

Augustus Matthiessen: His Studies on Electrical Conductivities and the Origins of his “Rule”

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One of the most widely studied properties of metals is its electrical resistivity (or its reciprocal, electrical conductivity). The mathematical expression by which this property is quantitatively calculated (the sum of the contributions of the different scattering mechanisms acting independently of one another in the metals as resistances to the passage of an electric current) is currently known as Matthiessen’s rule. These scattering centers of conduction electrons can include lattice phonons, impurities, point defects, dislocations, grain boundaries and the surfaces of the specimens, the extent of the participation of each of them being determined as a function, the extent of the participation of each of them being determined as a function, the extent of the participation of each of them being determined as a function of parameters, such as the average electron velocity in the direction of the force imposed by the applied field, or drift velocity, and the mobility of the electron. This expression, as well as other findings related to the dependence of conductivity on temperature and the establishment of a standard unit of resistance in the second half of the 19th century, originated from the whole research program on this property carried out by the 19th century British scientist Augustus Matthiessen, but were neither fully, nor literally, formulated by him. The purpose of this article is to show the real achievements of Matthiessen in

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the scientific context of events in the 19th century, especially in that specific area of electric technology. A summary account of subsequent scientific developments, mostly theoretical, is finally given, in order to help understand how this work was completely reconceptualized more than a half of century later in the light of the then still emerging quantum-mechanical electron theory of metals.

I. EDUCATION AND EARLY CAREER

Augustus Matthiessen was born January 2, 1831, in London, the son of William Matthiessen, a merchant who died while Augustus was quite young, and his wife, Jane. A paralytic seizure he had while a child of two- or three-years old, produced a permanent and severe twitching of Matthiessen’s right hand. Despite the liking he manifested for chemistry from his early youth, upon leaving the school, Matthiessen was sent to learn farming as the only occupation that was thought to fit his physical situation. With only a passing interest in agricultural chemistry, he went to the University of Giessen to obtain instruction in experimental chemistry under the direction of Justus Liebig (1803–1873) [1], [2]. His studies began on April 24, 1852, successfully incorporating teaching and research with professors such as Johann Heinrich Buff (1805–1878) and Heinrich Will (1812–1890) in physics and chemistry, respectively. Slowly but surely, Matthiessen began to understand the importance of precision and

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rigorous quantification in scientific work. After graduating on June 18, 1853, Matthiessen spent nearly four years at Heidelberg, where he was tutored by Robert Wilhelm Bunsen (1811–1899) and Gustav Robert Kirchhoff (1824–1877). Bunsen, with an excellent scientific reputation and a special focus on practical work, and Kirchhoff, who combined exceptional mathematical talent and experimental knowledge, likely had a significant influence on Matthiessen's scientific activity and molded his work style [3].

The work which first brought Matthiessen into notice was the continuation of Robert Bunsen's line of research related to the electrolytic preparation of some alkali and alkaline-earth metals, as well as the study of some of their specific physical properties, such as color, specific gravity, and atomic volume [4]–[7]. Calcium, strontium, magnesium, barium, and lithium, were successively and successfully studied by Bunsen and Matthiessen over a period no more than three years [8].

II. STUDYING ELECTRICAL CONDUCTIVITIES OF METALS AND ALLOYS

The studies of the electrical conductivities of these metals, and later of many others more carried out immediately afterwards in Kirchhoff's laboratories, became the opening to Matthiessen's research in this area. In 1849, Kirchhoff had made what can very probably be considered the first absolute determination of resistance. His skills for working out the solution of each new physical problem he faced, as well as his way for approaching it in mathematical terms, very probably influenced the character of Matthiessen's later investigations on conductivities and other subjects.

