M. Grant Norton

A Modern History of Materials

From Stability to Sustainability

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Introduction

Since our distant ancestors shaped flint, a polycrystalline sedimentary rock, into rudimentary tools, the majority of human history has been defined by the materials we use—stone, bronze, and iron. But it is over the relatively short period of just 100 years that technological change enabled by innovations in materials science has been particularly rapid—speeding up at unprecedented rates following the patenting of the silicon integrated circuit in 1961. Compare, for instance, the original Motorola StarTAC flip phone from 1996 with a 2022 iPhone 13. They contain many of the same elements in about the same proportions but that is largely where the similarity ends. The transition from the flip phone to the iPhone 13 with all its functionality has happened in a little over two decades. In that time, computers have become exponentially more powerful. In 1996, there were as many as 5 million transistors on an individual integrated circuit. By 2022, that number had exceeded 50 *billion*. Integrated circuits are just one example among numerous others that illustrate the amazing developments in materials, and how we process them, that have happened within the past one hundred years.

Another example of recent rapid advances in materials science is the ubiquitous rechargeable lithium-ion battery, which was commercialized in 1991 enabling an unprecedented, electrified, mobility revolutionizing everything from how we communicate to how we travel. Even as battery performance has increased, with the use of advanced materials, innovations in processing have been able to lower costs to the consumer. Purchasing a lithium-ion battery in 1991 would have cost over $7,500 per kilowatt-hour. Nowadays, a battery with the same power costs less than $180. To put that number into perspective, a Tesla Model S 75D has a 75 kilowatt-hour battery.[1] In 1991, that battery alone would have cost more than half a million dollars!

While completely new materials, like the components of a lithium-ion battery, have been developed over the past century, there are many modern versions of ancient materials, for instance, Corning's Gorilla Glass, which released in 2007 now protects over 8 billion mobile devices. Gorilla Glass shares many of the same chemical constituents—primarily silica—as the Roman glasses produced two thousand years ago. What is distinctly different is the clarity of the glass and the innovative way in which it is processed to overcome the material's inherent low tensile strength.

The 1920s and each of the three decades immediately following were monumental in their far-reaching impact in how we understand, see, and make materials creating a foundation for everything that follows. It is this period, beginning in 1920, that marks the modern age of materials with the awarding of the Nobel Prize in Physics to Swiss metallurgist Charles-Edouard Guillaume. This marked the first time the award had been given to a metallurgist or indeed for a metallurgical discovery.

In ancient times, Guillaume might have been a skilled metalworker smelting, casting, and forging metals to meet a variety of community needs from weapons and tools to domestic items and religious ornaments. Much like his early counterparts working with bronze Guillaume was fascinated by the properties of metals and how those properties could be changed by alloying. The combination that made Guillaume famous was an alloy of iron and nickel named *Invar*, short for *Invar*iable. Invar ushered in an era of what came to be known as "precision metallurgy" where the properties of an alloy could be precisely tailored for a specific application by controlling its composition.[2] With its remarkable stability, Invar would find immediate use in the precise measurement of distance and time. Today, it is manufactured in large-scale quantities for applications that also rely on that stability.

A major development that enabled the rapid technological changes and shift in our relationship to materials over the past century was the creation of quantum mechanics. This new field changed how we *understand* the very structure of materials, in a way that would fundamentally alter how we explain and control their properties. The importance of quantum mechanics is reflected in the number of Nobel Prizes awarded to those scientists most closely associated with its development.

At the end of the twenties, the 1929 Nobel Prize in Physics was awarded to Prince Louis-Victor Pierre Raymond de Broglie for his discovery of "the wave nature of electrons". This was followed closely in the 1930s with Nobel Prizes to Werner Heisenberg for "the creation of quantum mechanics" and to Erwin Schrödinger and Paul Dirac for "new productive forms of atomic theory". Then, in 1945, the Nobel Prize in Physics was awarded to Wolfgang Pauli for his discovery of "a new law of Nature", which determined how the electrons were arranged in an atom.

