday civil life, and of a true age of metallic conduits, allowing the users to pull many wires in the same enclosure, in many different types and sizes, to be used inside and outside of factories and homes, complement, only partially, the multiple new uses of metals and alloys from the first decades of the twentieth century.

Inventions in the field of electronics marked the beginning of a new era in which metals processing played a lead role too. Tungsten (wolfram), nickel, strontium, and barium, among other metallic materials, in pure condition or as alloys, were involved in the initial steps of construction of vacuum tubes, so critical to the development of electronic technology until the 1950's, and which later played a central role in the development of radio, television, radar and the digital computer. Germanium participated in the construction of the first transistors invented in 1948, which marked the obsolescence of vacuum tube technology. Germanium-indium alloys, which accelerated the commercialization of transistors in the late 1950's, were the precursors of the alloying process still used in the present day silicon technology. Copper, aluminum, or another metal, frequently gold-plated, still are the raw materials of the pins or the other connectors in the outer packaging of the microprocessors, originally invented in 1971. Electronic components from the 1960's and 1970's, designed for military and aerospace applications that required long duration, heat radiation and corrosion resistance, contained heavier gold-plated caps, leads, pins and connectors. Although in significant less amounts, most common circuit boards that can be found in normal computers still incorporate precious electronics components as gold, or alternatively silver, palladium, and, sometimes, platinum.

This explosion in the materials development required for the emerging electronic technologies produced considerable quantities of new and improved, although often expensive, materials and composites in different sizes and presentations. The need for evaluation of their corresponding thermal properties under conditions that cannot be satisfied sometimes using the classical known methods stimulated studies around improved or new techniques based on different principles.

The by then recently improved guarded-hot-plate method was highly recommended for insulating materials, but not for metals. Disadvantages such as heat leakage, small temperature gradients across the sample thickness, and requirement for very flat surfaces in order to cut down existing unaccounted interfacial heat transfer resistances due to contacts that definitively cannot be made uniform at the molecular level, were sufficient to rule out the use of this method with metals. The fact that heat losses are far more significant with increasing temperatures has led additionally to that no one of the many guarding schemes described in the literature can be effectively implemented above 1000 °C, so the accuracy of the measurements falls well below 10%.

3.1. The hot wire technique

A new –this time- transient method, the hot wire technique, initially based in the radial heat flow, emerged in the study of the thermal conductivity of metals. Its application in this field was, however, not focused on their solid condition, but on an area of particular importance form the thermal management viewpoint: molten metals. Interest in these substances, and in the knowledge of their thermal conductivities, at or around room temperatures, is currently associated with two main purposes: for reducing thermal interface resistances and for liquid cooling. Both applications are continuously increasing in importance because their significant contribution to the currently longed reductions in the overall thermal resistances of different process of electronic complex systems, such as casting and welding, for example. The incidence of heat transfer problems in the use of sodium, for example, for heat pipes and in the determination of the efficiency of nuclear and solar power plants, are other examples that highlight the importance of the knowledge of thermal properties of these molten materials. The process of heat transfer accompanying solidification in the semiconductor industry, to cite another example, determines the degree of perfection achieved in crystal growth and the heat dissipated in integrated circuits, following steps of sputtering, printing, or vapor deposition. Soldering, the most important industrial application of liquid metals at high temperatures, has been looking for lead-free solders to replace the historically used alloys of tin and lead, in order that the electronics community meets the Directive on the restriction of the use of certain hazardous substances in electrical and electronic equipment adopted in February 2003 by the European Union. Except for the much higher thermal conductivities compared to traditional heat transfer fluids, liquid metals offer the additional advantage of having the ability to pump more efficiently because of their characteristic low electrical resistivity.

Although molten metals systems are relatively simple in theory from a structural viewpoint, their obtaining at conditions well above room temperature create measuring difficulties because the problem to deal with high accuracy and to model molecularly the complex system melt-detector-atmosphere. Until a few years ago, there was not a single technique that could be used to measure thermal conductivity of molten metals or alloys at high temperatures with even the modest accuracy of 5–10%, with discrepancies reported of as much 50% over a wide range of temperature among results discussed in different reports. Besides the usual issues of purity, homogeneity and thermal stability of the samples, difficulties with metals are associated with their possibilities of oxidation (a layer of which can affect the resistance), and, over all, with the problem to isolate the conduction process from the simultaneous presence of the other two mechanisms of heat transfer, convection and radiation, especially at the high temperatures at which most metals are liquid. The imposition of a temperature gradient on the liquid sample, very sensitive to a gravitational force, creates both natural convection and an acceleration of all masses towards the center of gravitation, and making the bodies fall and fluids move downwards. This natural convection can only be eliminated by the absence of gravity, or reduced to a negligible effect in microgravity conditions.

While steady state techniques are unable to eliminate convection and the heat losses associated, transient methods can minimize its consequences by performing measurements whose duration are short compared with the time for the onset of the effects of significant loss of heat transfer related with the inevitable flow. The evolution in measurement techniques to transient methods was natural and logic as advances in instrumentation caught up with theory. From a simple viewpoint, transient techniques are based on generation of a non-temperature field inside the sample. In the hot wire technique, the thermal conductivity is determined by observing the temporal evolution of the temperature of a very thin metallic wire immersed in, or surrounded by, the test material after a step change in voltage has been applied to it. The voltage applied acted as a nearly constant heat flux of heat, producing so a temperature field throughout the material which increases with the time. The temperature change of the wire, which acts itself both as a temperature sensor and as a line source of constant heat flux per unit length, is evaluated from the resistance change. The thermal conductivity is then directly evaluated from the slope of the line relating the temperature rise in the wire to the logarithm of time. The additional difficulty arising with electrically conducting sample such as molten metals because of the electrical leakage through the samples has been overcome by using insulator coatings of optimized thickness on the wire. Alumina and silica have been used with this purpose.