The first paper published by Kirchhoff in Matthiessen's name on the electrical conductivity of the above-mentioned metals (with barium's exception), besides potassium and sodium, embodied the experimental results obtained by Matthiessen in the physical laboratory [9]. The required wires were formed in a device he designed to press out small portions of metals into thin samples by means of steel pressure equipment. The determination of the resistances was made by using a slightly modified apparatus constructed by Kirchhoff on the basis of an electrical circuit popularized more than a decade before by Charles Wheatstone (1802–1875). Other publications of his, including the reports of the experimental data of conductivities for 25 metals, followed this paper [10]–[12].

Almost simultaneously, Matthiessen showed interest in alloys made of two metals because of the multiple industrial applications he predicted for them. He proceeded to determine not only the electrical conductivities of upwards of 200 alloys of variable composition [13], but also their tenacities and specific gravities. Years later, he would publish a classification of the metals employed in the different alloys in order to try to establish some general rules

about the behavior of the conductivities of these materials compared to those of their individual component elements. 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. Lead, tin, zinc, and cadmium belonged to the first group, while bismuth, mercury, antimony, platinum, palladium, iron, aluminum, gold, copper, and silver, and as he thought, in all probability most of the other metals, belonged to the second group. The alloys were accordingly again divided, this time 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 [14]. 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 the alloys, showed very acceptable agreements. Another comparison, this time between the magnitudes of the electric conductivities of the alloys and those of their constituents, allowed him to work in the opposite way as well, and get information about the real nature of the alloys and state if some chemical combination could really exist there. In the same way, the fact that the preparation of copper of the greatest conductivity had great practical importance in connection with telegraphy also touched Matthiessen. The significant discrepancies showing between his results and previous similar observations made by other researchers forced Matthiessen to embark on the study of the probable influence of minute quantities of other metals, metalloids, and impurities on the magnitude of the electric conductivity of copper [15].

III. IMPROVING TEMPERATURE DEPENDENCE RELATIONS OF ELECTRICAL CONDUCTIVITIES

The next step in Matthiessen's researches was related to the study of the temperature dependence of electrical conductivity for metals. The results provided by continuous technological advances, in the then still new science of electricity, as well as in its interactions with other sciences, marked great influence on emerging communication systems, the design of instruments for measuring temperature, and the establishment of a standard unit of resistance, among other subjects. A knowledge of the above-mentioned temperature dependence became essential for most of the new developments. The first notice of this dependence had very probably been due to the British scientist Henry Cavendish (1731–1810) [16]. The first mathematical relation established corresponded to the

Russian physicist and Professor at the University of Saint-Petersburg, Emil Khristianovich Lenz (Heinrich Friedrich Emil) (1804–1865) [17]. Working with eight different metals, and with the assistance of the least-squares method, Lenz had established the following general quantitative relation, in modern terms, between both variables [18], [19]:

$$\sigma = \sigma_0 + yt + zt^2$$

where σ represented the electrical conductivity at a temperature t , σ_0 the conductivity at 0 °C, and y and z two particular coefficients for each specific substance. A decade later, the French physicist Alexandre-Edmond Becquerel (1820–1891), more known for his studies on solar radiation and on phosphorescence, had included the effect of heating on the electrical conductivities of a fewer number of metals, as well as some liquids and solutions [20]. Becquerel had arranged the results for electrical resistance R as a function of both the so-called coefficient of the increment of resistance by unitary change of temperature, and the temperature,

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

where R_0 represents the electrical resistance of the metal at 0 °C, and A a specific coefficient for each substance. This research had been followed by separate works carried out on the subject between 1858 and 1860 by the Norwegian neurophysiologist, physicist, and professor at the University of Christiania, Adam Frederik Oluf Arndtsen (1829–1919) and the Prussian industrialist and telegraph entrepreneur Ernst Werner Siemens (1816–1892). Arndtsen decided to use a parabolic equation of second order to represent the available experimental data [21],

$$R = a + bt \pm ct^2$$

a , b , and C being specific parameters for each one of the six metals and two alloys experimentally studied. Siemens, who sought a general, easily reproducible, and sufficiently accurate standard measure of resistance required for the then continuous invention of many delicate measuring instruments, was able to build a table including the relative conducting power of nine metals at the temperature t (with the resistance of mercury as the unit), which followed the general formula [22]

$$\sigma = \frac{a}{1 + bt \pm ct^2}$$

Matthiessen's first research on the influence of temperature on the electric conducting power of metals was published in 1862. The paper describes the apparatus (see Fig. 1) and the corresponding procedure in the minute detail that characterized all his scientific work [23].