With the revolutionary quantum mechanical description of the atom, it became possible to explain, for instance, the layered structure adopted by graphite, which acts as the anode electrode of most commercial lithium-ion batteries. Or why one form of carbon—graphite—is a good conductor of electricity while diamond, also comprised of just carbon atoms, is a very poor electrical conductor. Or why silicon solar cells absorb only certain frequencies of the Sun's radiation and how we might go about increasing cell efficiency. Our entire view of the material world since the 1920s is through the lens of quantum mechanics.

Closely following the development of quantum mechanics in the 1920s, which changed how we understand the structure and behavior of materials, was another major innovation in the modern history of materials: the commercialization in the late 1930s and 1940s of the electron microscope. This invention would eventually allow us to clearly see the structure of a material with atomic resolution providing, even in its earliest days, an experimental explanation for many of the properties of materials that had never before been possible.

Since its commercialization, the electron microscope opened an exciting new world beyond what was possible using light microscopy and far beyond what we could see with the naked eye. With its superior resolution, the electron microscope became the essential imaging technique—the workhorse—for observing materials and phenomena at the nanoscale, enabling the eventual development of the field of nanomaterials.

The fourth innovation that defines not only the era of modern materials science but also the modern world itself is our ability to shape materials. Since our ancestors' earliest use of stone tools, we have developed methods to shape materials for our needs. A major breakthrough in our ability to shape materials was the development in the early 1950s of new techniques for growing crystals that would never be found in nature. The fabrication of large, high-purity, defect-free crystals of silicon would become essential for the creation of integrated circuits, the "silicon chips" at the heart of every one of our electronic devices. These are the devices that increasingly impact almost every aspect of our daily lives.

In the 1960s, we saw another innovation in materials processing that would enable a further defining material for our modern world: the glass optical fiber. There are currently over one billion kilometers of optical fiber deployed around the world enabling the transmission of information over long distances, literally at the speed of light.

Each decade during the past 100 years has witnessed not only advances in understanding, synthesizing, and characterizing materials but also the creation of new materials. As an example, the 1930s and 1940s saw the rapid development of a range of materials synthesized from fossil fuel precursors. These were materials with no natural analogs, materials that were purely the result of human ingenuity. The two most widely used—and frequently discarded—of these organic polymers (plastics) are polyethylene, first made in 1933, and polyethylene terephthalate, first made in 1941. While satisfying many of what have become essential applications, polymers along with their chemical precursors are creating an unprecedented array of environmental and human health hazards that were largely unforeseen at the time of their discoveries.

The latter half of the twentieth century and moving into the twenty-first century saw the discovery and development of what have become key innovations in modern materials science: nanomaterials, high-temperature superconductors, lithium-ion batteries, solar cells, and the materials that enable quantum computing. Our relationship with materials impacts almost every aspect of our daily lives, from how we make them, to how we use them, and finally how we dispose of them. That relationship currently looks for the most part like, *take—make—use—dispose*.[3] While this consumerist model may have served well enough for some in the past, it is not sustainable for the future. The visible result of this behavior is obvious with the ever-growing mountains of plastic waste. But the problem extends beyond plastics to include all the metals that we dispose of rather than recycling them at the end of their product's useful life. In the absence of some technological miracle, going forward we will require a more circular economy based on the 4 Rs of sustainability: reduce, retain, recycle, and regenerate.

This modern history explores a wide range of materials and the technologies they enabled. Each of the chapters in this book highlights discoveries and innovations that have occurred within the past century together with some relevant background and context. In each of the chapters, scientists whose important contributions led to the amazing materials described in this book are highlighted. Many of these scientists were awarded Nobel Prizes for their work.

Chapter 1, **A Measure of Stability**, begins this modern history of materials in 1920 with the announcement of the award of the Nobel Prize in Physics to metallurgist Charles-Edouard Guillaume for his discovery of the anomalous properties of the metal alloy *Invar*, a material that defined stability and whose importance has continued to increase over time.

Chapter 2, **A Quantum of Solace**, traces the history of quantum mechanics and the giants of science who gave us this new way of looking at the material world.