Although the first heated-wire experiments go back to 1780 with the discussions about the possibility that gases could conduct heat [39], it was in 1931 when the technique was employed by first time to measure the thermal conductivity of solids and powders, besides some liquids [40]. From that time the technique has been in continuous evolution, and the arrival of new technologies associated with electronics made possible the very accurate measurements of small and transient resistance changes in periods that not exceed one second. A pioneer modification proposed in 1970's introduced an automatic Wheatstone bridge to measure the resistance difference of two wires (identical except for their length), with gold springs to always ensure their tautness. The new arrangement subtracts the end effects by automatic compensation through the electrical measurement system, and allows a considerable reduction in the duration of each experimental run. In this way, it has been possible to work with higher precision by eliminating completely the already discussed effects associated with natural convection and reducing other time-dependent errors [41]. Different recent adaptations of the instrument (Fig. 20) had allowed the determination of molten metals such as indium, gallium, mercury, tin, and lead with a reported accuracy of about ±2% [42].

Another transient technique, using this time a thin, plane, electrically insulated resistive element, usually in a spiral pattern, as both the temperature sensor and the heat source, instead the wire, is also occasionally utilized to determine thermally characterization of another different class of metallic substances such as composite materials [43]. Thermal conductivity of metallic powders is an important thermophysical property in, for example, the emerging rapid manufacturing process of selective laser melting for rapid mold manufacturing and other design applications. Mechanical properties and appearance of the consolidated material manufactured through layer by layer powder deposition and successive laser beam irradiation based on computer aided design data are directly influenced by the powder materials utilized and the corresponding fabrication parameters. Polymer composites filled with metal particles, on the other hand, are of extreme interest for heat dissipation applications like in electronic packaging, in computer chips, besides other fields of engineering. In these compounds, whose thermal characterization is close to the properties of metals, whereas their mechanical properties and the respective processing

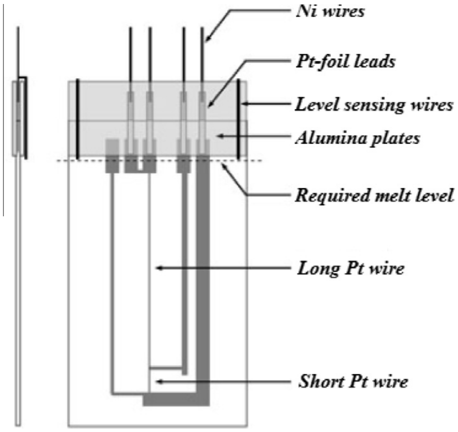

Fig. 20. Transient hot-wire instrument with two wires.

methods are typical for plastics, the fact of adding fillers to plastics changes the behavior of the polymers and significantly increases the thermal conductivity of the system. With an appropriate method of sample preparation, the transient plane source technique is recommended to be used for thermal conductivities in the range 0.005–500 W/m · K over a wide temperature range.

3.2. Laser-flash technique

The length of time required for making reliable measurements, the large sample sizes required in some cases by these techniques, and the difficulty to extend the measurements to high temperatures became significant limitations for the existing steady-state and most transient methods for determining thermal properties. In 1961 a team composed by the physicist in charge of the High Temperature Physics Section of the Naval Radiological Defense Laboratory (NRDL) in San Francisco, William J. Parker, the electronic scientist Robert J. Jenkins, the also physicist C. Press Butler, the electronic engineer Ralph Rudkin, and the student in engineering physics at the University of California, Gaynor L. Abbott, was asked for to establish a program for measuring the high temperature thermal properties of metals, alloys, ceramics, and composites by using a then available high-intensity carbon-arc image furnace [44]. The program responded to the needs of the Navy Bureau of Aeronautics for high temperature thermal property data to be used in the calculation of temperatures in applications such as the aerodynamic surfaces of their high speed vehicles and their rocket-nozzle guide vanes. Both, the flash method they would developed years later and the respective apparatus they would design for use it had roots in the experiences that the members of the team had with nuclear tests, as well as close similarity with the equipment they used for them.

NRDL had been initially established at the end of World War II to develop techniques for decontaminating ships which had passed through regions of radioactive fallout, and later broadened to include the study of other effect of nuclear weapons. The characterization of the thermal radiation from the fireball associated with nuclear detonations involved the establishment of scaling-laws and the development of the above mentioned furnace to reproduce high radiant fluxes in the laboratory as a function of time, weapon yield and atmospheric conditions. A high intensity xenon flash lamp with similar spectral distribution to that of the fireball was used as the source of thermal radiation in order to obtain the atmospheric transmission factor by measuring radiant flux as a function of distance. A radiant power of a few megawatts for a period of less than one millisecond made possible to distinguish the pulse delivered by the lamp from the background light at night in the San Francisco Bay area over distances of up to 24 km. A complete group of facilities and equipment, which included a moving truck for locating the instrumentation for recording the transmitted light pulse, and that obtained the energy received as a function of distance, filters, oscilloscopes, cameras, and photomultipliers, collaborated to obtain the atmospheric transmissions as a function of wavelength.

The underlying theory behind the technique involved subjecting the entire front face of a specimen of dense material to a very short, instantaneous, and spatially uniform impulse of radiant energy, causing a temperature rise on the other side (rear face), which is measured with an infrared remote sensor. Although all these requirements were not fully completed, several additional assumptions were added to the original supposed one dimensional heat conduction. No heat losses from the specimen front, side and back surfaces; homogeneity and isotropy of the specimen material; uniform distribution of the incident energy at the front surface; infinitesimal pulse (or, in other words, negligible duration of the radiation pulse from the flash lamp in comparison with the characteristic time for the temperature excursion of the sample); opaque material, and thermophysical properties and density invariance of the specimen with temperature within the experimental conditions, were the most important of these assumptions.