Matthiessen determined the conducting power of the wires or bars of silver, copper, gold, zinc, tin, arsenic, antimony, bismuth, mercury, and the metalloid tellurium, each at about 12 °C, 25 °C, 40 °C, 55 °C, 70 °C, 85 °C, and 100 °C. From the mean of the eight observations made with each wire, four at each temperature on heating, and four on cooling, Matthiessen deduced the same general formula previously proposed by Lenz for representing its dependence with temperature, but he also determined new sets of coefficients for each one. Table 1 shows the mean of the formula found for some metals, with the conducting power of each one at 0 °C taken equal to 100. The other conclusion at which he arrived, that 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 (a mean value for the ten metals of about 29.3%) did not receive later experimental support and consequently was never explored further.

Two years later, Matthiessen published a new article on the effect of temperature, this time on alloys [24]. The conclusions of the study showed great similarity in their behavior to 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 deduced specific equations of dependence for fifty-three alloys composed of two metals and three alloys composed of three metals. Table 2 shows the results for some alloys of definite chemical formula. Table 3, on the other side, shows the variation of these formulas for alloys including the same metals, but with different compositions. All the values were reduced to 0 °C as mentioned for pure metals.

The set of equations proposed on the basis of Matthiessen's results became classics in the study of electric properties. They were, however, limited to the range of temperatures between the freezing and boiling points of water. In addition, the study did not include important metals such as platinum, which had begun to be considered the most valuable metal for constructing pyrometric instruments. The equations, including the coefficients determined by Matthiessen, gave a close agreement with experimental observations between the narrow limits indicated, but were wholly inapplicable for temperatures exceeding 200 °C, where the term t^2 began to predominate and to produce absurd values for R . These limitations were solved in the following decades by scientists such as the German engineer Carl Wilhelm (later Charles William) Siemens (1823–1883)—Ernst Werner's brother—[25] and the French physicist Justin-Mirande René Benoît (1844–1922) later Director of the Bureau International