In Chapter 3, **Seeing Is Believing**, the focus is on the electron microscope, an instrument critical to our understanding of a whole range of materials. The chapter also provides a very brief history of scanning tunneling microscopy, a technique with the ability to provide atomic resolution images of the surfaces of materials.

Chapter 4, **Made to Measure**, looks at three very different methods of making materials that have become essential to our modern lives—pulling single crystals of silicon, drawing ultra-pure optical fibers, and blowing thin sheets of polyethylene—as well as a fourth method, 3D printing, which offers enormous potential for more sustainable manufacturing processes.

Chapter 5, **There's *Still* Plenty of Room at the Bottom**, follows the history of nanotechnology, from Michael Faraday's experiments at the Royal Society in London on the colors produced by "finely divided" gold particles to Don Eigler at IBM moving a single xenon atom back and forth across a platinum surface. Three nanomaterials—gold nanoparticles, carbon nanotubes, and graphene—are discussed in this chapter, from their discovery to the search for applications.

Chapter 6, **The Future of Mobility**, is about a technology that has been essential in enabling our mobile world: lithium-ion batteries. This chapter describes the history of the lithium-ion battery from the early work in 1913 that demonstrated the potential of a battery containing a lithium electrode up to the awarding of the Nobel Prize in Chemistry to the three scientists who brought the battery into commercial use creating a revolution in portable electronics ushering in a mobile more-electric world.

Chapter 7, **Here Comes the Sun**, discusses solar cells, widely regarded as one of the key technologies necessary for a sustainable, carbon-free, future. Chapter 7 begins by considering the two main approaches used to capture solar energy and convert it into electricity. But the focus of this chapter is photovoltaics. While the first photovoltaic cells were dominated by silicon, recent research has identified other materials that can capture an even greater fraction of the sun's energy for higher efficiency devices.

In Chapter 8, **Certain About Uncertainty**, we look from the materials perspective at the history of the rapidly advancing technology of quantum computing, a direct outcome of the research in the 1920s in quantum mechanics discussed in Chapter 2.

Chapter 9, **Promises Unmet**, discusses several developments in materials science that have produced great excitement in the field but have, as yet, failed to live up to their promise and potential: specifically, carbon nanotubes, introduced in Chapter 5, as well as one of the most exciting discoveries of the twentieth century, high-temperature superconductivity. The chapter concludes with a short discussion of why some of the potential importance of a material or a particular study may be overblown to raise the perceived impact of the work.

Chapter 10, **A Green New Deal**, looks at our history of materials usage and the increasing demand for many critical raw materials. It also addresses some of the challenges in the creation of a circular economy based on the four principles of reduce, retain, recycle, and regenerate. In that context, this chapter looks at some recent studies to upcycle plastics into valuable raw materials that can be used to make new plastics or converted into valuable added chemicals such as waxes and oils. It concludes by examining some of the historically successful approaches to recycling metals and the challenges specifically associated with recycling lithium, the essential element of the lithium-ion battery.

Notes

1. Ritchie H (2021) The price of batteries has declined by 97% in the last three decades. https://ourworldindata.org/battery-price-decline. Accessed 4 Aug 2022.
2. Cahn RW (2001) The Coming of Materials Science. Pergamon, Amsterdam, p 145.
3. Ashby MF (2016) Materials and Sustainable Development. Elsevier, Amsterdam, p 202.

Contents

1

A Measure of Stability

With the Great War in the past, just, for many Americans the 1920s seemed to offer enormous optimism and a great deal to celebrate. It was a time to spend some money, kick-back, and have fun. After a slow start at the beginning of the decade, the stock market was on its way to scaling unprecedented new heights (before, of course, its almighty collapse in October 1929 and the onset of the Great Depression). The economy of the United States was booming with consumers clamoring for the latest technology whether radios to listen to the popular Waldorf-Astoria Orchestra on WJZ Newark or the Eveready Hour, named after the famous battery, or washing machines and refrigerators—the symbols of modern middle-class convenience and comfort. For those who could afford it, there was Henry Ford's Model T, offering a new form of upward mobility for about $300. (Less than $5,000 in today's money.)