Specific conditions of the new technique allowed the obtaining of thermal diffusivities instead the thermal conductivities determined by previous methods. First measurements, began in 1957, were on metals. The corrections for radiation losses from the faces at high temperatures limited the use of the method to 1000 °C. In order to satisfy the requirements of the Bureau of Aeronautics for data of metals at much higher temperatures it was necessary to replace the carbon-arc image furnace as heat source. Following essays, initially with tungsten, were made using the already known electrically heated wire technique. The measurement capability of the method was quickly extended to include heat capacity, which was determined from the rate of decay of the temperature in the uniform-temperature region of the wire after the power was turned off. Molybdenum and rhenium were added some time later to the short list of metals whose data were already available.

After exploring different alternatives for the heat source, a solution emerged: a xenon flash lamp, much smaller, of course, than that used in the simulated nuclear tests, but serving basically the same purpose. Parker deduced the particularly simple relation for the diffusivity α:

$$\alpha = \frac{1.38z^2}{\pi^2 t_{1/2}} \tag{10}$$

where z is the thickness of the specimen and $t_{1/2}$ the time required for the rear face temperature to reach half its maximum. Thermal conductivity k could be determined by:

$$k(T) = \alpha(T)c_p(T)\rho(T) \tag{11}$$

where c_p and ρ are the heat capacity and bulk density of the material.

Beginning with a copper specimen, 6 mm thick, the authors reported data for thermal diffusivity, heat capacity and thermal conductivity for silver, iron, nickel, aluminum, tin, zinc, and four alloys, at 22 °C and 135 °C (Fig. 21) [45]. Some years after the first patent on infrared laser was awarded to Bell Laboratories in 1960, this light source was incorporated in the technique, changing its original name for ‘laser-flash’. Since then, the technique has been in permanent evolution, and its many variations and modifications based on a variety of models for different applications and have been extended worldwide, being almost unanimously considered the most useful for high temperature measurements of thermal diffusivities not only of metals, but also a wide range of materials including ceramics, coatings, composites, glasses, insulating solids, polymers, and refracting materials, among others [46].

The main advantages associated with this method are the simple sample preparation with small size required, and the elimination of the problem of the thermal contact resistance, while the heat losses are minimized by making the measurements in a time short enough so that very little cooling can take place. The main disadvantage is the requirement of density data of the material analyzed to calculate thermal conductivity. One of the occasional largest sources of error is related with the possible non-uniformly heating of the front surface of a specimen by the laser source because irregular spatial profiles of the pulse due to multimode oscillation. Non-uniform heating deviates heat flow inside of the specimen from one-dimensional heat flow on which the standard mathematical model of the laser flash method is founded.

Actual laser flash apparatus allows applications to solid materials in the 100–2800 K temperature range, 1×10^{-7} to 1×10^{-3} m^2/s thermal diffusivity range, and 0.015–1000 W/m · K thermal conductivity range, with accuracy, in the case of pure metals, of

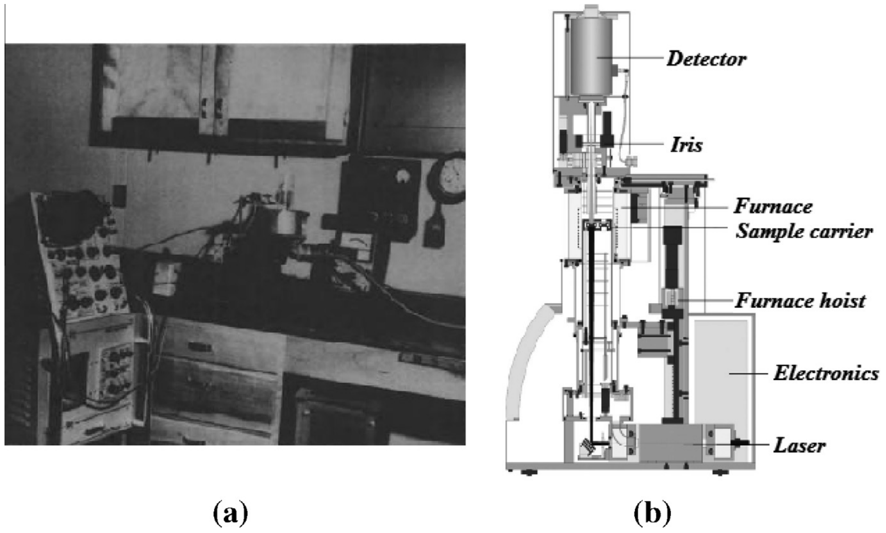

Fig. 21. Laser flash technique (a) first set-up for measuring thermal diffusivity by the flash method; (b) measurement part of the NETZSCH LFA 457 Microflash.

generally better than 3%. The specimens in the average experiments have usually the shape of a disk. Their diameter and thickness depending on the nature of the material and the temperature range of measurement, but normally varied between 6 and 16 mm, and between a fraction of a millimeter and 6–7 mm, respectively [47]. Technique has been improved by the introduction of a system of concurrent testing of multiple large samples (30 mm diameter and up to 5 mm thickness), with both properties, thermal conductivities and specific heats, being measured in the same test. This improvement does not only solve in great extension the limitation when dealing with some composite materials for which small samples are considered non-representative of the larger body, but also allows the achievement of required constant conditions for the whole experiment. The reported results show accuracies of ±2–3% for the multiple sample configuration. The sample chamber of modern modular apparatus include a sample robot for up to 6 simultaneous samples and three user exchangeable furnaces that allow measurements from -125 up to $1600\,^{\circ}\mathrm{C}$.