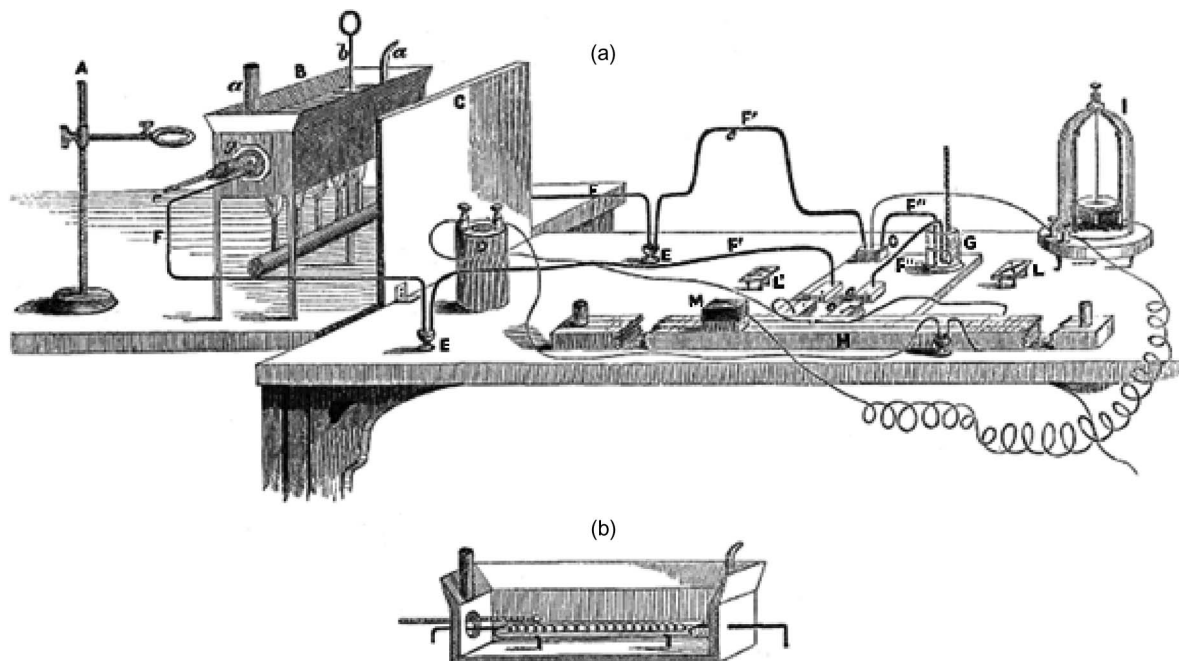


Fig. 1. Matthiessen's apparatus. (a) Arrangement of the entire assembly. B is the trough in which the wires (soldered to two thick copper wires, bent as shown in the figure, and ending in the mercury cups E, which were connected with the apparatus by two other copper wires, F', of the same thickness) were heated by means of an oil bath; C a piece of board placed in such a manner as 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 on which 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], (b) Disposition of the wire to be studied on a small glass tray in the trough (Credit: Ref. [23]).

des Poids et Mesures (BIPM) [26], [27]. They extended the coverage of the mathematical expression in the range of higher temperatures (0–860 °C), including, besides the above-mentioned platinum, other metals previously not considered such as gold, magnesium, and thallium. Other extensions on low temperatures were also later separately reported by the French physicists Louis-Paul Cailletet (1832–1913) and Edmond Bouty (1846–1922) [28], as well as by the British physicists James Dewar (1842–1923) and John Ambrose Fleming (1849–1945) [22], [29], [30], [49], covering temperatures that reached –200 °C.

Table 1 Matthiessen's Analytical Expressions for the Relative Electrical Conductivities of Ten Different Metals (Credit: Ref. [23])

Silver	$\lambda = 100 - 0.38287t + 0.0009848t^2$
Copper	$\lambda = 100 - 0.38701t + 0.0009009t^2$
Gold	$\lambda = 100 - 0.36745t + 0.0008443t^2$
Zinc	$\lambda = 100 - 0.37047t + 0.0008274t^2$
Cadmium	$\lambda = 100 - 0.36871t + 0.0007575t^2$
Tin	$\lambda = 100 - 0.36029t + 0.0006136t^2$
Lead	$\lambda = 100 - 0.38756t + 0.0009146t^2$
Arsenic	$\lambda = 100 - 0.38996t + 0.0008879t^2$
Antimony	$\lambda = 100 - 0.39826t + 0.0010364t^2$
Bismuth	$\lambda = 100 - 0.35216t + 0.0005728t^2$
Mean of the above ...	$\lambda = 100 - 0.37647t + 0.0008340t^2$

A very significant deduction that Matthiessen made from his study was 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 followed that the formula for the correction for temperature for a specific alloy could be easily determined knowing only its composition and its resistance at any temperature.