The 1920s was a decade of rapid change. Prohibition officially went into effect on January 17, 1920. While reformers rejoiced, organized crime flourished with notorious gangsters such as Al "Scarface" Capone and George "Bugs" Moran capitalizing and profiting from the booming market in illegal alcohol. Women won the right to vote on August 18, 1920, when the 19th Amendment to the United States Constitution was finally ratified. Many politicians including Ohio Republican and 29th President Warren G. Harding pushed for isolationism and there was a major religious revival among conservative Christians. And in a futuristic monoplane named the

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Spirit of St. Louis, Charles Lindberg's solo crossing of the Atlantic Ocean was to usher in the age of modern aviation.

In entertainment and sports, the 1920s were a time of innovation and exceptionalism. Louis Armstrong and the Hot Five were wowing audiences with the new jazz music. Charlie Chaplin was causing confusion and uproar on the silver screen with some of his most famous and popular movies. Ballerina Ana Pavlova was dazzling audiences across the world as *The Dying Swan*. At the 1920 Summer Olympics—the first games since the War—held in the Belgian city of Antwerp, Ethelda Bleibtrey won gold in all three women's swimming contests, on the way breaking five world records. And Babe Ruth was knocking them out of the park at Yankee Stadium and ballparks the length and breadth of the country at the beginning of what would be a fourteen-year record-breaking career with the New York Yankees.

Across the pond, while the immediate post-war years were good for some in Europe there were major challenges the continent had to address with emerging signs of even greater troubles ahead. Britain and France were faced with the crippling debts of war, a deep economic recession, and high unemployment. In Italy, the situation was worse with the economic problems being compounded by the enormous number of casualties the country had suffered coupled with the demoralization brought about by its string of wartime defeats. Collective feelings of disillusionment and despair led the king of Italy to turn to the leader of the Fascist party, Benito Mussolini, to form a government. This decision quickly led to a one-party police state, another sign of trouble ahead.

Germany was on the brink of economic collapse with the requirement to pay reparations to the Allies of 132 billion German marks (roughly $400 billion in today's dollars)—an absolutely staggering amount of money at the time—and the imposed cuts to its industrial and manufacturing base. Russia was engulfed in a vicious civil war that would last until 1922. Whilst Ireland was in the midst of a War of Independence pitting the Irish Republican Army against the British Army and its partners in the Royal Irish Constabulary and the Ulster Special Constabulary, which would lead to a ten-month long civil war.

In Stockholm, the Nobel Foundation was doing what it had done uninterrupted every year since 1901, awarding the Nobel Prize in Physics.

Less well known—at least outside the village of Fleurier—than Louis Armstrong, Charlie Chaplin, Ana Pavlova, Babe Ruth, and possibly Ethelda Bleibtrey, was Swiss scientist Charles-Edouard Guillaume winner of the 1920 Nobel Prize in Physics for, as the Nobel Foundation in Sweden noted, "recognition of the service he has rendered to precision measurements in Physics by

Fig. 1.1 Charles-Edouard Guillaume (ETH-Bibliothek Zürich, Image Archive Portr_08563)

his discovery of anomalies in nickel steel alloys."[1] Awarding the 1920 Nobel Prize in Physics to Charles-Edouard Guillaume, pictured in Fig. 1.1, was the first time the prize had gone to a metallurgist or for a metallurgical discovery. But it certainly would not be the last time a metallurgist, or indeed a materials scientist, or the discovery of a new material would be recognized by the Nobel Foundation.

While many around the world during the 1920s clamored for change, Charles-Edouard Guillaume's career was dedicated to the unchanging—the establishment, reproduction, and delivery of global standards.

Born in Fleurier in 1861 Charles-Edouard Guillaume is certainly the village's most famous son. At the time of his birth, Fleurier—the village of flowers—was best known for watchmaking with almost a quarter of its albeit small population engaged in supplying high quality timepieces to countries as far afield as China, the United States, Egypt, and Turkey. Watchmaking ran in the Guillaume family. Charles' grandfather, Alexander Guillaume, established a successful watchmaking business in London, which he passed down to his three sons. Charles' father relocated the business to Switzerland, settling in the little village of Fleurier in the canton of Neuchâtel.

