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# Studies on the temperature dependence of electric conductivity for metals in the Nineteenth Century: a neglected chapter in the history of superconductivity

*(Estudos sobre a dependência com a temperatura da condutividade elétrica de metais no século XIX: um capítulo menosprezado na história da supercondutividade)*

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Two different lines of research had significant contributions to the discovery of superconductivity: the liquefaction of gases and the studies of the temperature dependence of the electrical conductivity, or resistance, of pure metals and alloys. Different publications have described and discussed the achievements in the first one of these subjects. The second subject had not received, however, the same attention. This article tries to fill this gap by presenting an account showing details of the evolution of the ideas, the first essentially experimental contributions to the subject and their corresponding responsible persons.
**Keywords:** superconductivity, electrical resistance, temperature, dependency relation, history, metals, alloys.

Duas diferentes linhas de pesquisa deram significativa contribuição à descoberta da supercondutividade: a liquefação de gases e os estudos da dependência da condutividade ou resistência elétrica com a temperatura, em metais puros ou ligas. Diferentes artigos descrevem e discutem as conquistas da liquefação ao passo que a segunda não recebeu, contudo, a mesma atenção. Este artigo busca preencher esta lacuna, apresentando um histórico detalhado da evolução de idéias, das primeiros resultados experimentais e dos pesquisadores nelas envolvidos.
**Palavras-chave:** supercondutividade, resistência elétrica, dependência com a temperatura, história da supercondutividade em metais e ligas.

## 1. Introduction

The traditional accounts about the discovery of superconductivity, whose first century is commemorated this year, show it as a consequence, in some way accidental, of the experimental researches on the liquefaction of the by then so called 'permanent' gases. A previous article on this subject is mainly focused on the historical evolution of these events [1]. This conception is, however, historically incomplete, since parallel achievements developed in a different line of research made equally significant contributions to the identification of the new phenomenon. The necessity for disposing of appropriate thermometric instruments for the each time more extreme and limited regions of low temperature in order to replace those, by then, unpractical gaseous ones, forced the carrying out of researches focused on the application of different physical principles and materials in order to fill this objective. The studies on the electrical conductivity, or resistance, of pure metals and alloys and their temperature dependence aroused the interest of scientists of different nationalities in the second half of the nineteenth century and the first half of the twentieth century, and contributed not only to the understanding of the electrical properties of those materials but also to the proposal of several theoretical models on electric conduction. The purpose of this article is to expose an account of the more relevant facts related with this second line of knowledge, including details of the first essentially experimental contributions to the subject and their corresponding responsible persons.

## 2. The concept of electrical conductivity in the eighteen century and the first studies on its dependence with temperature

Although the first real theoretical advancement on electrical conductivity of metals came with the German physicist Paul Karl Ludwig Drude (1863-1906) by

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putting forth his famous free electron theory [2], the establishment of electricity as an imponderable elastic fluid transferable from one body to another had been discovered around one hundred and eighty years before by the British scientist Stephen Gray (1666-1736), sweeping so away the old idea of an electrical effluvia inseparably attached to a body in which they were excited [3,4]. Stimulated by the reading of the accounts of the physicist and compatriot his Francis Hawksbee (1666-1713) [5,6], and after some experiences on related subjects as assistant to the also British natural philosopher Jean Theophilus Desaguliers (1683-1744), Gray, a dyer by profession and an amateur naturalist by inclination, carried out in 1720 a series of experiments using a hemp thread that allowed him to demonstrate that electricity could be conducted by some materials for distances as great as 233 m, while others did not conduct electricity at all [7]. Although initially almost ignored, the early Gray's ideas on electrical communication came to the fore nine years later, and became of the public domain with a new publication in 1731 [8].

No further significant progress was made on this subject until 1734, when the French scientist and Superintendant of the Jardins du Roi, Charles François de Cisternay du Fay (1698-1739), suggested the existence of two kinds of electric fluid, vitreous and resinous, which could be separated by friction and neutralized each other when they combined [9]. The so-called "two-fluid" theory of electricity proposed by du Fay, based on experiments with the attraction and repulsion of different electrified substances, was later contrasted with that of "one-fluid" theory suggested by the American scientist Benjamin Franklin (1706-1790), which considered only one fluid either present, positively or negatively charged [10]. With the classification of substances as conductors or insulators and the establishment of the electricity flow direction from positive to negative, the basis for the behavior of the new property was ready.

It is the British natural philosopher Joseph Priestley (1733-1804) the first in trying, although with great imperfections, the estimation of electrical conductivity in metals by using static electricity. He determined the relative scale of conduction power between two metals by measuring the amount of fine test melted after passing similar discharges through wires of identical length and diameter [11]. The first notice about the dependence of electrical conduction with temperature, however, is very probably due to the British scientist Henry Cavendish (1731-1810). Accurate measurements he did in 1776 of relative resistances of an iron wire and solutions of common salt allowed him to identify better conduction powers for warmer solutions than for colder ones [12]. The first more reliable measurements for metals with voltaic electricity are attributable to the British chemist Humphry Davy (later Sir) (1778-1829), who carried out researches in 1821 by which not only clearly proved the differences existing between the conducting power of different materials and its dependence with temperature, but also found the relation of this power to the other physical variables such as weight, surface and length of the conducting body, as well the conditions of electro-magnet action [13]. Working as nearly as possible with similar wires (diameter being more than one-tenth of an inch and lengths of three inches) of platinum, silver wire, copper, tin, iron, lead, gold and palladium, Davy found much greater differences in the behavior of different materials than he initially expected, and, over all, what he considered the most remarkable result, which was the significant variation of the corresponding conducting powers with temperature, being lower in some inverse ratio as the temperature was higher. One year before the publication by the German physicist Georg Simon Ohm (1789-1854) of the well-known mathematical theory of the galvanic circuit, and based on the Davy's work, the French scientist Antoine César Becquerel (1788-1878) compiled in 1826 a list of conductive powers of nine metals (relative to that of cooper), which was considered as a reference work and used as a guide on the subject for several decades [14].

## 3. The first analytical relations of dependence

The first mathematical relation for the temperature dependence of electrical conductivity was established by the Russian physicist and Professor at the University of Saint-Petersburg, Emil Khristianovich Lenz (Heinrich Friedrich Emil) (1804-1865) (Fig. 1), widely known by the discovery of two fundamental physical laws on the phenomena of induction and the thermal action of a current (the latter now better known as Joule's law) [15]. After finishing some electromagnetic experiments on the influence of various factors in the induction of the electrical currents by magnets, and before starting those that led him to the establishment of the law that bears his name, Lenz was involved in studies on the electrical resistance and conductivity in metals. In an article published in 1832 [16] he revealed how the lecture of a paper written by the Italian physicist Leopoldo Nobili (1784-1835) and his countryman, the science administrator Vincenzo Antinori (1792-1865), on the electrical phenomena produced by a magnet [17], suggested him the idea for the new subject of research. The paper describe the way they used for determining the order in which four different metals (cooper, iron, antimony and bismuth) were adapted to produce the electric current by magnetism. The Lenz's exact words were: "it is particularly striking that the order is the same as that which these metals occupy, also, in reference to their capacity of conducting electricity, and the idea suddenly occurred to me whether the electromotive power of the spirals did not remain the same in all metals; and whether the stronger current in the one metal did not arise from its being a better conductor of electricity than the others. With this in view, I examined four metals, cooper, iron, platinum and brass" [16].

Figure 1 - Emil Khristianovich Lenz.