With its evolution, the method has gained in versatility. Sources of energy pulses different to the usual neodymium (Nd) glass laser, such as flash lamps, electron beams and other types of lasers, have been also used, although modifying, of course, the pulse shape [48]. Thermal conductivities of semitransparent materials have been measured after attach large opaque layers or to be coated on the front surface to prevent laser penetration, and on the rear surface to prevent the infrared detector from viewing the sample [49]. The layered arrangement enabled the study of different temperature-sensitive materials, thin films, or other materials which would be very difficult to measure using other transport property measurement methods. If good adhesion is not achieved, this coating procedure can potentially be however a significant source of error. Similar successful results have been achieved with materials not included in the original development, such as molten liquids [50] and with some highly advanced material systems, as it is the case of the layered thermal barrier coatings (TBC) with metallic substrates and metallic bond coats [51]. The thermal conductivities of these widely materials to enable gas turbines to operate at higher gas temperatures and increasing efficiencies while reduce the requirements for cooling air and the thermal fatigue of structural components, had also been determined by laser flash technique with acceptable accuracy after some specified conditions were taking under consideration. The promissory results obtained with this layered arrangement enabled the study of different temperature-sensitive materials, thin films, or other materials which would be very difficult to measure using other transport property measurement methods. It is perhaps no exaggeration to say that the method has been one of the major instrument in generating the thermal diffusivity data published in the scientific literature during the past few decades.

4. 1980–2010's: New frontiers of materials science and engineering technology

The explosion of new materials for all the many emerging technologies in the last quarter of the twentieth century, especially electronics and particularly solid-state devices, has produced objects that very quickly went from being considered no more than a curiosity to be the heart of information technology. The analysis of an important difference was maybe one of the main factors responsible for this spectacular transformation. While electrical charge flows only in metals and superconductors, heat, on the other hand, flows in all materials. It should be then possible to identify the fundamental and technological limits for the control of heat flow in solids, in a similar way to the possibility the man had to control the flow of charge in conductors. It was necessary recognize two fundamental length scales – wavelength and mean free path – associated with the two energy carriers by which heat flow predominantly occur in solids: electrons in metals, and lattice vibrations – or phonons – in insulators and semiconductors. The design and fabrication of solid structures that overlap in size with these mentioned length scales was a logic way to gain control of heat flow. It was nanotechnology, as well as its corresponding manufacture techniques that allowed the fabrication of structures with sizes in the 1–100 nm range, which provided the possibility to manipulate, initially to some extent, heat flow in solids through the interplay of confined size with electron/phonon wavelengths and mean free paths.

Thanks to the different behavior of the matter at this physical scale, and the subsequent knowledge of its novel optical, electric, magnetic, thermal and/or mechanical properties, among others, exhibited by the nanomaterials, their science and engineering developments have impacted energy, healthcare and biotechnology, space exploration, transportation, besides that more widely popularized application related to information technology, computing and telecommunication, among others. These nanomaterials, found in the form of clusters, multilayers, thin films, or nanocrystalline materials (usually expressed according to their dimensionality by 0, 1, 2 and 3), present as common components, metals amorphous and crystalline alloys, semiconductors, oxides, and nitride and carbide ceramics in different presentations.

With the move of electronic industry toward nanometer designs and the many and continued performance improvements in electronic components, such as higher power computer chips and power converters, a very important challenge began to become increasingly prominent. The significantly increased heat generation at small size scales required not only more efficient strategies for microscale heat dissipation, but also new demands on packaging technology in order to identify the appropriate special materials for manufacturing the substrates or baseplates acting as heat sinks and in which the high-performance electronic devices need to be mounted to allow effective thermal management. As the devices and packages become smaller heat losses fluxes reached values at the die of 300 W/cm^2 and beyond. If this large amount of waste heat is not effectively dissipated, the electronic equipment will exceed its safe operating temperature limits, influencing its damage threshold and jeopardizing its functionality and reliability. The fact that in a recent economic projection of the global market for thermal management products it is reported that by 2016 the thermal management technologies market will be worth nearly US $ 11 billion, compared with a 2010 value of US $ 7.5 billion and US $ 8 billion in 2011, with a compound annual growth rate of 6.4% in this period, and the thermal management hardware accounting about 84% of the total thermal management market, makes clear the importance of this new element [52].

Thin films are, unarguably, one of the most multifaceted representatives of these new nanomaterials and key components of modern micro/nano electronics. Their usual application in metallization and as interconnects in the semiconductor industry as well as structural elements in microelectromechanical systems (MEMS) make of their study something very relevant in the context of this paper. The 1980's can well be summarized as the 'thin' decade. Sheets, wafers, and films provided by several processes, and stimulated by the new requirements in microelectronics, began to flood the market. Metals, or metallic compounds, regarding the 'protagonist' of this paper, serve many different uses in thin films: conductors (aluminum, copper, and gold in some radio-frequency devices), contacts to semiconductors (platinum silicide), resistors (tin oxide, metal films coated with nickel chromium), 'glue' layers when some noble metals do no adhere well to substrates (titanium or chromium for gold and platinum), barrier to prevent unwanted reactions between thin films or diffusion of unwanted atoms (alloys and compounds as tungsten–nitride or titanium–tungsten), optical materials for displays and optical light emitting devices (indium doped tin oxide), photomasks (chromium), catalysts in chemical sensors, microreactors, and fuel cells (palladium and platinum), magnetic materials (nickel and nickel alloys), electron emitters (molybdenum), and protective coatings (nickel and chromium), among others [53]. Reliable thermophysical property values of thin films began to be indispensable not only for the optimal design of these highly integrated electronic devices, but also for the studies on the heat management between interconnects and interlayer dielectric materials for microprocessors, to cite just one example.