Guillaume's early education was at the Neuchatel gymnasium or grammar school. Then at seventeen he enrolled in the Zürich Polytechnic, which was later to become the Swiss Federal Institute of Technology in Zürich or ETH Zürich for short. There the young Guillaume studied mathematics. Under the direction of Heinrich Friedrich Weber, Guillaume was awarded his PhD from the University of Zürich in 1883 for a thesis on electrolytic capacitors. (Zürich Polytechnic was not able to award doctorates at that time.)

In 1883 electrolytic capacitors, the topic of Guillaume's dissertation, represented a relatively new technology but one that was important for the emerging electrification of cities around the world and was certainly an area suitable for active research at one of Europe's most prestigious universities. A university that would include not only Guillaume among its famous alumni, but other Nobel Prize winning physicists including Wilhelm Röntgen, the discoverer of X-rays, and Albert Einstein. Einstein, who had been nominated many times, was the favorite to win in 1920, but this again proved not to be his year. Einstein was *awarded* the Nobel Prize in Physics in 1921, the year after Guillaume, for his explanation of the photoelectric effect and *received* his Nobel one year later in 1922. During the selection process in 1921, the Nobel Committee for Physics decided that none of the year's nominations met the criteria as outlined in the will of Alfred Nobel. According to the Foundation's statutes, the Prize can in such cases be reserved until the following year. In Einstein's case it appears that the Nobel Committee did not want to give the award for relativity, which they considered unproven. The compromise was to make the deferred prize for the photoelectric effect, which had been published several years earlier in 1905.

So, what is an electrolytic capacitor, a device that fascinated a young Charles-Edouard Guillaume? Inside an electrolytic capacitor is a metal foil, which acts as the anode or positive electrode. The metal foil is selected for its ready ability to form an oxide layer on its surface, in the same way as rust, iron oxide, forms on a piece of old iron. The earliest electrolytic capacitors used aluminum foil because of the strong bond formed between the oxide layer and the underlying metal.[2] Other suitably oxidizable metals including tantalum and niobium would become increasingly important as the technology developed and more applications were found for these devices.

Tantalum and niobium oxides offered an advantage over aluminum oxide because they are more reliable and can operate stably over a wider range of temperatures. That latter property—stability—was something that would be extremely important to Guillaume later in his professional career.

A feature of all electrolytic capacitors is that because of the presence of the oxide layer formed on the anode, they permit an electric current to flow in one direction only in a process known as rectification. In the late 1880s with the transition from Thomas Edison's low voltage direct current (DC) distribution of electric power to Nikola Tesla's more practical and efficient alternating current (AC), there was a residual need for local low voltage DC electricity. Rectifier function using capacitors could perform the necessary AC to DC conversion improving upon the cumbersome and expensive motor generators that were prevalent at the time.

One example of an important application that required a DC electrical source was to recharge batteries. These were used for, among other things, electric vehicles, which were beginning to appear in the 1800s throughout Europe, in Hungary, the Netherlands, England, France, and in the United States. Although gasoline-fueled internal combustion engines would rapidly come to replace battery power during the nineteenth century, electric vehicles were destined to become an increasingly significant part of the automobile market two centuries later led by companies such as Tesla and the lower profile China-based Kandi. Some recent modeling by the International Monetary Fund predicts that by the early 2040s—midway through the twenty-first century—electric vehicles may represent 90% of all the vehicles on the road.[3] These will all require batteries that can be quickly and conveniently charged and recharged using DC electrical power.

Electrolytic capacitors and their smaller relatives the chip capacitor gained even greater importance with the invention of the transistor, marking the dawn of the electronics age.

The canton of Neuchâtel, which includes the village of Fleurier and the city of Neuchâtel itself has boasted two Nobel Prize winners. In addition to Charles-Edouard Guillaume, who was the first, Daniel Bovet was awarded the 1957 Nobel Prize in Physiology or Medicine for "his discovery relating to synthetic compounds for the blocking of the effects of certain substances occurring in the body, especially in its blood vessels and skeletal muscles."[4] Allergy sufferers are the beneficiaries of Bovet's most well-known discovery, antihistamines. These are used in allergy medications to block the neurotransmitter histamine, which causes the unpleasant runny nose and itchy watery eyes that accompany a mild allergic reaction.