In a later paper, read before the Academy of St. Petersburg on June 7, 1833, Lenz revealed details of his research. A pair of identical spirals were built for each metal under investigation and connected in series into a single circuit whose free ends were joined by cooper lead wires to a galvanometer very similar to that invented by Nobili. By using a circuit with an electromotive force which was free of the uncertainty implied by the internal resistance of the battery, Lenz was able to find the electric conductivity of each one of the studied metals at different temperatures and found with considerable degree of accuracy the magnitude of their respective changes with this variable. The ballistic method based on the original conception of an instantaneous, impact-like effect of induction current he employed for measuring this and other electric and magnetic quantities, allowed him to determine values at between six and twelve different temperatures for, initially, silver, copper, brass, iron and platinum [18], and sometime later, gold, lead and tin too [19]. According to the particular analytical style that characterized his research and differenced it from that of most of contemporaneous colleagues, Lenz worked the whole set of experimental values with the assistance of mathematical methods, mainly that of least squares, looking for the establishment of a general quantitative relation between both variables. The relation he found for this specific case was (*using his own notation*)

$$\gamma_n = x + yn + zn^2 \ ,$$

where $\gamma_n$ represented the electrical conductivity at a temperature $n$, $x$ the conductivity at 0 °C in the Reaumur scale, and $y$ and $z$ two particular coefficients for each specific substance (Table 1).

Table 1 - Lenz's specific coefficients for electrical conductivity of eight metals. Credit: Ref. [19].

| | |
|---|---|
| *für Silber* $\gamma_n$ | $=136{,}250-0{,}49838\ .n+0{,}00080378.n^2$ |
| *für Kupfer* $\gamma_n$ | $=100{,}000-0{,}31368\ .n+0{,}00043679.n^2$ |
| *für Gold* $\gamma_n$ | $=79{,}792-0{,}170284.n+0{,}00024389.n^2$ |
| *für Zinn* $\gamma_n$ | $=30{,}837-0{,}127726.n+0{,}00023733.n^2$ |
| *für Messing* $\gamma_n$ | $=29{,}332-0{,}051685.n+0{,}000061316.n^2$ |
| *für Eisen* $\gamma_n$ | $=17{,}741-0{,}083736.n+0{,}00015020.n^2$ |
| *für Blei* $\gamma_n$ | $=14{,}620-0{,}060819,n+0{,}000107578.n^2$ |
| *für Platin* $\gamma_n$ | $=14{,}165-0{,}038899.n+0{,}00006586.n^2$ |

Lenz determined as well the ranges in which the formulas could be utilized for each one of the studied metals. Researches carried out more than a decade later by the German physicist and mathematician Johann Heinrich Müller (1809-1875) showed a favorable comparison between the results found by application of these formulas and the experimental values [20].

The next essay on the subject was carried out more than a decade later by the third son of the previously mentioned A.C. Becquerel, the French physicist Alexandre-Edmond Becquerel (1820-1891) (Fig. 2), more known by his studies on solar radiation and on phosphorescence. The author did not make, however, any reference to the Lenz's work, and the research included not only the effect of heating on the electrical conductivity for a larger number of metals, but also for some liquids and solutions.

The apparatuses he used for the study incorporate several changes in order to improve the accuracy regarding that used by Lenz, and are schematically shown in Fig. 3 [21]. A first step for the evaluation of the temperature influence on the conduction power was its determination at a reference value (around 12.75 °C). The corresponding device included (Fig. 3a) a differential galvanometer having two separate wires in its coil (one of them of the metal to be studied) and placed on the board SS', a couple FF' formed by one cylinder of amalgamated zinc immersed in a saturated sodium chloride solution and other of cooper in a solution of sulphate of the same metal, an early version of a Wheatstone rheostat DEE'D' for the introduction of a conductor wire in the circuit, and a device RAA'R' where the wire whose conductivity was to be determined was placed.

If the wires was be made of two different metallic conductors of equal conducting power connecting the poles of the same galvanic pair or battery, and so that both currents shall be in opposite directions through the galvanometer, the needle of the latter would be stationary, and this became the test for the equality of the conduction powers of the two metals. A quantity denominated equivalent of resistance must to be determined in terms of a number of divisions in the rheostat for a definite length of wire of the metal to be studied. The rheostat was made to furnish a measure of the resistance to conduction of a given length of wire, and on this way the length of the other wire must to be conditioned according its conduction power in order to maintain the equilibrium of the needle. If the nature of the connections remaining the same, the apparatus was arranged so that scarce any change could be made in either circuit, beyond that of the length of the wire, and the corresponding variations in the length of the wire under study could be read off in a graduated scale.


Figure 2 - Alexandre-Edmond Becquerel.

The study of the effect of temperature included a simple arrangement (Fig. 3b), in which the wire under investigation was putted around a metallic tube CD to form a helix whose convolutions were not touching, and introduced along with the bulb of a thermometer into a bath of oil. Two thick connecting parts of cooper, whose resistance to electrical conduction could be neglected regarding that of the wire, were connected with the extremities of the latter in the bath, and the whole arrangement was then immersed in a water bath. The increase of the equivalent of resistance in the wire due to heating it from the ambient temperature to the boiling point could be then accurately measured by allowing the heated bath to cool gradually. The obtained results allowed Becquerel to conclude that the increase of resistance by unitary change of temperature ($dr/dt$) was a characteristic constant for each metal studied. Although without the primary purpose for explicitly establish an analytical equation for estimating conductivities, Becquerel arranged the results as a function of both, the so called coefficient of the increment of resistance ($dr/dt/$ resistance at 0 °C) and temperature,

$$R = R_0\,(1 + at)\,,$$

where $R_0$ represents the electrical resistance of the metal at 0 °C. The Table 2 presents the coefficients he estimated for a number of metals.

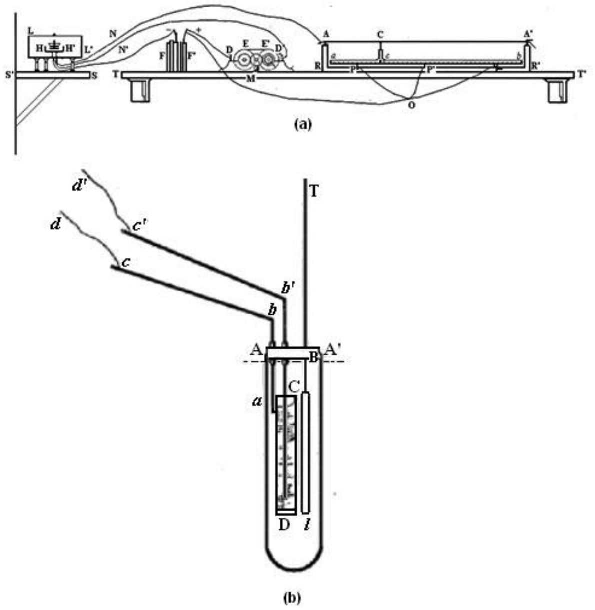


Figure 3 - Becquerel's equipment. Credit: Ref. [21].

