# A Centennial Report

## Alan Cottrell

> I...still believed that I was the victim of deception when I observed the phenomenon of the ray."
> Röntgen recounting his discovery of x-rays at Würzburg, 1895
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> MAJORANA: There are scientists who "happen" only once in every 500 years, like Archimedes or Newton. And there are scientists who happen only once or twice in a century, like Einstein or Bohr.
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> FERMI: But where do I come in, Majorana?
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> MAJORANA: Be reasonable, Enrico! I am not talking about you or me. I am talking about Einstein and Bohr.
>
> S. Chandrasekhar
> *Truth and Beauty* (1987)

## Influences on Society

This past century has seen an incredible change in developed society: It is the information revolution, based on radio, television, telecommunications of many kinds, computers everywhere, the Internet, intelligent monitoring and control systems, and a host of other services. One materials development has made all this possible: the silicon chip. The triumphal outcome of the second half-century's intense research and development of semiconductors is that silicon chips are now made in millions and are the heart of all these information systems.

Second only to the silicon chip in shaping modern society is the revolution in plastics, polymers, and synthetic fabrics, the familiar products of which surround us everywhere. A century ago there was only celluloid. Now numerous such materials are in everyday domestic use, with an inexhaustible variety of different applications in an incredible range of forms.

Another prominent development has been the introduction of aluminum, both for simple but ubiquitous domestic utensils and, in a much more demanding role, for aircraft structures, which has made the era of cheap mass air transport possible. The main materials development underlying this has been the large-scale electrolytic reduction of the ore using low-cost electricity, but improvement of the metal by alloying was also important.

Less spectacular, but perhaps even more important, has been the massive production and widespread use of structural steel, again a fruit of cheap production on a truly heroic scale. In fact, steel remains to this day the cheapest way of buying sheer tensile strength.

## Electrons in Metals

J.J. Thomson's discovery of the electron in 1897 led to a remarkably rapid application in materials science: Drude's 1900 theory of metals. His picture of free electrons in a metal owed much to the classical kinetic theory of gases, and it delivered golden rewards in its explanation of why metals are such extremely good conductors, not only of electricity, but also of heat. It gradually became clear, however, that some major change to the theory was necessary. For example, the free-electron gas has almost no specific heat, unlike a classical gas. This problem could not be evaded by assuming that there are very few free electrons, because experimental facts such as the Hall effect proved precisely the contrary.

The answer had to wait a quarter of a century, until quantum mechanics arrived. In 1928, Sommerfeld cleared up most difficulties by the simple step of replacing the classical gas laws in Drude's theory with quantum-mechanical ones. This introduced the famous concept of the energy-band structure for the itinerant electrons, all levels of which are completely filled up to the Fermi level. With this modification, free-electron theory became so successful that even today, three-quarters of a century later, this quantized free-electron picture is what immediately comes into a physicist's mind when thinking about a metal.

Most of the basic theoretical work on metals since then has been focused on understanding why this simple theory works so well. Why do the lattice ions appear so ineffective as obstacles to the movement of the electrons? Why do the electrons not scatter one another intensely? Why are only some solids metals, whereas others are insulators? A first answer to the first question came very early, from Bloch's 1928 theory showing that a perfectly periodic crystal lattice does not scatter

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free electrons. Electrical resistance comes from the scattering of electrons by deviations from this periodicity, due to thermal vibrations, impurity atoms, and lattice defects. Much later, pseudopotential theory completed this story in 1959, showing that through the Pauli exclusion principle, the lattice atoms are inherently almost transparent to free electrons (in good metals, at least). The second question had an early answer in the realization that most electrons in the band distribution are unable to scatter one another because there are no empty quantum states within energy reach into which they could go. Later, Landau's theory of the Fermi liquid elegantly cleared this up in 1957.

The problem of why some materials are metallic and others are not has lingered through most of the 20th century. A great early step toward its solution was taken by Goldhammer in 1913, followed by Herzfeld in 1927. They started from insulators, in which the atoms were assumed to retain their valency electrons, denying these their freedom. But it was known that volumetric compression, by reducing the spacing between atoms, increases the polarizability, leading ultimately to a polarization catastrophe in which the dielectric constant becomes infinite, implying that the atoms are no longer able to hold on to their electrons. This was interpreted as the transition of the material from the nonmetallic to the metallic state.