The study of their thermophysical properties, so much important for the thermal characterization of these nanomaterials, the understanding of the heat diffusion mechanism, and the careful thermal design of those microelectronic devices in which they will be utilized, has not be however as advanced as the study of other of their also electrical, magnetic and optical properties because measurements of thermal energy transfer in thin films were, and still are, much more difficult than measurements of other properties. Besides the experimental technique itself, two additional difficulties affect the determination of thermophysical properties in the case of thin films. First, with the drop of the thickness of thin-films into the submicron regime came the realization that bulk and thin-film thermal properties differ markedly because of structure imperfections, the different mechanisms that govern conduction at small length scales and to various materials, and the phonon scattering at the latter's both sides of interfaces [54]. It is even not exaggerated to say that what maybe makes the objects in the nanometer scale so interesting is this difference in properties.

The easy way of the extrapolation from a bulk measurement to the film usually leads then to misleading results. Since universal behavior cannot be expected however for these differences and the impossibility for predicting them from theory, the properties of each particular material must to be measured separately. The second problem is associated with the fact that material properties must to be measured in a film as it is processed in a final application. The variety of reported values of thermal conductivity provides evidence of the dependence both on the type of deposition process used with the materials that are implemented in the structure substances materials that are going to be implemented in the structure — Low-Pressure Chemical-Vapor-Deposition (LPCVD), Plasma Enhanced Chemical Vapor Deposition (PECVD), etc.) and on their processing parameters [55]. Since thermal conductivities are strongly deposition techniques dependent, differing for each manufacturer, it is usually recommended to use tabulated values found elsewhere only as guidelines, and characterize each deposited film *in situ* individually. A project of a database system for thermophysical property data, developed by the National Metrology Institute of Japan (NMIJ) to store comprehensive information on thin films, identifying constituent elements, phases, compositions and method of synthesis, is thought will take still long time to collect all the required information [56]. For the usual typical layered films it is not only required the measurement of the thinner films of higher thermal conductivities composed the whole material. A point is usually reached where the intrinsic thermal conductivity of each film is comparable to the interface resistance between the stacked layers, being then also necessary the measurement of the property for such interfaces.

The measurement of the thermal properties of thin films has been very challenging [57]. Steady state techniques are not optimal for thin-film measurements because they offer little sensitivity for characterizing individual thin films in multilayer samples, multiple contacts are required to extract the relevant data, and they generally require significant fabrication on the sample. Application in the nanometer ranges of these classical direct determinations of the cross-plane thermal conductivity to a thin-film-on substrate system, in which it is required the finding out the temperature drop across the film thickness, faces however two main difficulties not found in the case of bulk materials: (a) the creation of a reasonable temperature drop without a large temperature rise in the substrate, and (b) the experimental measurement of the temperature drop across the film [58]. Typical transient methods, on the other hand, measure either the time response of the material of interest to a heating signal or the thermal response to sinusoidal heating generated by an alternating current. The most widely used thermal conductivity measurement techniques for these new materials can be appropriately grouped into frequency-domain and time-domain methods, typically represented by the electrically heated 3-ω method in the first of the cases and for the time-domain thermoreflectance method (TDTR) using ultrafast lasers in the other.

4.1. The 3-ω technique

The 3-ω method, based on the temperature-dependent electrical resistivity of metals and involving the diffusion of heat into a medium from a periodically oscillating source located on the surface, has become a very effective method for measuring the thermophysical properties of thin films. Closely related to the hot-wire technique, the method uses a thin metal micro-bridge deposited on the surface of the specimen serving simultaneously as an electrical-source and as a temperature sensor. The thermal penetration depth is varied by tuning the driving frequency, which provides sensitivity in determining the thermal properties of the tested sample. In the basic method, a small sinusoidal electric current $I(t) = I_0\cos(\omega t)$ at angular frequency ω is passed through the metallic heater, generating temperature oscillations at angular frequency 2ω. The amplitude of this temperature oscillation is a function of the geometry, heating power, and thermophysical properties of the material of interest. These thermal waves perturb the sensor resistance at a frequency 2ω, subsequently generating a small voltage signal at frequency 3ω, which is finally related with the thermal properties of the sample. Taking the average temperature over the entire resistor, one-dimensional flow and other usual suppositions, the following analytical solution to the heat diffusion equation can be derived

$$\Delta T = \frac{P}{\pi l k_s}\int_0^\infty \frac{\sin^2(\eta b)}{(\eta b)^2\sqrt{\eta^2+q^2}}d\eta \qquad (12)$$

where P, l, and b represent the heating power, the length, and the half-width of the thin metal strip, respectively, k_s the thermal conductivity, η the variable of integration, and the factor $q\ (=\sqrt{i2\omega/a})$, with a as a constant, comprise the frequency dependence of the temperature oscillation on top of the surface of the sample. Eq. (12) has not analytical solution, and can only be solved numerically to a certain degree. The linearization for the limit case for thermal penetration enough large compared to the thin metal strip width, led to the approximation

$$\Delta T \approx -\frac{P}{2\pi l k_s}\left(\ln(2\omega)+\ln\left(\frac{b^2(\rho c_p)_s}{k_s}\right)-2\xi\right)-\frac{P}{4lk_s}i \qquad (13)$$

where ξ is a constant roughly equal to 0.922. If, as it has been proven, the real part of these temperature oscillations as a function of the natural logarithm of the frequency is a straight line, the slope of the curve allows the direct finding of the thermal conductivity of the substrate. This situation is not usual for transient measurement techniques, where independent measurements of the thermal diffusivity and volumetric heat capacity are usually required to obtain the thermal conductivity of the material.

A basic measuring system is schematically shown in Fig. 22. One of the arms of the Wheatstone bridge of the electric circuit includes the measuring element, while the others are high-class resistors and potentiometers. A vacuum chamber including a heating panel on which the sample with a sensor strip is mounted, serves to maintain nearly adiabatic conditions for the measurements. The differential signal from the bridge, containing the pre-extracted signal $V_{3\omega}$ is amplified by an analog amplifier. One the signals are recorded, the data collected is transmitted to a computer for further numerical processing.