A few time later, in the second semester of 1848, the Irish astronomer and physicist, Rev. Dr. Thomas Romney Robinson (1792-1882), made a contribution to the subject, which have been almost ignored by historians. Unsatisfied as he was, on one side with the imperfect state of the rheometric knowledge and the unsteady action of the batteries implied in the experiments carried out by Davy, and with the range of temperature covered by the researches of both, Lenz and Becquerel, (little above of that of boiling water) on the other, Robinson meant to find a more general relation between conductivity and temperature based on his strong belief about a close relation between it and the molecular forces and the structure of matter. The main difference in the equipment used was the inclusion of a pyrometer to measure the temperature by expansion of a wire of the material to be investigated [22]. Although he apparently identify the analytical expression

Table 2 - Becquerel's coefficients of increment of resistance for several metals. Credit: Ref. [21].

| | Coefficient d'augmentation de résistance pour 1 degré. |
|---|---|
| Mercure | 0,001040 |
| Platine | 0,001861 |
| Or | 0,003397 |
| Zinc | 0,003675 |
| Argent | 0,004022 |
| Cadmium | 0,004040 |
| Cuivre | 0,004097 |
| Plomb | 0,004349 |
| Fer | 0,004726 |
| Étain du commerce contenant peut-être du plomb | 0,005042 |
| Étain assez pur | 0,006188 |

$$R = R_0 + bT,$$

(where $R_0$ was the resistance at 0 °C, $b$ its change for one degree) as the more appropriate to represent the results of his experiments, Robinson also understood that it was required to introduce corrections due to the heating effect of the current on the rheostat and resistance coils by which they were measured. The formula to which he finally arrived, whose results showed close agreement with the experimental values, would be

$$R = R_0 + bT - cR^2I^2,$$

where $I$ is the electric current. The coefficients $a$, $b$ and $c$, specific again for each substance, could be determined by minimum squares techniques or ordinary elimination on the basis of experimental values of successive trials. The initial promising results showed for platinum wires of different thickness quickly became strongly limited. The possibility to extend these experiments to other metals was minimized because of the difficulty to find any determination of similar expansions to that gotten for platinum, with the only exceptions of iron and copper. The oxidation in the pyrometer of the first of these metals did not permit, however, to get consistent results. Cooper also oxidized, but the film of the oxide acted as a coating and protected the interior, prevented changes in the diameter of the wire for temperatures below 480 °C. With results for only platinum and cooper, the research had not important diffusion among the then scientific community.

## 4. Arndtsen, Siemens and the improvements of accuracy and coverage

The separate works on the subject by the Norwegian neurophysiologist, physicist, and professor at the University of Christiania, Adam Frederik Oluf Arndtsen (1829-1919) (Fig. 4) and the German Ernst Werner Siemens, complete this first chapter of the history. Regarding the first, it was very probably that his early interests on phenomena related with nerve conductivity and transmission, and in general on the uses of electricity in medicine in general, motivated him to carry out researches on the electrical resistance in metals at different temperatures. Knowledgeable, as he was, of the Lenz's work, the primary objective Arndtsen had with the experiments was to eliminate some sources of error he indentified in previous researches, in order to improve the accuracy of the by then known results. These mistakes were mainly focused in the significant influence the contact between the wire and the warm liquid had, specially at high temperatures, on the conductivity measurements. With this purpose in mind, Arndtsen modified twice the arrangements used by his predecessors by working first in his native land, and later at Gottingen in the laboratory of one of his professors, the German physicist Wilhelm Eduard Weber (1804-1891).

Figure 4 - Adam Frederik Oluf Arndtsen. Credit: Courtesy of Justervesenet (Norwegian Metrology Service).

In order to make the above mentioned corrections, the first arrangement included the covering of the metallic wire $L$ with silk, its winding up around a test tube of a little diameter, and the soldering of the free ends of two thick and short cooper wires $ab$ and $bc$ (with lengths appropriately conditioned as it is exposed above) completed with caps fully filled with mercury. The new disposition was then placed into other wider glass test tube provided with a thermometer and closed with corks, and the whole device was immersed in a water or oil bath carefully kept at constant temperature. The whole assembly was coupled to a simple Wheatstone's differential galvanometer $AA$ and the rheostat $R$ as the basic elements of the circuit. The essential differences of the second arrangement regarding the first one were the introduction not only of a previously calibrated copper wire *ce* placed on a board $R$ and coupled to the motor $B$ for carry out the rheostat function, but also of a differential galvanometer $A$ with multipliers $a$ and $b$ and the respective reel $M$ in the assembly of the whole equipment. This latter modification had as objective to amplify in the scale $F$ the effect of the current, further deflecting the needle $m$, improving so the accuracy of sensitivity, and, as consequence, the accuracy of measurements [23]. Both arrangements are shown in the Fig. 5.

To the only metals studied in the first series of experiments, cooper and platinum, Arndtsen subsequently added silver, aluminum, brass, iron, lead, and the alloy argentan, or German silver, composed this latter by nickel, copper and zinc. The experiments showed a proportional resistance increasing with temperature for most of the metals under investigation, it meant silver, copper, aluminium and lead, confirming so the previous Becquerel's findings. Regarding brass, argentan and iron, the changes in resistance with temperature were far from to be simply proportional and Arndtsen decided to use a parabolic equation of second order for represent the corresponding experimental data. Some of the formulas he found, valid in the range studied, 0 to 200 °C, are shown in Table 3.

Arndtsen observed that, with the only exception of iron, the proportional increase in the resistance for the six different metals investigated varied very little, and that if the resistance at the freezing point was called 100, the numbers representing the increase for one centigrade degree in the metals he investigated lied, again with the exception of iron, between 0.327 and 0.413. This fact allowed him to speculate that if still more carefully investigations were carried out and absolutely pure metals were employed, perfectly accordant numbers could be obtained. This little difference led the German physicist and mathematician Rudolf Julius Emanuel Clausius (1822-1888) to suggest a very simple and original new class of relation between both variables. After glance at the Arndtsen's results, and without an apparent connection in his mind with any theoretical consideration, Clausius observed that they very closely approached the coefficients of expansion [24]. By leaving of consideration the quadratic member occurring in iron and taking the mean of the whole of the first coefficients, he obtained the following expression for the resistance at the temperature $t$ as a function of the resistance at the freezing point $R_f$

$$R = R_f \,(1 + 0.00366\; t)\,.$$

From this equation he followed that, although the number of metals investigated was still too small and the agreement of the numbers too imperfect to enable him to arrive to a "safe" conclusion, the resistance of simple metals in the solid state was nearly in proportion to the absolute temperature. Almost a quarter of a century later, this speculation was taken up again by the Polish physicist and chemist Zygmunt Florenty Wróblewski (1845-1888), who inferred from it the fact that the electric conductivity of metals would be null at the temperature of zero absolute. This inference can be considered the first explicit, although unconscious, reference to the phenomena what would be later called superconductivity. Although Wróblewski carried out researches on this subject working with copper, the technical limitations by then existing only allowed him to reach temperatures of about -200 °C, and he was therefore unable to establish conclusive experimental support about this fact [25]. It seems that no further investigations about this relation were later proposed and the speculation did not go further away.

Table 3 - Arndtsen's equations for electric resistance of some metals as a function of temperature. Credit: Ref. [23].

| | |
|---|---|
| Silber | $w_t = 241190 + 823{,}471 . t$ |
| Kupfer | $w_t = 244370 + 901{,}456 . t$ |
| Aluminium No. 2 | $w_t = 427616 + 1555{,}924 . t$ |
| » » 1 | $w_t = 476218 + 1622{,}903 . t$ |
| Messing | $w_t = 949086 + 1577{,}381 . t - 2{,}5948 . t$ |
| Argentan | $w_t = 1289815 + 499{,}623 . t - 0{,}71946 . t^2$ |
| Eisen | $w_t = 1626643 + 6718{,}686 . t + 8{,}5745 . t^2$ |
| Blei | $w_t = 2631490 + 9914{,}665.$ |

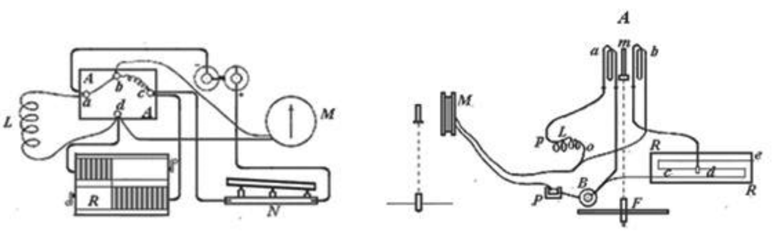

Figure 5 - Two assemblies used by Arndtsen. Credit: Ref. [23].