Guillaume's Nobel Prize winning discovery had actually occurred twenty-four years earlier, in 1896, while he was working at the International Bureau of Weights and Measures (*Bureau International des Poids et Mesures*, BIPM) in Sèvres, France, just outside Paris. But the award reflected more than just a single discovery, it recognized the years of important research that Guillaume had performed at the Bureau including establishing and distributing the metric standards.

Located on the left bank of the iconic Seine River, Sèvres already had a strong connection with materials even before the establishment of the BIPM. Since 1756, Sèvres had been well known for the manufacture of elaborately decorated porcelain having established itself along with Meissen in Germany and The Potteries in the United Kingdom as one of the most important sites for the manufacture of European porcelain. Among its notable customers the Sèvres Porcelain Factory welcomed French king Louis XV, who became its principal shareholder and financial backer. Russian empress Catherine II was also a much-valued customer. The czarina's commission was one of the largest and most celebrated ever made by the Sèvres factory. It took multiple iterations before Catherine approved the final design: "After lengthy negotiations about the decorative scheme, the czarina settled on a composition with various Neoclassical elements—stiff bunches of flowers, ample scrolls, and, most important, depictions of cameos, which she collected with enthusiasm."[5]

In 1920, the year Guillaume's Nobel Prize was awarded, Sèvres would again achieve international recognition. This time it was not for its beautiful ceramics or its exacting standards but as the location for the signing of the Treaty of Sèvres between the victorious Allied powers and Turkey, effectively ending the Ottoman Empire. The treaty was signed in the exhibition room at the Sèvres porcelain factory but was never ratified. A treaty described "as brittle as the porcelain that was produced there."[6]

Formation of the International Bureau of Weights and Measures in 1875 in its historic home in the Pavillon de Breteuil coincided with the signing of the Meter Convention (*Convention du Mètre*) or Treaty of the Meter as it is more frequently known in the United States. Seventeen nations, including the United States, were the original signatories. As of January 2023, there are sixty-four Member States and thirty-six Associate States and Economies of the Meter Convention, which forms the basis of all international agreements on units of measurement. The Bureau's task, as home of the International System of Units (SI) and the International Reference Time Scale (UTC), is to ensure worldwide unification of physical measurements.

Guillaume joined the International Bureau of Weights and Measures in 1883 straight after completion of his PhD. His appointment as an assistant researcher came at an important time in the history of the Bureau and for how we measure the world. In 1889, six years after Guillaume had joined, the Bureau embarked on an ambitious program; the approval and worldwide distribution of metric standards. Among his duties, Guillaume was charged with making precise copies of the standard meter, which was kept safely in the Pavillon de Breteuil. The bar was an alloy consisting of 90 parts platinum to 10 parts iridium that had been developed by chemist Henri Sainte-Claire Deville.[7] Both platinum and iridium are highly resistant to corrosion and very stable. The 90/10 alloy had an additional property that was very important. Its dimensions were found to barely change with temperature. If kept outside subjected to the vagaries of the weather the length of the platinum-iridium meter bar would vary by only 0.2 mm between the coldest and warmest average monthly temperatures in Paris.[8] As Guillaume said of the platinum-iridium alloy during his Nobel Lecture on December 11, 1920: "The hardness, permanence, and resistance to chemical agents would be perfect for standards that would have to last for centuries."

Guillaume was correct. Although the original meter bar made of platinum and iridium has lasted well over 100 years it is no longer used to define the metric unit of length. After 70 years, the 1889 platinum-iridium International Meter preserved at the Pavillon de Breteuil lost its position as the primary length standard being replaced by increasingly precise measures to define one meter. Measures that are convenient, can be reproduced, and are unaffected by variables such as temperature. In October 1960 the meter was redefined to an optical standard equivalent to a very precise 1,650,763.73 wavelengths of the orange light, in a vacuum, produced by the element krypton-86 (^{86}Kr).[9] In 1984, the Geneva Conference on Weights and Measures improved upon the definition by stating that a meter is the distance light travels, again in a vacuum, in 1/299,792,458 s with time being measured by a cesium-133 (^{133}Cs) atomic clock.