The original idea of the method came from the Italian physicist and politician Orso Mario Corbino (1876–1930), who discovered that a third-harmonic voltage component, which is usually several orders of magnitude smaller than the fundamental, appears when an alternating current is applied through a resistive heater [59]. In this way, Corbino seems to be the first to notice that the temperature fluctuations of an ac heated wire gives information about the thermal properties of the material. The technique was initially developed to measure the thermal diffusivity of metal filaments used in incandescent light bulbs. The objective was the understanding of the observed short lifetimes of metal filament lamps compared to carbon filament ones due to burnout [60]. Systematic investigations, exploiting the method for calorimetric studies to measure frequency dependent heat capacities of metals and alloys used as heaters in the experiments, were carried out mainly in the 1960's [61]. Two decades later the method was applied to measure the thermal diffusivity of liquids near the glass transition by using the third harmonic detection technique with planar heaters, which, at the same time, showed its spectroscopic capability [62]. The understanding of the fundamental difficulty posed by dc measurements at room temperatures, in which a significant percentage of the heat that is originally intended to flow through the solid radiates out of the sample, ratified the selection of ac measurements.

The definitive takeoff of the method arrived with the seminal contribution made by the Professor David G. Cahill and collaborators who, after working with a line heater deposited by first time on the surface of a solid material, developed the above described analytical solution for determine the thermal conductivity of materials in this state [63]. The new measurement technique was initially introduced for measuring the thermal conductivity of bulk samples of poor thermal conductors free from errors of blackbody radiation. Since then, it has been extended to different types of materials. Its major field of application is the thermal characterization of the in-plane and cross-plane thermal conductivity of relatively thin films or superlattices [64], and nanowires and nanotubes [65], where its accuracy is unquestionable. It is also employed to measure the thermal conductivities and heat capacities of nanofluids and electrically conducting liquids [66]. The Cahill's approximation remains regularly true mainly at low frequencies. Later improvements had allowed the development of a technique that employs 3-ω measurements at low and high frequencies separately in order to simultaneously determine the thermal conductivities of the film and substrate [67].

Three-ω was motivated by a fundamental difficulty of dc measurements at room temperatures, in which a significant percentage of the heat that is originally intended to flow through the solid radiates out of the sample. With the ac measurements the equilibrium is reached after only few oscillation cycles, there is less vulnerability to radiation losses at sufficient excitation frequency, and the heat affected region reduced since the magnitude of the temperature oscillations decay exponentially away from the resistive line heater.

The applicable temperature range for the method runs from 30 K to 1000 K depending on the thermal properties of the substrate and the heater geometry, although very high temperatures are not usually accessible for semiconductors. One of the reasons for the attractiveness of the method lies in its ease of implementation. It only requires a simple setup composed of a heating element directly placed onto the sample, a Wheatstone bridge circuit to cancel the common mode, and a lock-in amplifier to perform the read-out. It is the relative simplicity of the setup and the easy of the experimental data post-processing without any fitting procedures, what made the 3-ω method so attractive in the field.

Average accuracy in the order of 5%, reduction of the equilibrium times to few minutes after only few oscillation cycles, and a decreased effect of black body radiation due to both the small surface area of the metallic lines and the exponential decay of the magnitude of the temperature oscillations decay away from the resistive line heater (even at 1000 K the calculated error due to radiation does not exceed 2%) are the maybe more important advantages of the 3-ω method over other techniques. Non-reusability and flimsiness of the traditional 3-ω sensor, the smooth specimen surface requirement, destructiveness to the specimen surface, are, on the other hand, some of the more relevant general deficiencies of the method from the viewpoint of practical applications. Significant limitations may occur regarding two specific situations. Considering thin films, on the one hand, the method does

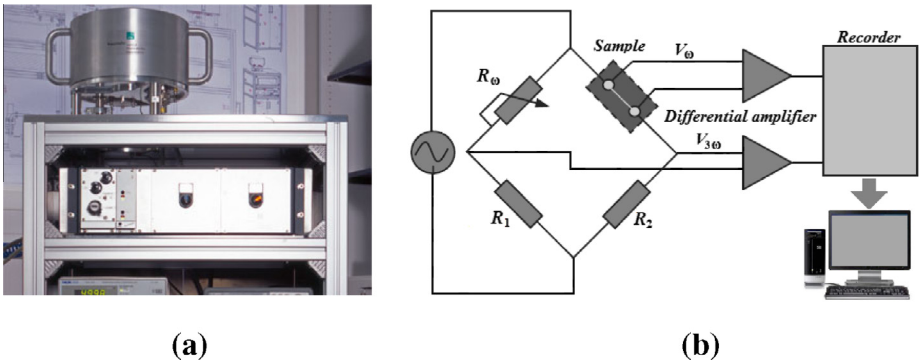

Fig. 22. 3-ω technique (a) measurement setup (Fraunhofer Institute for Physical Measurement Techniques IPM), (b) schematic arrangement.

not offer distinction between the intrinsic thermal resistance of a film and the interfacial thermal resistance. The sample preparation regarding electrically conducting, or semiconducting materials, on the other hand, offers challenges because the need to electrically isolate the metal microbridge from the sample, thus introducing an additional thermal resistance and reducing both, the accuracy and the sensitivity of the technique [68]. Regarding this same subject, the long time-consuming microfabrication of the required electrical heating/sensing elements on the sample surface, could render scanning operations difficult and measurements of rough or electrically conductive samples challenging.

4.2. Time-domain thermoreflectance

The conventional laser-flash method is useful to observe the thermal energy transfer in disk-shaped specimens of known thickness on a macroscopic scale. The order of ten microseconds of the response time of the infrared radiation thermometers used in this method is too long however to observe the temperature response of submicrometer and nanometer thin films after a picosecond pulse heating. This is because the heat diffusion times across these very little structures are shorter than one nanosecond, whereas the heat diffusion times over one millimeter in bulk specimens are longer than ten times this value.