About 1860 the inventor and industrialist Ernst Werner Siemens (1816-1892) (Fig. 6) investigated the law of change of resistances in wires by heating and proposed several equations and methods for testing resistances and use them for determining faults. His interest on the subject was not casual, but arouse as a consequence of preceding researches, mainly related with electrical communication, which had allowed him to developments such as the invention of the pointer telegraph, the magneto-electric dial instrument giving alternate currents, and the instrument for translating on and automatically discharging submarine cables, among others. The subject of telegraphy was closely associated with the then system of electrical measurements and with the invention of many delicate measuring instruments. The requirement of other standards of measurements in order not only to some quantities could be gauged, but also consistent work could be done, led W. Siemens and other contemporary scientists to the identification of a general, easily reproducible, and sufficiently accurate standard measure of resistance.

Figure 6 - Ernst Werner Siemens.

W. Siemens adopted in this search the resistance of mercury as the unit, and embarked on its more accurate possible experimental determination at different temperatures. Among the enough criteria for its choice were facts such as that it could be easily be procured of sufficient, almost indeed of perfect purity, the nonexistence of different molecular states that could affect its conducting power, a smaller dependence of its resistance with temperature regarding other metals, and a very considerable specific resistance that allowed that numerical comparisons founded on it as a standard were small and convenient. As every experimenter would then be able to provide himself with a standard measure as accurate as his instruments permit or require and to check the changes of resistance of the more convenient metal standard, W. Siemens understood the necessity for establishing a comparison between the conducting power of mercury and some solid metals. By using identical experimental procedures with all materials under investigation, he was able to build a table including the relative conducting power of nine metals at the temperature $t$ (Table 4) [26]. The results showed very acceptable agreement with those presented by Arndtsen regarding common metals in both studies.

Table 4 - Siemens's conducting powers of nine metals at a temperature $t$ compared with that of mercury at 0 °C. Credit: Ref. [26].

| | |
|---|---|
| Quecksilber | $\frac{1}{1+0{,}00095t}$ |
| Blei | $\frac{5{,}1554}{1+0{,}00376t}$ |
| Platin | $\frac{8{,}257}{1+0{,}00376t}$ |
| Eisen | $\frac{8{,}3401}{1+0{,}00413t+0{,}00000527t^2}$ |
| Neusilber | $\frac{10{,}532}{1+0{,}000387t-0{,}000000557t}$ |
| Messing, | $\frac{14{,}249}{1+0{,}00166t-8{,}00000203t^2}$ |
| Aluminium | $\frac{31{,}726}{1+0{,}003638t}$ |
| Kupfer | $\frac{55{,}513}{1+0{,}00368t}$ |
| Silber, hart | $\frac{56{,}252}{1+0{,}003414t}$ |

## 5. The researches of Augustus Matthiessen

The maybe most widely known and integral researches in the nineteenth century on the electric conductivities of metals and their relation with different variables, including temperature, were carried out by the British chemist and physicist Augustus Matthiessen (1831-1870) between 1857 and 1864. It was during the studies at Heidelberg that his interest in electrical subjects arose. From 1853 he spent nearly four years under the direction of German chemist Robert Wilhelm Eberhard Bunsen (1811-1899), isolating for the first time the metals calcium and strontium in the pure state by means of electrolytic methods. The studies of the electrical conductivities of these metals, and later of many others, carried out in the laboratories of the German physicist Gustav Robert Kirchhoff (1824-1887), became the opening to researches in the area. Kirchhoff had made in 1849 what can be very probably considered the first absolute determination of resistance, and his skills for not merely working out the solution of each new physical problem he faced up to after it had been so formulated, but also for stating it in terms of mathematics, very probably influenced the character of Matthiessen's later investigations on conductivities and other areas.

A first paper published by Kirchhoff in Matthiessen's name on the electric conductivity of the two above mentioned metals, besides potassium, sodium, lithium and magnesium, embodied the experimental results obtained by Matthiessen in the physical laboratory [27].The required wires were formed in a device he designed to press out small portions of metals into thin samples by means of a steel pressure, while the determination of the resistances was made by using a slightly modified apparatus constructed by Kirchhoff on the basis of the Wheatstone's method. Other publications his, including experimental data of conductivities for twenty-five metals, followed this paper [28].

Almost simultaneously Matthiessen also showed interest in alloys made of two metals because of the multiple industrial applications he predicted for them [29], and proceeded to determine not only the electrical conductivities of upwards of 200 alloys of variable composition [30], but also their tenacities and specific gravities. He decided to classify the metals employed in the different alloys in order to try to state some general rules about the behavior of their conductivities compared to those in individual condition. The classification included two great groups: those which, when alloyed with one another, conducted electricity in the ratio of their relative volumes, and others which, when alloyed with one of the metals belonging to the first class, or with one another, do not conduct electricity in the ratio of their relative volumes, but always in a lower degree than the mean of their volumes. To the first class belonged lead, tin, zinc, and cadmium, whereas to the second belonged bismuth, mercury, antimony, platinum, palladium, iron, aluminum, gold, copper, silver, and, as he thought, in all probability most of the other metals. The alloys were consequently divided into three groups: those made of the metals of the first class with each other; those made of the metals of the first class with those of the second class, and finally those made of the metals of the second class with each other. The comparison between the obtained experimental values and those calculated by assuming a proportional participation of each metal in the whole value according to its relative volume in alloys showed very acceptable agreements. Other comparison, this time between the magnitudes of the electric conductivities of the alloys and those of their constituents, allowed him too to work in the opposite way, and get information about the real nature of the alloys and to state if some chemical combination would really exist there or not. On the same way, and because of the preparation of cooper of the greatest conductivity had great practical importance in connection with telegraphy and his results showed significant discrepancies regarding previous similar observations by different researchers, Matthiessen embarked as well in studies about the probable influence of minute quantities of other metals, metalloids and impurities on the quantitative magnitude of this property [31].

Matthiessen's first researches on the influence of temperature on the electric conducting power of metals were published in 1862. The paper describes the apparatus and the corresponding procedure in the minute detail that characterized all his scientific work [32]. Figure 7a shows the disposition of the whole apparatus. $B$ is the trough in which the wires (soldered to two thick copper wires, bent as shown in the figure, and ending in the mercury-cups $E$, which were connected with the apparatus by two other which were connected with the apparatus by two other copper wires, $F'$, of the same thickness) were heated by mean of an oil-bath; $C$ a piece of board placed in such a manner in order to prevent the heat of the trough from radiating on the apparatus; $G$ a cylinder glass including the normal wire soldered to the wires $F''$; $H$ a wire of German silver stretched on the board, $I$ the galvanometer, $K$ the battery, $L$ and $L'$ two commutators fitting into four mercury-cups at $o$, and $M$ the block to make the observations. In addition, $a$ identifies the tubes for filling the space between the inner and outer troughs with oil, and $d$ a glass tube allowing the thermometer $c$ to pass freely. The way as the wire to be studied was placed on a small glass tray in the trough is shown separately in the Fig. 7b.