IV. CONTROVERSY ON ELECTRICAL RESISTANCE STANDARDS

Between 1860 and 1866, Matthiessen had a bitter confrontation with E. W. Siemens, called by some the “metals controversy,” about the choice of the best electric resistance standard [23], [31]–[34], [50]–[52]. By the beginning of the second half of the 19th century, a mixture of resistance “standards” were available, though none were completely satisfactory. A certain copper wire, one foot (300 mm) long, 1.8 mm diameter, and weighing 100 grains (6.48 g), proposed by the English scientist Charles Wheatstone (1802–1875) in 1843, did not receive wide acceptance by the scientific community of the time. A similar fate met the longer arbitrary unit of resistance known as the “etalon,”

Table 2 Matthiessens's Analytical Expressions for the Temperature Dependence of Electric Conductivities of Some Alloys of Definite Chemical Formula (Credit: Ref. [24])

Alloy.	Formulae for the correction of the conducting-power for temperature.
Sn ₃ Pb	$\lambda = 12.002 - 0.046645t + 0.0001042t^2$
Sn ₃ Cd	$\lambda = 14.558 - 0.059337t + 0.0001728t^2$
Sn ₂ Zn	$\lambda = 16.747 - 0.065044t + 0.0001460t^2$
Pb Sn	$\lambda = 10.139 - 0.038358t + 0.00008536t^2$
Zn Cd ₁	$\lambda = 25.619 - 0.096978t + 0.0002049t^2$
Sn Cd ₁	$\lambda = 21.658 - 0.083368t + 0.0002038t^2$
Cd Pb ₃	$\lambda = 9.155 - 0.032041t + 0.00006647t^2$

also consisting of a copper wire, but measuring 7.62 m length, 0.667 mm diameter, and weighing 22.49 g, suggested five years later by the German Engineer Moritz Hermann von Jacobi (1801–1874). Both examples of standards did not come into wide use, partly because of the little effective demand they had at the time they were proposed.

The stage of progress reached in the following decade by the science of electricity, and especially by the art of telegraph, contributed decisively to increasing the need for a single universal standard with which any resistance, anywhere in the world, might be compared. Although it was not the only critical problem associated with the technical and commercial success of the telegraphic enterprise, the long undersea cables that began to be built in the late 1850s showed each time more clearly the inadequateness of the rough methods of electrical measurements used with contemporary overhead lines. In 1860, Werner Siemens introduced a new arbitrary unit based on the re-

sistance, at a temperature of 0 °C, of a column of pure mercury, of a uniform cross-sectional area of 1 square mm, and a length of 1 m (equivalent to the current value of 0.9407 international ohm) [35]. This proposal received considerable acceptance on the European continent, but was criticized by Matthiessen, who argued that impurities dissolved from the connecting wires would alter the conductivity of the mercury [36]. Matthiessen's opinion was clearly founded in his experience with the inclusion of mercury cups in the apparatus he used for measuring electrical conductivities (see Fig. 1), and the great care he had taken to prevent it from compromising the measurements by chemical contamination. Matthiessen thought that the best material for building such a material standard of resistance was an alloy of equal volumes of pure gold and pure silver (by weight, two parts gold to one part silver), and he proposed a hard-drawn wire of this gold-silver alloy of 1 mm length and 1 mm diameter calibrated to 100 resistance

Table 3 Matthiessen's Analytical Expressions for the Variation of the Temperature Dependence of Electric Conductivities of Some Alloys Including Variations in Their Composition (Credit: Ref. [24])