But back in 1889, Guillaume was faced with the challenge of duplicating the standard meter bar, which because of the amazing stability and the rarity of its constituent elements was incredibly expensive. A single meter cost 7,000 crowns. (At the time a very spacious terraced house for a working London professional, his family, and at least one live-in servant could cost around 400 crowns a year.)[10] It would simply cost too much money to make duplicates for the ever-growing number of member states. If platinum and iridium were too expensive, were there lower cost metals that could be used instead?

Seeking a solution, Guillaume began investigating other alloys that might be used to make duplicates of the standard meter bar.

Nickel satisfied many of the properties necessary to make an unchanging standard. It was "unaffected by the passage of time, rigid and of average expansibility." The challenge turned out to be not in the excellent properties of pure nickel but in finding a factory that could make a bar of the appropriate quality that was "perfectly sound and crack-free."[11] Maybe, instead of pure nickel, an alloy containing nickel might be formulated that had both the desired properties coupled with an ease of manufacture.

Research in iron-nickel alloys was already taking place on both sides of the English Channel (*la Manche*). In Paris, at the request of the Ordnance Technical Department (*Section technique de l'artillerie*) J.R. Benoit was studying the properties of steel alloys containing nickel and chromium with a view to developing a length standard. While in London in the Siemens laboratory at King's College, John Hopkinson was observing some curious magnetic properties of alloys of iron and nickel when they were plunged into solid carbon dioxide (dry ice) at a temperature of −78°C.[12]

While interesting, the steel alloys being studied by Benoit and Hopkinson were not suitable for use as standard measures of length. In fact, they were entirely unsuited for this demanding application because they had a high coefficient of thermal expansion (sometimes abbreviated CTE and often represented by the Greek letter α). A high coefficient of thermal expansion means that the dimensions of a material are strongly affected by changes in temperature. By a stroke of good luck, a bar of steel containing 30% nickel—considerably more than was present in the earlier alloys—arrived at the Bureau in Sèvres in 1896. Unexpectedly, Guillaume found that this alloy with its extra amount of nickel had a very low expansivity—one-third lower than that of platinum. Encouraged by this fortuitous result Guillaume continued his studies of iron-nickel (ferronickel) alloys with, as he says, "stubborn obstinacy." He prepared a range of ferronickel alloys with nickel contents from 30% all the way up to 60% then measured how much their dimensions changed with temperature. The composition with the lowest coefficient of thermal expansion contained 64.4% iron and 35.6% nickel. In fact, this alloy exhibited the least amount of thermal expansion of any metal or alloy known at the time. What was particularly surprising to Guillaume about this result was that it did not follow the commonly accepted "rule of mixtures", which would predict that the coefficient of thermal expansion of the alloy should not be less than that of the individual component with the lowest value.

On the suggestion of Marc Thury, a professor at the University of Geneva, Guillaume named this remarkable alloy "Invar", short for *invar*iable. As

Guillaume commented in his 1904 paper published in the journal *Nature*: the succinct name was adopted to avoid saying "steel containing about 36 per cent of nickel, which is characterized by possessing an extremely small coefficient of expansion or by the fact that its specific volume is practically invariable when considered as a function of the temperature."[13] Naming the new alloy Invar was certainly less of a mouthful.

As an invariable measure of length Invar was invaluable. It offered the physical benefits of the platinum-iridium alloy, but at a fraction of the cost. Using Invar, it was now economically feasible for Guillaume to make multiple duplicates of the standard meter bar for distribution throughout the world. Moreover, with its superlative stability it did not take long for Invar to find application in a number of fields in addition to its use as the universal standard of length. One of those was in clockmaking—an application that Guillaume, whose family had a history in the trade, was quick to recognize.[14]

Before the advent of the quartz clock, time was most reliably kept by a pendulum clock measured by the period of swing of a pendulum—a weight (known as a bob) attached to the end of a metal rod. To maintain accurate time keeping it was necessary for the metal rod to always be the same length regardless of temperature (the same requirement for the standard meter bar). If the rod expands the pendulum becomes longer, the clock will lose time. Conversely, a decrease in temperature will cause the clock to gain time. Before the advent of Invar the warming of the steel rods used in pendulum clocks resulted in a loss of ½ second per degree Celsius a day (0.28 s per degree Fahrenheit a day).