Matthiessen determined the conducting power of the wires or bars of silver, copper, gold, zinc, tin, arsenic, antimony, bismuth, mercury, and the metalloid tellurium at about 12°, 25°, 40°, 55°, 70°, 85°, and 100 °C, and from the mean of the eight observations made with each wire (four at each temperature on heating, and four on cooling), deduced the same general formula previously proposed by Lenz for representing its dependence with temperature, but determining new sets of coefficients for each one on the basis of the new accurate experimental data. Table 5 shows the mean of the formula found for some metal, with the conducting power of each one taken equal to 100 at 0 °C. Some conclusion he arrived, by which the conducting power of all pure metals in a solid state would seem to vary in the same extent between 0 °C and 100 °C, it meant 29.307%, did not received additional experimental support and consequently did not extend in the time.

Two years later he published a new article on the effect of temperature, this time on alloys [33]. The conclusions of the study showed great similarity in the behavior of the alloys regarding those of the metals which composed them. By using a very similar apparatus he was able to find that the conducting-power of alloys decreased (with exception of some bismuth alloys and few others) with an increase of temperature and to deduce specific equations of dependence for fifty-three alloys composed by two metals and three alloys composed by three metals. The Table 6 shows the results for some alloys of definite chemical formula; Table 7, on the other side, shows the variation of these formulas for alloys including the same metals but different composition. All the values were reduced to 0 °C, as mentioned for pure metals.

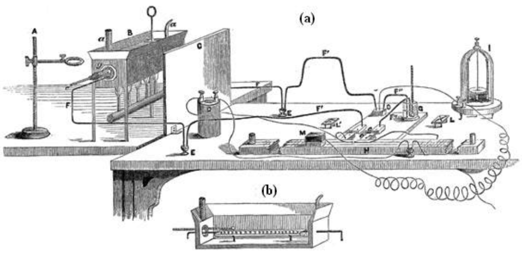


Figure 7 - Matthiessen's apparatus. Credit: Ref. [32].

Table 5 - Matthiessen's analytical expressions for the relative electrical conductivities of ten different metals. Credit: Ref. [32].

| | |
|---|---|
| Silver .................. | $\lambda=100-0{\cdot}38287t+0{\cdot}0009848t^2$ |
| Copper.................. | $\lambda=100-0{\cdot}38701t+0{\cdot}0009009t^2$ |
| Gold .................... | $\lambda=100-0{\cdot}36745t+0{\cdot}0008443t^2$ |
| Zinc ..................... | $\lambda=100-0{\cdot}37047t+0{\cdot}0008274t^2$ |
| Cadmium ............ | $\lambda=100-0{\cdot}36871t+0{\cdot}0007575t^2$ |
| Tin ..................... | $\lambda=100-0{\cdot}36029t+0{\cdot}0006136t^2$ |
| Lead .................. | $\lambda=100-0{\cdot}38756t+0{\cdot}0009146t^2$ |
| Arsenic ............... | $\lambda=100-0{\cdot}38996t+0{\cdot}0008879t^2$ |
| Antimony ............ | $\lambda=100-0{\cdot}39826t+0{\cdot}0010364t^2$ |
| Bismuth ............... | $\lambda=100-0{\cdot}35216t+0{\cdot}0005728t^2$ |
| Mean of the above ... | $\lambda=100-0{\cdot}37647t+0{\cdot}0008340t^2$ |

Table 6 - Matthiessens's analytical expressions for the temperature dependence of electric conductivities of some alloys of definite chemical formula. Credit: Ref. [33].

| Alloy. | Formulæ for the correction of the conducting-power for temperature. |
|---|---|
| $Sn_6$ Pb ................................ | $\lambda=12{\cdot}002-0{\cdot}046645t+0{\cdot}0001042t^2$ |
| $Sn_4$ Cd ................................ | $\lambda=14{\cdot}558-0{\cdot}059337t+0{\cdot}0001728t^2$ |
| $Sn_2$ Zn ................................ | $\lambda=16{\cdot}747-0{\cdot}065044t+0{\cdot}0001460t^2$ |
| Pb Sn ................................ | $\lambda=10{\cdot}139-0{\cdot}038358t+0{\cdot}00008536t^2$ |
| Zn $Cd_2$ ................................ | $\lambda=25{\cdot}619-0{\cdot}096978t+0{\cdot}0002049t^2$ |
| Sn $Cd_4$ ................................ | $\lambda=21{\cdot}658-0{\cdot}083368t+0{\cdot}0002038t^2$ |
| Cd $Pb_6$ ................................ | $\lambda=\ 9{\cdot}155-0{\cdot}032041t+0{\cdot}00006647t^2$ |

A very significant conclusion Matthiessen derived from the study was the deduction of the fact that the absolute difference between the observed and calculated resistances of an alloy at any temperature equaled the absolute difference between the observed and calculated resistances at 0 °C. On this basis it was followed that the formula for the correction for temperature for a specific alloy could be then easily be determined with only knowing its composition and its resistance at any temperature.

Table 7 - Matthiessen's analytical expressions for the variation of the temperature dependence of electric conductivities of some alloys including the same metals with composition. Credit: Ref. [33].

| Alloy. | Volumes per cent. | Formulæ for the correction of the conducting-power for temperature. |
|---|---|---|
| Lead-silver ........................ | 94·64 of Pb | $\lambda=\ 8{\cdot}880\ -0{\cdot}032149t\ +0{\cdot}00007070t^2$ |
| Lead-silver ........................ | 46·90 of Pb | $\lambda=12{\cdot}731\ -0{\cdot}024986t\ +0{\cdot}00003947t^2$ |
| Lead-silver ........................ | 30·64 of Pb | $\lambda=21{\cdot}874\ -0{\cdot}043652t\ +0{\cdot}00005687t^2$ |
| Tin-gold.............................. | 90·32 of Sn | $\lambda=\ 8{\cdot}2418-0{\cdot}025418t\ +0{\cdot}00005472t^2$ |
| Tin-gold.............................. | 79·54 of Sn | $\lambda=\ 4{\cdot}7963-0{\cdot}014006t\ +0{\cdot}00003020t^2$ |
| Tin-copper (hard drawn)............ | 93·57 of Sn | $\lambda=12{\cdot}034\ -0{\cdot}044328t\ +0{\cdot}00009781t^2$ |
| Tin-copper (hard drawn)............ | 83·60 of Sn | $\lambda=12{\cdot}764\ -0{\cdot}042457t\ +0{\cdot}00008734t^2$ |
| Tin-copper (hard drawn)............ | 14·91 of Sn | $\lambda=\ 8{\cdot}8223-0{\cdot}0048266t+0{\cdot}000002593t^2$ |
| Tin-copper (hard drawn)............ | 12·35 of Sn | $\lambda=10{\cdot}154\ -0{\cdot}0067656t+0{\cdot}00001203t^2$ |
| Tin-copper (hard drawn)............ | 11·61 of Sn | $\lambda=12{\cdot}102\ -0{\cdot}0083587t+0{\cdot}000003674t^2$ |
| Tin-copper (hard drawn)............ | 6·02 of Sn | $\lambda=19{\cdot}716\ -0{\cdot}019626t\ +0{\cdot}00001390t^2$ |
| Tin-copper (hard drawn)............ | 1·41 of Sn | $\lambda=62{\cdot}463\ -0{\cdot}16713t\ \ +0{\cdot}0003136t^2$ |
| Tin-silver ............................ | 96·52 of Sn | $\lambda=12{\cdot}384\ -0{\cdot}047293t\ +0{\cdot}0001014t^2$ |
| Tin-silver ............................ | 75·51 of Sn | $\lambda=13{\cdot}706\ -0{\cdot}051720t\ +0{\cdot}0001172t^2$ |
| Zinc-copper (hard drawn) ......... | 42·06 of Zn | $\lambda=21{\cdot}793\ -0{\cdot}029939t\ +0{\cdot}00002916t^2$ |
| Zinc-copper (hard drawn) ......... | 29·45 of Zn | $\lambda=21{\cdot}708\ -0{\cdot}027632t\ +0{\cdot}00002698t^2$ |
| Zinc-copper (hard drawn) ......... | 23·61 of Zn | $\lambda=28{\cdot}298\ -0{\cdot}040039t\ +0{\cdot}00003832t^2$ |
| Zinc-copper (hard drawn) ......... | 10·88 of Zn | $\lambda=46{\cdot}934\ -0{\cdot}095947t\ +0{\cdot}0001423t^2$ |
| Zinc-copper (hard drawn) ......... | 5·03 of Zn | $\lambda=60{\cdot}376\ -0{\cdot}14916t\ \ +0{\cdot}0002473t^2$ |