Alloy.	Volumes per cent.	Formulae for the correction of the conducting-power for temperature.
Lead-silver	94.64 of Pb	$\lambda = 8.880 - 0.032149t + 0.00007070t^2$
Lead-silver	46.90 of Pb	$\lambda = 12.731 - 0.024986t + 0.00003947t^2$
Lead-silver	30.64 of Pb	$\lambda = 21.874 - 0.043652t + 0.00005687t^2$
Tin-gold.....	90.32 of Sn	$\lambda = 8.2418 - 0.025418t + 0.00005472t^2$
Tin-gold.....	79.54 of Sn	$\lambda = 4.7963 - 0.014006t + 0.00003020t^2$
Tin-copper (hard drawn).....	93.57 of Sn	$\lambda = 12.034 - 0.044328t + 0.00009781t^2$
Tin-copper (hard drawn).....	83.60 of Sn	$\lambda = 12.764 - 0.042457t + 0.00008734t^2$
Tin-copper (hard drawn).....	14.91 of Sn	$\lambda = 8.8223 - 0.0048266t + 0.00002593t^2$
Tin-copper (hard drawn).....	12.35 of Sn	$\lambda = 10.154 - 0.0067656t + 0.00001203t^2$
Tin-copper (hard drawn).....	11.61 of Sn	$\lambda = 12.102 - 0.0083587t + 0.00003674t^2$
Tin-copper (hard drawn).....	6.02 of Sn	$\lambda = 19.716 - 0.019826t + 0.00001390t^2$
Tin-copper (hard drawn).....	1.41 of Sn	$\lambda = 62.463 - 0.16713t + 0.0003136t^2$
Tin-silver	96.52 of Sn	$\lambda = 12.384 - 0.047293t + 0.0001014t^2$
Tin-silver	75.51 of Sn	$\lambda = 13.706 - 0.051720t + 0.0001172t^2$
Zinc-copper (hard drawn)	42.06 of Zn	$\lambda = 21.793 - 0.022939t + 0.00002916t^2$
Zinc-copper (hard drawn)	29.45 of Zn	$\lambda = 21.708 - 0.027632t + 0.00002698t^2$
Zinc-copper (hard drawn)	23.61 of Zn	$\lambda = 28.298 - 0.040039t + 0.00003232t^2$
Zinc-copper (hard drawn)	10.88 of Zn	$\lambda = 46.334 - 0.095947t + 0.0001423t^2$
Zinc-copper (hard drawn)	5.03 of Zn	$\lambda = 60.376 - 0.14916t + 0.0002473t^2$

as the best possible reference for comparisons of resistance [37]. Matthiessen's initial opposition to mercury on the grounds of its chemical susceptibility to impurities went very quickly beyond the limits of strictly scientific, when he attacked Siemens' chemical expertise, contending that the Prussian was incompetent to evaluate the corrupting effect of impurities on mercury. The German answered also in kind, questioning Matthiessen's ability as a chemist, and particularly in his handling of mercury and interpreting its behavior. These undiplomatic comments, each published in important journals, turned a scientific controversy into a recurring "discursive slippage between expressing distrust in the [other] measurer, in the measurement practices, in the metal undergoing measurement, or in the inappropriate use of research" [31, p. 126].

Three years later, in 1861, a committee appointed by the British Association for the Advancement of Science (BAAS) to investigate the establishment of units and construction of material standards for electrical resistance [38] chose to reject both Matthiessen's original proposal of a gold-silver alloy for the standard, as well as the Siemens' mercury construction, subsequently recommending instead the use of a cheaper alloy of silver-platinum. The polemic about the use of mercury as a reliable material to build universal resistance standards continued for years, even after Matthiessen's death, becoming an overtly nationalistic matter.

In 1861, Matthiessen became a Fellow, and afterwards a member, of the Council of the Royal Society (see Fig. 2). The following year, he was elected to the lectureship on chemistry at St Mary's Hospital, a post which he held until 1868, when he was appointed to a similar job at St. Bartholomew's Hospital [1]–[3]. His work on the physical and electrical properties of metals and alloys earned him the Royal Medal from the Royal Society in 1869, which identified this work as one of "the two most important contributions to the advancement of natural knowledge" [39]. Shortly thereafter, a charge of indecent assault on a young man left Matthiessen distraught, and, after leaving a note stating that he was not guilty of the charges, he committed suicide in his laboratory by poisoning himself with prussic acid on October 6, 1870, thus ending his short, but productive scientific career [29], [40], [41], [53]. There is no known portrait of him, and very little additional information of his private life is publicly known. Perseverance, an acute power of observation, a distinct power of generalization, and a marked degree of manipulative skill, despite his physical limitations, are some of the characteristics of his work unjustly ignored by historians of science. Although his investigations on the properties of pure metals and alloys had immediate practical applications, Matthiessen's great fondness for experimental inquiry, obsession with accuracy, and sound choice of worthy subjects for study, according to the scientific and technical requirements of his times, were elements that characterized all of his short, but fruitful scientific research [42].