Picosecond thermoreflectance, alternatively referred to as time-domain thermoreflectance (TDTR), provides a direct optical heating method for measuring heat diffusion on nanometer length scales by using radiation energy as the heat source. The basic principle of these transient thermal reflectance (TTR) methods is to heat a sample by laser irradiation and probe the changes in the surface reflectivity of the heated material as a function of time after a short pulsed heating event (see Fig. 23). The source of energy in the TTR method is normally provided by a pulsed laser with short pulse duration. The sample should be metallic or coated with a thin metal layer, in order to guarantee the reflectances and reflectance's temperature coefficients sufficiently high required for the method to provide sufficient thermoreflectance signals. The sensitivity of the technique is determined by the extent of the change in the reflectivity with changes in the temperature.

Ultrafast thermoreflectance techniques often employ subpicosecond lasers. Repeated laser pulses are divided into two beams. The pump beam excites a sample and the probe beam measures the changes in the reflectivity or diffraction, which is temperature-dependent. Both pulses originate from the same short pulse laser system. The pump pulse is focused onto a small spot on the sample surface. A fraction of this pulse is absorbed within a depth of about 10–20 nm from the film surface, and creates a local region of excitation within this spot size. The temperature of the heated surface decreases because of the thermal energy transfer from the film surface to the inner part of the film. The initial temperature distribution in the depth direction thus created is proportional to the adsorbed light distribution. The probe weaker pulse is focused onto the excitation region. In TDTR method, probe beam arrives at the sample surface delayed with respect to the pump by means of a variable optical path. The monitoring of the intensity of the reflected probe beam [69], the measurement of the angular deflection of the probe beam [70], and the detection of the displacement of the surface of the sample by an interferometric method [71] are some of the different classical detection schemes proposed for the method. Since the reflectivities of metals are sensitive to their temperatures and approximately proportional to them in a wide but limited temperature range, the normalized temperature profiles can be obtained from the normalized reflected light intensity. Analytical solutions of the diffusion problem are then used to determine the thermal conductivity of the material following an iterative matching process between the solutions and the experimental results. Changes in reflectance and transmittance can then be used to determine properties of the film. In the case of metals, the change in reflectance is related to changes in temperature and strain.

The idea of using a pulse to capture a transient event originated with the advent of high-speed spark photography [72]. The first probe registered experiment was carried out in 1867 by the German physicist August Toepler (1836–1912), when used a 2 µs spark to initiate a sound wave and then photographed the propagation using a second spark triggered with an electrical delay [73]. Other relevant first facts are more recent. The first pump–probe experiment conducted with an ultrashort laser pulse and an optical delay was used to measure the transient reflectance response of a germanium sample subjected to a 10 ps pulse [74].

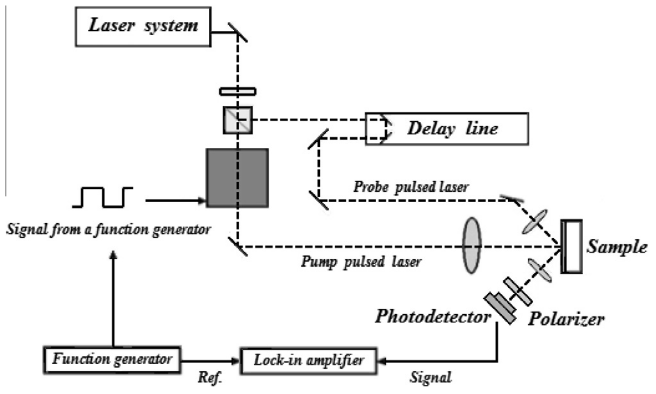

Fig. 23. Schematic diagram of the experimental setup used in the time-domain thermoreflectance technique.

A two-temperature model for describing heat transfer during ultrashort-pulsed laser heating in a metal was proposed the same year [75]. The first thermal transport experiments using picosecond thermoreflectance in films with thicknesses below a few hundreds of nanometers, for which the precise knowledge of the thermal properties of the substrate was not known, was made separately by Paddock and Eesley [76] and Young and collaborators [77] only in 1986. With their determination of the thermal diffusivity perpendicular to the surface of thick nickel films and silicium dioxide, respectively, they were able to demonstrate the capabilities of the technique for metal films of the order of 100 nm thick and the latter's independence of the result of the supporting substrate material. Years later the technique was used for measure the thermal conductivities of pure metals, such as lead, gold, aluminum, and titanium, at different temperatures [78], and metal–metal interfaces [79].

Improved optical designs, the elimination of erroneous images by adjusting signals and the corresponding improving sensitivity, have led to the extensive adoption of the TDTR technique to measure thermal conductivities of different materials in both bulk and thin-film formats, including nanomaterials and interfaces of nanomaterials, metal films, dielectric films, phase change materials, thermally anisotropic materials, superlattice structures, and layered nanolaminates, enabling experiments that were impossible decades ago [80]. Works using TDTR span the range for its use from the lowest thermal conductivity ever observed in a fully dense material ($0.05\ \mathrm{W/m \cdot K}$ for disordered thin films of the layered crystal WSe_2) [81] to the high thermal values for pure metals and thin diamond films of thickness near $1\ \mu m$ with highly non-uniform thermal conductivities owing to spatially varying disorder associated with nucleation and grain coalescence (including values above 1300 W/m K) [82]. Reported average accuracies are in the range of 5–10%.