## 6. Extension and consolidation of an analytical relation

The investigations of Arndtsen, W. Siemens, and Matthiessen were limited to the range of temperatures between the freezing and boiling-points of water, and do not comprise important metals such as platinum, which began to be considered as the most valuable metal for constructing pyrometric instruments. The equation, including the coefficients determined by Matthiessen for example, gives a close agreement with observation between the narrow limits indicated, but resulted wholly inapplicable for temperatures exceeding 200° Centigrade, when the term $t^2$ began to predominate and to produce absurd values for $R$. This had been clear for German born engineer Carl Wilhelm (later Charles William) Siemens (1823-1883) (Fig. 8), who in 1860, in the course of the testing of the electrical condition of the Malta to Alexandria telegraph cable, its manufacture and submersion, identified the potential danger of the heat that could be spontaneous generated within a large amount of cable, either when coiled up at the works or on board ship, due to the influence of the moist hemp and iron wire composed its armature. In considering the ways by which such increase of temperature might happen, his attention was directed to the importance for studying the relation between electric conductivity and temperature. This study additionally led some time later to made use of this relation for the design of a new thermometer. The instrument, which really worked as an electric thermometer, was further perfected by C.W. Siemens and applied as a pyrometer to the measurement of furnace fires.

Figure 8 - Wilhelm (William) Siemens.

As a consequence of this design, C.W. Siemens undertook to carry out a series of detailed experiments in order to find a more widely applicable equation [34]. His work was initially focused on platinum, the metal he considered in many aspects the most suitable one for extending the enquiries to high temperatures, and that Matthiessen had been left out of consideration in his researches. C.W. Siemens carried out then three series of experiments using equal number of different assemblies. In the first one the wire was wound upon a cylinder of pipeclay in helical grooves to prevent contact between the convolutions of the wire. This wire was then placed together with a delicate mercury thermometer, first in a cooper vessel contained in a bath of linseed oil, and then in a larger vessel, packing with sand between the two in order to the too sudden radiation and the consequent change of temperature. Wire was then connected with a Wheatstone's bridge and a sensitive galvanometer. The bath was then very gradually heated by a series of small burners, being the resistances read off at intervals of 4 to 5 °C whilst the oil was kept in continual motion. When the highest point had been reached, the bath was allowed to gradually cool down measurements were taken at the same points of temperature as before. This methodology was repeated several times until about six readings of the resistance at each point of temperature had been obtained. The second assembly (Fig. 9) replaced the wire in the pipeclay by a spiral contained in a glass tube and hung by its leading wires in a rectangular air chamber. The space between the walls was filled with sand in order to insure too a very steady temperature inside. Three mercury thermometers with the bulbs around the platinum coil in the same horizontal plane were inserted through the cover of the double chamber. Five small burners heated externally the box, which, together with the flames, were always surrounded by a metallic screen in order to prevent irregular looses of heat by radiation or by atmospheric currents. Measurements of the resistance were then taken at the same regular intervals of temperature previously mentioned. The third assembly made use of the same platinum wire, with the only difference that chamber containing the tube and wire was filled with linseed oil.

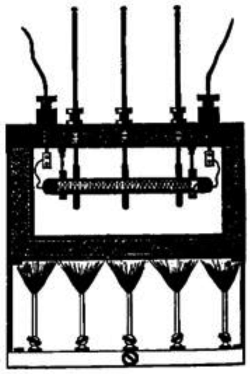

Figure 9 - C.W. Siemens's apparatus. Credit: Ref. [34].

As no general conclusion could be drawn from the bearing of only one metal, C.W. Siemens decided to carry out similar researches with coils of comparatively pure cooper, fused iron (or mild steel), iron, silver and aluminum, which were in a similar way gradually heated and cooled in metallic chambers containing the bulbs of mercury thermometers, and for higher temperatures of air thermometers, and the electrical resistances were carefully determined. The progressive increase of electrical resistance was thus directly compared with the increasing volume of an incondensable gas between the limits of 0 and 470 °C. The experiments were described by C.W. Siemens in 1871 in a Bakerian lecture delivered at the Royal Society in which he presented the possibility of temperature measurement by measuring the corresponding resistance variations of a metal conductor. Although a committee designated two years later determined the inconvenience for to use the platinum wire proposed as a sensor by C.W. Siemens for temperature measurement because of a thermal hysteresis it exhibited, the investigations led to the formulation of a new formula for the electric dependence of conductivity. He was convinced that the new formula should be based upon a rational dynamic principle and the application of the mechanical laws of work and velocity to the vibratory motions of a body which represented, according him, 'its free heat'. If this heat was considered to be directly proportional to the square of the velocity with which the atoms vibrate and it was assumed that the resistance which a metallic body offered to the passage of an electric impulse from atom to atom was directly proportional to the velocity of the vibrations representing its heat, it followed that the resistance increased in the direct ratio of the square root of the free heat communicated to it. In mathematical terms, the equation should to take an initial form,

$$R_t = \alpha T^{1/2},$$

where $T$ symbolized temperature by first time in an absolute scale, and $\alpha$ a specific and experimentally determined coefficient for each metal in particular. C.W. Siemens analyzed however that this exclusively parabolic expression would make no allowance for the possible increase of resistance due to the increasing distance between adjoining articles with increase of heat and the ultimate constant resistance of the material itself at the absolute zero. He speculated that the first of these contributions should depend upon the coefficient of expansion $\beta T$ and the second one only upon the nature of the metal. Once these contributions were considered, the expression took the form

$$R_t = \alpha T^{1/2} + \beta T + \gamma,$$

where $\beta$ and $\gamma$ symbolized usual specific coefficients for each metal. Table 8 shows the individual equations for each one of the metals under consideration.