V. CONCLUDING REMARKS

Current descriptions of the so-called "Matthiessen's rule" range from simple to fairly complex. A very simple one, for example, states that "the electrical resistivity consists of two parts, the ideal resistivity ρ_i , characteristic of the pure metal, and the residual resistivity ρ_r , which is because of impurities, strains, etc., and which varies from specimen to specimen" [43]. The other, more elaborate one, states that "the partial resistivities arising from the scattering of the conduction electrons at different types of scatterers," ["... such as phonons, impurities, point defects, dislocations, grain boundaries, and the surface of the specimen..."], "are additive" [44]. Historically speaking, these statements, and of several frequently quoted alternative formulations of some of Matthiessen's experimental conclusions (which he had never formulated as a rule), became modern reconceptualizations.

Theoretical and experimental work carried out in the first quarter of the 20th century became the first signal that the original empirical relation developed about six decades before, later known as "Matthiessen's rule," had not appropriate scientific support [43]. The new available results showed that the suggested approach of additivity of the resistances involved in a given case, somewhat hidden during that period, was far from exact and could only be considered to be a good first approximation. A number of scientific developments in solid-state physics that occurred at the close of the 19th century, but especially since the 1920s, marked, among other things, not only the rediscovery of the relation, but also the beginning of different studies in order to both probe its real experimental foundations and provide a sound theoretical basis for it [45]. Experimental researches on cathode rays carried out by the English physicist Joseph John "J. J." Thomson (1856–1940) in the mid- and late-1890s constituted a definitive step toward understanding the nature of electrical conduction by extending conclusions about electrical phenomena in gases to the electrolysis of liquids and conduction in metals [34], [46], [47], [54]. This research followed previous theoretical works of the Irish physicist and mathematician Joseph Larmor (1857–1942) and the Dutch physicist Hendrik Antoon Lorentz (1853–1928) on a new definite concept of the electron and its role as the universal subatomic carrier of electricity [48], as well as one experiment, carried out by the Dutch physicist Pieter Zeeman, who was also reconceptualizing the electron [49], [50], [55].

The introduction in the 1900s of the free electron theories of electronic conduction in models such as that proposed by the German physicist Paul Karl Ludwig Drude (1863–1906) [51]–[53], followed by the application to the problem of Fermi-Dirac statistics by his compatriot Arnold Johannes Wilhelm Sommerfeld (1868–1951) [54], showed that precise quantitative calculations of the properties of specific metals could be undertaken [55], [56]. Drude's model, although it provided an explanation of the