To overcome this loss of accuracy, pendulum clocks would employ expansion-compensation mechanisms to reduce the effect of temperature changes. One widely used mechanism was the gridiron pendulum invented by John Harrison in 1721. The gridiron consists of alternating parallel rods of two metals—for instance the two metals might be steel and brass—each having a different coefficient of thermal expansion. Temperature changes are accommodated by the upward expansion in one material (in our example, brass) being compensated with the downward expansion of the other metal (iron). But the complexity of the compensation mechanism was not ideal and a simpler approach was definitely needed. This sounded like a perfect job for Invar, which quickly found its way into pendulum clocks only two years after the discovery of its remarkable properties. The Riefler regulator clock developed in 1898 by Sigmund Riefler was the first clock to use an Invar pendulum giving the timepiece an unprecedented accuracy of 10 ms per day, a "gold standard" in precision. Riefler's new form of pendulum was exhibited at the 1898 World's Fair in Munich. By 1900, Invar pendulum rods were used for

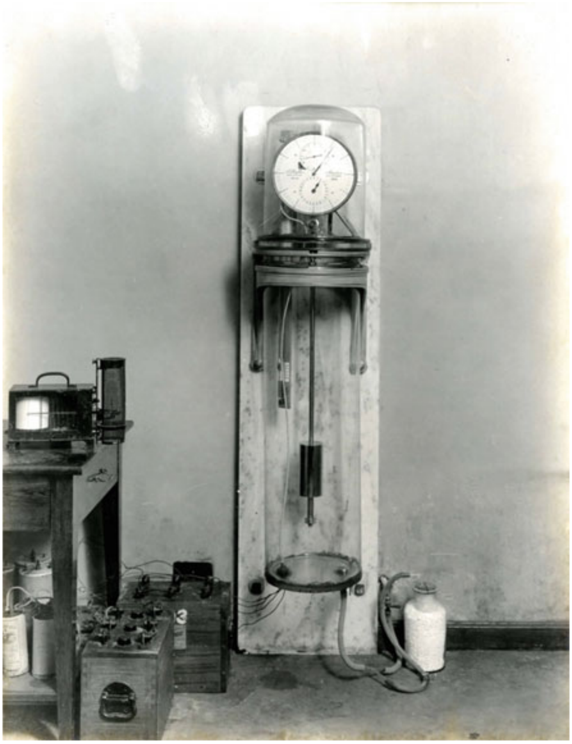

Fig. 1.2 A Riefler clock with its Invar pendulum. This specific clock was purchased in 1904 by the National Bureau of Standards from the firm Clemens Riefler in Germany (Credit NIST)

the highest precision clocks and could be found in nearly every astronomical laboratory. Invar had made the need for complex compensation mechanisms in timepieces redundant. An example of a Riefler clock, purchased by the National Bureau of Standards in 1904, is shown in Fig. 1.2.[15] Riefler clocks served as the national time interval standard until 1929, when it was replaced by the Shortt clock that also used a pendulum and bob made of Invar.

A quick fifteen-minute taxi ride east from Sèvres, home of the International Bureau of Weights and Measures, will take you to Paris's most famous landmark—the Eiffel Tower. Erected in 1889 as a temporary exhibit for the World's Fair, the Eiffel Tower with its 7,300 tons of wrought iron became the tallest structure in the world reaching 1,063 feet at its tip. It would hold that record for over 40 years. Because of the extreme height of the tower the French Service Geographique was concerned about the *sideways* movement of the monument whether caused by wind or by temperature changes, but "for want of an appropriate method no attempt was then made to study the