Table 8 - C.W. Siemens's analytical expressions for the electric resistances of several metals. Credit: Ref. [34].

| | |
|---|---|
| For platinum— | $r = \cdot 0021448 T^{\frac{1}{2}} + \cdot 0024187 T + \cdot 30425$ |
| | $r = \cdot 039369 T^{\frac{1}{2}} + \cdot 00216407 T - \cdot 24127$ |
| | $r = \cdot 092183 T^{\frac{1}{2}} + \cdot 00007781 T - \cdot 50196$ |
| For copper— | $r = \cdot 026577 T^{\frac{1}{2}} + \cdot 0031443 T - \cdot 29751$ |
| For iron— | $r = \cdot 072545 T^{\frac{1}{2}} + \cdot 0038133 T - 1 \cdot 23971$ |
| For aluminium— | $r = \cdot 05951436 T^{\frac{1}{2}} + \cdot 00284603 T - \cdot 76492$ |
| For silver— | $r = \cdot 0060907 T^{\frac{1}{2}} + \cdot 0035538 T - \cdot 07456$ |

Improvements in the range of coverage in both directions of the scale of temperature of the general forms of the relation between conductivity and temperature would become the last significant contributions to the subject in the nineteenth century. The first of them is due to the work of the French physicist and later Director of the Bureau International des Poids et Mesures (BIPM) Justin-Mirande René Benoît (1844-1922) (Fig. 10), who, with an early training in medicine, turned very quickly to studies in physics, and conducted in 1873 a series of experiments on the temperature dependence of electrical resistance in metals as a requirement to receive his *Doctoral ès Sciences Physiques* [35]. By employing the differential galvanometer for measuring resistances, Benoit was able to determine between five and eight measurements of electric resistances of nineteen metals at equal number of different temperatures, covering a range that varied between the melting point of ice and the boiling point of cadmium, it meant 0 and 860 °C. The experimental results were numerically treated in order to find the optimum coefficients for each metal by the method of least squares on the basis of the above mentioned form of the equation originally proposed by Lenz. Table 9 lists the analytical equations derived for all the metals included in the study. In the graphical results shown in the Fig. 11 for some metals the resistance of each at 0 °C is supposed equal to 1, and each ordinate indicates the experimental increase at the corresponding temperature [36].

Figure 10 - J.-René Benoît.

Table 9 - Benoit's analytical expressions for the electric resistances of nineteen metals. Credit: Ref. [35].

*Variation de la résistance avec la température.*

| | | |
|---|---|---|
| Acier | $R_t = R_0$ | $(1 + 0,004978\,t + 0,000007351\,t^2)$ |
| Fer | » | $(1 + 0,004516\,t + 0,000005828\,t^2)$ |
| Étain | » | $(1 + 0,004028\,t + 0,000005826\,t^2)$ |
| Thallium | » | $(1 + 0,004125\,t + 0,000003488\,t^2)$ |
| Cadmium | » | $(1 + 0,004264\,t + 0,000001765\,t^2)$ |
| Zinc | » | $(1 + 0,004192\,t + 0,000001481\,t^2)$ |
| Plomb | » | $(1 + 0,003954\,t + 0,000001430\,t^2)$ |
| Aluminium | » | $(1 + 0,003876\,t + 0,000001320\,t^2)$ |
| Argent | » | $(1 + 0,003972\,t + 0,000000687\,t^2)$ |
| Magnésium | » | $(1 + 0,003870\,t + 0,000000863\,t^2)$ |
| Cuivre | » | $(1 + 0,003637\,t + 0,000000587\,t^2)$ |
| Or | » | $(1 + 0,003678\,t + 0,000000426\,t^2)$ |
| Argent $(\frac{750}{1000})$ | » | $(1 - 0,003522\,t + 0,000000667\,t^2)$ |
| Palladium | » | $(1 + 0,002787\,t - 0,000000611\,t^2)$ |
| Platine | » | $(1 + 0,002454\,t - 0,000000594\,t^2)$ |
| Laiton | » | $(1 + 0,001599\,t)$ |
| Bronze d'aluminium | » | $(1 + 0,001020\,t)$ |
| Maillechort | » | $(1 + 0,000356\,t)$ |
| Mercure | » | $(1 + 0,000882\,t + 0,000001140\,t^2)$. |

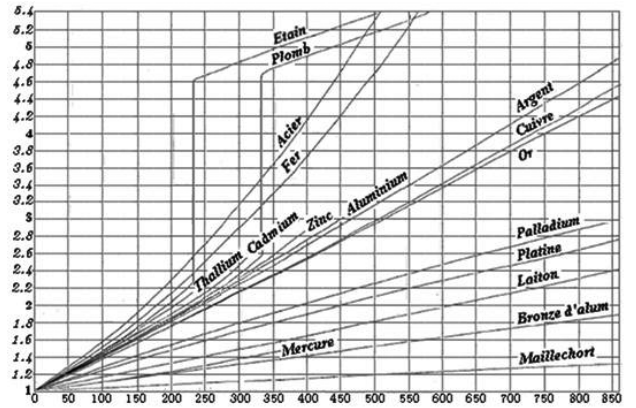


Figure 11 - Graphical behavior of resistance according the Benoit's results. Credit: Ref. [35].

Other extensions, this time on low temperatures, were later reported on the same line of investigation that in the second decade of the twentieth century would led Kamerlingh Onnes to his important discovery, it means in the whole framework of the researches on liquefaction of gases, and by using the excessive cold so produced for the determination of several properties of matter. The French physicist Louis-Paul Cailletet (1832-1913), one of the two responsible for the first liquefaction of oxygen, reported in 1885 the results of experimental measurements carried out jointly with his colleague Edmond Bouty (1846-1922) on conductivities of mercury, silver, magnesium, tin, copper, iron and platinum in the new range between 0 and -123 °C [37]. If it is important to remark that their experiments proved again the regular decreasing in the electrical resistance with the drop in temperature for most of the metals, that the coefficient of variation was appreciably the same for all, and that the results acceptably agreed the general form of the analytical formulas previously proposed, the most relevant facts for the present history are the speculations they venture to do on the basis of these results. In a short sentence concluding the paper the authors considered that although their experiments do not enable them to form any precise idea of what would take place in those conditions as "very probably that the resistance would become extremely small and therefore the conductivity very great at temperatures below -200 °C", and what could be considered one of the first, if not the first one, although unwitting predictions about the existence of the phenomena of superconductivity, that "if the same law (that proposed according the Matthiessen and Benoit's results) held at low temperatures, the resistance of a metal, varying like the pressure of a perfect gas under constant volume would furnish a measure of the absolute temperature, and would cease to exist at absolute zero". This hypothesis complemented the previously mentioned by Clausius, but on a slightly more supported basis.

About a decade later researches carried out by the British physicist James Dewar (later Sir) (1842-1923) and John Ambrose Fleming (1849-1945) strengthened the information about the electrical behaviors of metals at still lowest temperatures, thanks to the increasing availability of each time more complete appliances for the production of large quantities of the liquid gases necessary as refrigerant agents. With great experience on the subject thanks to previous researchers that had allowed him to liquefy hydrogen by first time, Dewar embarked with his colleague in specific investigations on the measurement of electrical conductivities of eight metals (nickel, tin, iron, platinum, aluminium, gold, silver and copper), seven alloys (platinoid, german silver, platinum-iridium, platinum-silver, palladium-silver, platinum-rhodium and phosphor-bronze), and carbon at the temperatures produced by the evaporation of liquid oxygen when boiling under normal or under reduced pressures, it means of about -200 °C [38]. The initial research was complemented one year later by adding other metals (palladium, zinc, lead, magnesium, cadmium and thallium) and alloys (gold-silver, aluminium-silver, aluminium-copper, manganese-steel, nickel-steel, copper-manganese, titanium-aluminium, silverine and copper-nickel-aluminium) in the whole study [37]. Figure 12 shows some of the preliminary results. The experimental results showed that the order of the conductivity of the metals at very low temperatures was different from the order at ordinary temperatures, but what was more important, after extrapolate their data they dared to speculate that "the electric specific resistance of all pure metals will probably vanish at the absolute zero of temperature" [39].