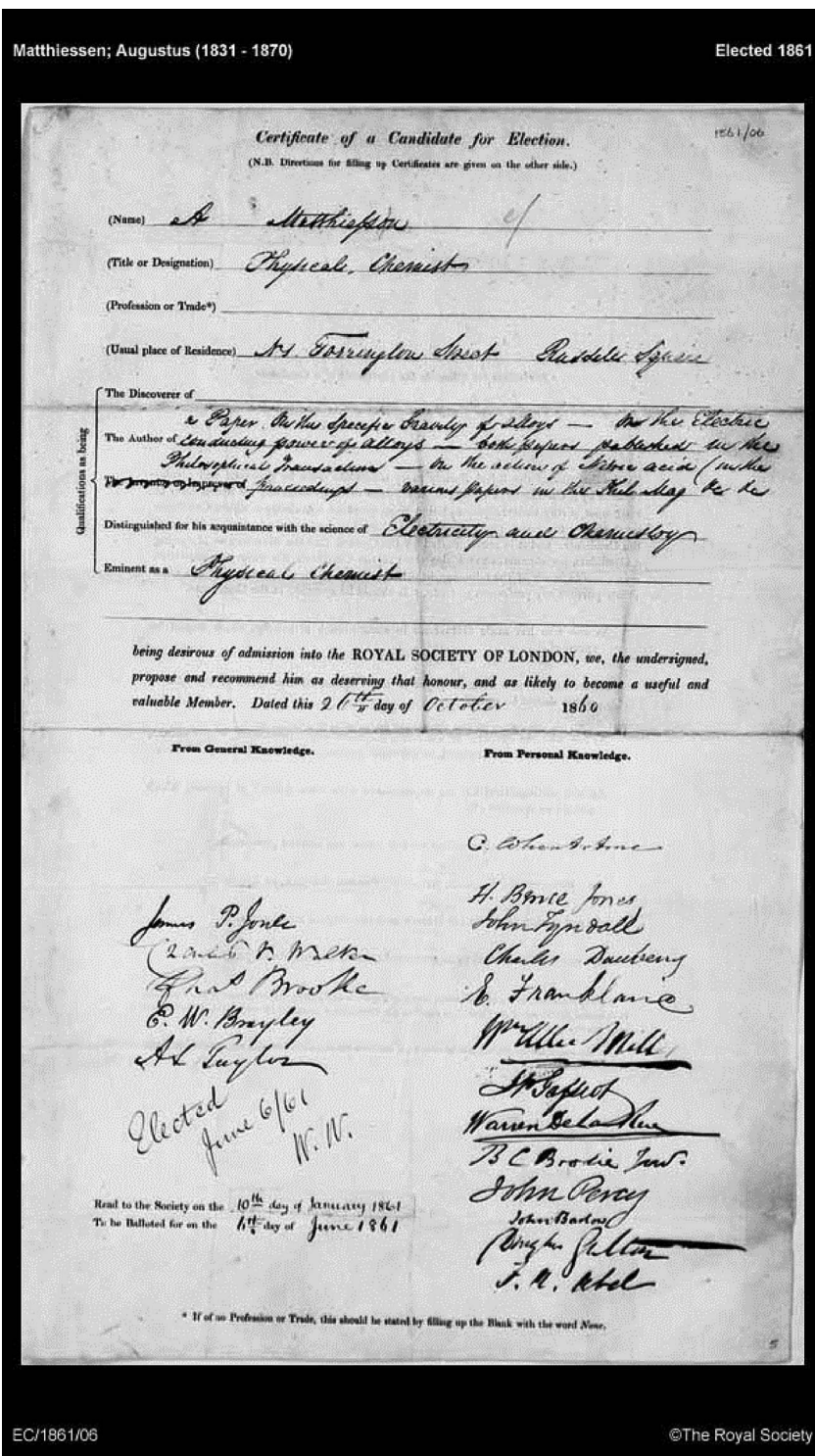


Fig. 2. Matthiessen's certificate for election as a Fellow of The Royal Society (Credit: Centre for History of Science, Royal Society).

phenomenon of electrical resistance and became the first attempt to explain the behavior of electrons in a metal, failed to treat the electron as a classical particle. Sommerfeld's work, although built on the concepts of quantum statistics and spinning electrons, failed too for

not satisfying all the specific restrictions on the behavior of electron particles imposed by quantum mechanics. The quantum-mechanical study of the wave function of electrons in a lattice carried out by the Swiss physicist Felix Bloch (1905–1983) as part of his doctoral

dissertation in 1928 [57] filled this void, contributing to the foundations of band theory embracing metals, semiconductors, and insulators, and providing the theoretical basis for “Matthiessen’s rule.”

The extension of measurements of the electrical resistances of alloys initiated at about the same time, especially at very low temperatures, served to show that the “Matthiessen’s rule” was only an approximation and not universally valid. The origin of the various deviations observed showed it

later to be a rather complex problem and that no single completely satisfactory explanation appeared to exist [58]. ■

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