The main advantage of the TTR method is that it is a non-contacting and non-destructive optical approach, both for heating a sample under test and for probing the variations of its surface temperature. The possibility the method has to obtain instant two-dimensional thermal maps with submicron spatial resolution and 5–50 mK temperature resolution enables the identification of whatever non-uniformity in the heating element or other thermal anomalies, which could not be detected from electrical measurements alone using, for example, the 3-ω method. The use of the method is attractive regarding, for example, the measurement of thermal conductivities of nanometer-scale thin-layer materials, because its use decouples the effect of interface conductance observed in other techniques with longer pulsed lasers, and avoids the difficulties encountered with contact methods of having to fabricate a measuring device into a sample, and then having to isolate and exclude the influence of that measuring device. These facts, together with its indisputable high accuracy and the prospects that improvements in laser performances make in the long term more sophisticated experiments possible become significant advantages for TDTR from the experimental viewpoint, once the high initial cost of the laser and optical equipment has been overcome. The possibilities for studying lateral heat flow in addition to just that through the thin film, and the measurement accuracy enhancement as well as the reduction in the time needed for it, by tuning compact laser sources over a wide wavelength range available, are some of the different current work items.

5. Concluding remarks

The determination of thermal conductivities of metals and other materials became an important issue from the nineteenth century, and even earlier. The importance originated in its impact on heat transfer processes, one of the most widely spread in chemical and other industries, and its decisive relation and incidence on other scientific matters. Several good examples may be mentioned around the scientific interest in this topic. The aforementioned studies on the solar heating influence near the earth's surface and the marked increase in the need for the most serviceable metals to be employed in boilers or fireboxes of locomotives in order to enable a much greater quantity of steam to be raised in a given time were maybe two of the most important. Other examples of specific areas benefited from the improved techniques of thermal measurements are related with the foundation of the electrical age and thereafter the increasing demand for materials with adequate values of a property closely related with thermal conductivity as it was the electrical resistance, the outstanding advances in metallurgical knowledge, allowing the development of new alloys and the extraction of metals that could not be separated previously.

Both, the material type and the range of thermal conductivity and diffusivity values over its corresponding operational temperature range influence the type of method to be used and the size, shape, and other additional specifications of the test specimen and apparatus required. Each one of the techniques developed for the determining of thermal conductivity has its own advantages as well as its inherent limitations If it is true that the transient methods, many of them involving periodic heating and based on the original and nowadays named 'classical Ångström's method', have become one of the preferred ways for current measurements of thermal properties, not only of metals, but also of different types of materials [83], other old and new techniques are equally used with the same objective. Although given different names, and using instruments of obviously greater precision and reliability, a look to current standard handbooks of properties measurements [84] show that some of the physical principles involved in methods such as, for example, those of Forbes and Lees, have however transcended time, and continue being used in modern determinations.

The temperature dependence of thermal conductivities of metals and alloys is not a different issue. Modern theoretical studies had shown that this strong relation is not a so simple matter, but a complex contribution of two mechanisms related with migration of free electrons and lattice vibrational waves. Without the availability of these current powerful models to explain the thermal, electrical, and optical properties of matter, and the modern theoretical and mathematical theories of heat conduction, scientists of the nineteenth century were, however, able to propose correlations that, although with obvious less accuracy, illustrated, to some extent, the dependence function in the same way as the different actually empirical correlations proposed [85].

A period that extended for several decades in the twentieth century seemed to show a transition from the use of steady-state methods to transient methods. The advantages shown over conventional methods included shorter times of measurement and wider measurement and working temperature ranges, as well as the possibilities to be used not only to measure the properties of various homogeneous materials but also to identify those of layered composite materials, and to simultaneously determine in a direct way, in some cases, both thermal diffusivity and the thermal conductivity [86].

The discovery of new materials over the following decades, with each time more complicated crystal structures and subsequently more complicated phonon scattering mechanisms, brought however new challenges to both the theory and experimental understanding of their behavior. The knowledge of their different properties, including those thermal, became each time more a priority issue. Metallic glasses, thin films, quasicrystals, and superlattice structures, joined many new nano-compounds to form a group of materials of great theoretical and technological interest whose characterization was, and still it is, urgently required.

New measurement techniques and analytical models have appeared, and continue doing it. Current successful techniques must to surely be still improved, and very probably also combined among themselves or with new ones, in order to not only satisfy the demanding requirements but also to expand their coverage to include surely new materials. Trends for the revival, in some cases, of classical principles used in old methods by using simple optimized apparatuses in order to make accessible techniques to a wide number of researchers are also on the way [87] Experiments based on these techniques have led to fundamental understanding of electron, phonon and photon interactions and transport in both bulk and micro/nanostructured solids as well as solid-state devices. There are still, however, many limitations [88].

Prospects of fields of research in the future should to cover a wide spectrum. Thermal transport across solid–solid interfaces, for cite an example, remains as one of the most challenging problems, and the fundamental understanding of the individual and collective role of interfaces on thermal conductivity is nowadays in only a partial state. Predictions from models developed for this subject rarely agree with experimental data mainly because they do not isolate contributions to heat transport by anharmonicity, electron–phonon coupling, interfacial disorder and chemistry. Theoretical and experimental studies on materials that reasonably expected will play each time more an important role in nanostructured materials and devices, such as carbon nanotubes and nanowires, to cite another example, are still uncompleted. Reduction in size of electronic devices provides the main driving force behind researches in nanotechnology and the superior high thermal conductivities of carbon nanotubes makes them an ideal element for providing high performance thermal-management materials. Metal composites filled with carbon nanotubes, showing remarkable reduced thermal-expansion coefficients, is in the focus of the possible innovative solutions for cooling matters. Studies on dissipation in the generally metallic multiwall carbon nanotubes (MWCNs) and the metallic or semiconducting (depending on the chirality in their crystal structure) single wall carbon nanotubes (SWCNs) are then surely one of those where progress will be made in the future.

Conflict of interest

None declared.

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