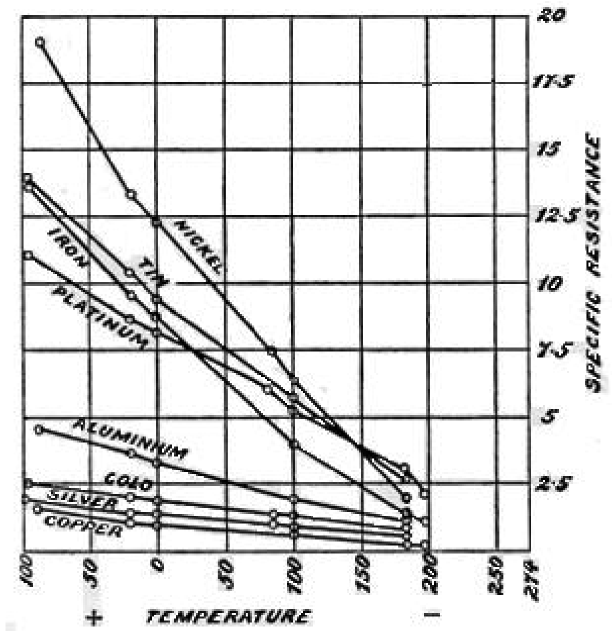


Figure 12 - Dewar's electrical conductivities of some metals at low temperatures. Credit: Ref. [38].

## 7. Concluding remarks

Several factors influenced the scientific studies on the temperature dependence of the electric conductivity of metals in the nineteenth century. The curiosity arisen for the still new science of electricity that characterized many subjects related with this discipline was very quickly complemented by interactions with other sciences, as for example medicine, and the usefulness that the results provided for the technological developments in emerging communication systems, the design of instruments for measure temperature, and the establishment of a standard unit of resistance. But while these motivations were diverse, the experimental methodology used along the full century was not so different. The introduction of the differential galvanometer by Becquerel and Wheatstone bridge in the first half of the century for the measuring of resistances became the maybe only significant modifications in the methodology followed by the different scientists involved in the subject, and the fact that the various results only correspond each other in an approximate way was not due to the diversity of apparatuses employed but circumstances such as the purity of the materials used, the procedure by which the corresponding wire was built and the accuracy of the measurements, among others. The general dependence equation between resistance and temperature established by Lenz about the first third of the century was basically retained and the extension in the number of metals included in the study, the accuracy and the coverage of temperatures would become the main modifications and the facts that helped to consolidate the relation.

The fact that the different involved researchers mostly worked with the same metals was not a merely coincidental matter. Criteria for the selection of the materials to be studied included, besides the obvious availability, conditions of the highest possible purity, relative good conducting power, and scientific and industrial usefulness in electrical and non-electrical areas. The weighted consideration of all these criteria provided good reasons for the joint study of their respective physical, thermal and electrical behaviors. Three metals, copper, aluminium, and platinum, become good examples. Because their high electrical conductivities and the ease with which copper could be drawn into rod and flexible and easily soldered wire this metal became in great demand. It was known, however, that this electrical conductivity varied with the presence of even small various impurities, and very few of its commercial grades reached the required standard of purity. The fire-refined copper was too poor an electrical conductor, but this did not matter for most of the usual non-electrical applications, such as the manufacture of domestic pots and pans, sheathing of ships's bottoms and fireboxes for locomotives; for electrical applications, however, it mattered very much. The appearing of a patent for the electrolytic refining of cooper in 1865 in order to replace the old fire-refining methods not only allowed precious metals to be recovered efficiently and economically, but provided a means of producing the desirable very pure copper. The introduction of the dynamo in the second half of the nineteenth century favored impetus in the production of both, copper and lead, being the electrical industry the greatest for these two metals, and in to a lesser extent practically all other non-ferrous metals. Aluminium is other case to mention. Nor Lenz nor Becquerel included it in the list of the metals to be studied, and the determination of its power conduction only aroused the interest of the scientific community in the second half of the century. The finding of a possibility by which it could become a challenger to copper in the field of electrical conductivity and for a number of other uses previously traditional the latter metal propelled increased interest in the evaluation of its properties and a later phenomenal rise in its production. Platinum, for mentioning the third example, was not only important in the nineteenth century because the property that would led it to be used in the resistance thermometer and subsequently to bridge the gap between scales and to establish as a new one in the each time greatest range of temperatures. Other properties such as its expansion with heat as glass did, which allowed wires to be sealed into glass tubes or vessels to carry an electric current, its high resistance to caustic substances even at high temperatures and its inertness to react with most of elements and compounds, made of it a valuable material in the chemical and physical laboratories from before the coming of the stainless steel.

Kamerlingh Onnes discovered the phenomenon of superconductivity on April 8, 1911. In no one of the different related publications that preceded the discovery, nor in his Nobel Lecture in 1913 he referred to the researches by Lenz, Arndtsen, Matthiessen, Benoit, the Siemens's brothers, or to whatever those by the other names mentioned along this article. The only references he occasionally did to Cailletet and Dewar were related with the apparatus or procedures that these scientists followed along their experiments on liquefaction. Although there is not historical evidence about the fact that Kamerlingh Onnes had information or not about the researches who preceded him in the study of electrical properties at low temperatures, and no one of the experiments carried out by the Dutch physicist seemed to have require of the utilization of analytical relations for the calculation of electrical conductivities or resistances, it is evident that the full knowledge he had on the temperature dependence of electrical conductivities of metals in the full range must to be based to a great extent in the lecture of the respective publications.

The developments of the relation between electrical conductivity and temperature for metals, as many others of the discoveries in electricity in the nineteenth century, favored significant improvements in other specific areas besides the later well-known discovery of superconductivity, as it was, for example, thermometry. The invention of resistance thermometers decisively made the establishment of reliable standards of electrical units much easier and allowed accurate measurements of especially by then high temperatures. Although not so quickly, the phenomena of superconductivity also found commercial use. In the same way that, for example, the electromagnet invented by the British physicist William Sturgeon (1783-1850) and later developed by American physicist Joseph Henry (1797-1878), quickly found application in the developing heavy industries, that the recognition by the Estonian-German experimental physicist Thomas Seebeck (1770-1831) of the fact that the flow of an electrical current could be regulated by heat marked not only the beginning of the study of thermoelectricity but also played an important role in the design of superconductors in the late twentieth century, or that the independent discoveries of the conversion of temperature differences directly into electricity, the presence of heat at an electrified junction of two different metals, and the heating or cooling of a current-carrying conductor with a temperature gradient by the French physicist Jean Charles Athanase Peltier (1785-1845), Seebeck, and the mathematical physicist and engineer William Thomson, 1st Baron Kelvin (1824-1907), respectively, brought about the phenomena of thermoelectric effect and found wide utilization in power generation and refrigeration, among others, the progressive understanding of the properties of superconducting materials had allowed their practical application in areas such as power transmission, superconducting magnets in generators, energy storage devices, particle accelerators, levitated vehicle transportation, rotating machinery, and magnetic separators. If the whole research program on liquefaction of gases from middle of the nineteenth century supplied the thermal frame that favored the discovery of superconductivity, the amazing amount of available experimental data of the temperature dependence of the electrical conductivities for metals, the continuously improved methodologies for the respective studies, and the analysis of the observed tendencies were the responsible of the not so much accidental discovery of this phenomena.

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