Strangely, this theory was overlooked for half a century, even though Pauling produced some comparable ideas in the meantime. The main high road of metal theory continued to be the free-electron theory, in which atomic interactions are virtually ignored. Sommerfeld's theory pointed to the essential condition: If there is a finite density of states at the Fermi surface, the material is a metal; otherwise, it is not. But why do various materials differ in this respect? Wilson gave an important answer in 1931, based on the Brillouin-zone structure of electron-energy bands. Metals require partly filled zones. In the absence of these, the material is an insulator. This theory ruled the roost for many years, even though a serious fault had been spotted in 1937. It predicted NiO to be a metal, whereas it is actually an insulator. The problem was that Wilson's theory is a "macroscopic" one in the sense of being based on free electrons, which react only to large numbers of crystal planes, so that local conditions involving individual atoms and how they respond to their

immediate neighbors—precisely what Goldhammer and Herzfeld had considered—were ignored. It was Mott in 1949 and Hubbard in 1963 who finally brought the theory back to a form close to the Goldhammer-Herzfeld one.

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Imagine a crystal of, say, sodium, but of such enormous lattice spacing that each atom is in effect isolated. Suppose that all the atoms are neutral, and then take the valency electron away from one of them and give it to another. This costs an ionization energy that is several times larger than the affinity energy regained from the receptor atom. This process is thus energetically unfavorable, and so the system stays preferentially in its all-neutral state (i.e., it is an insulator). Repeat the process at successively smaller lattice spacings. The resulting increased interaction between the atoms now broadens the electron-energy band; eventually by so much that the bottom of the band falls low enough to compensate for the difference between the ionization and affinity energies. It is now favorable for an electron to leave its parent atom and go into the bottom of the free-electron energy band, that is, to enjoy the freedom to go to any of the other atoms of the crystal. This is the transition to the metallic state, according to the Mott-Hubbard theory.

The stunning discovery of superconductivity by Kamerlingh-Onnes in 1911 began a century of exciting but largely frustrating research. On the practical side, the search for alloys with usefully higher superconducting temperatures met with only modest success, although sufficient for a few applications, notably in magnetic resonance imaging for medical diagnostics. This was matched by theoretical frustration. The most eminent theoretical physicists struggled vainly to understand the basic mechanism until Bardeen, Cooper, and Schrieffer eventually solved the problem in 1957. A subtle and minute attraction between the free electrons, due to their interactions with the lattice ions, produces a thin gap at the Fermi surface that enables this surface to become fixed in unsymmetrical positions representing the resistance-free perpetual flow of electric current. This convincing BCS theory appeared to have finally demolished the

great theoretical problem.

Not so. It returned to life with a vengeance in the wake of the extraordinary discovery of high-temperature superconductors by Bednorz and Müller in 1986. All the old frustrations have come back again. These high temperatures still fall tantalizingly short of room temperature, which is the holy grail of this subject. About the only thing that the theoreticians agree on, in trying to understand it, is that the mechanism is unlikely to be the BCS one. The problems here are plainly heading for the next century.

Alloys challenged electron theory in other ways. Their study was very active at the start of the 20th century and focused on the determination of their phase diagrams, inspired partly by (then) recently established principles of thermodynamics, such as the phase rule, and partly in the hope of discovering new alloys with useful properties. This work was successful, both scientifically (especially when reinforced in the 1920s by the x-ray determination of crystal structures of alloys), and in providing many important new materials. Some outstanding examples are the aluminum alloys, starting with duralumin, based on precipitation hardening following Wilm's discovery in 1911, although not understood until much later; stainless steel, notably the 18-8 austenitic type that is now found in virtually every household as well as throughout the chemical and food-processing industries; and the nickel-based superalloys, which since the 1940s, have made the gas-turbine aero-engine such a formidable power unit.

But alloys raised great perplexities. What was one to make of phases such as $CuZn$, $Cu_5Zn_8$, and $CuZn_3$? Their compositions were nonsensical, according to chemical valency orthodoxy. It was Hume-Rothery's great discovery in 1926 which revealed that large numbers of such alloys occur at the same ratios of valency electrons to atoms, and that they then mostly have the same crystal structures. To set them apart from classical chemistry, they became known as "electron compounds." They were first explained by Jones in 1934. He showed that for a given crystal structure, there is a critical valence-electron concentration, at about the electron-compound value, for which these electrons fit particularly well into the Brillouin-zone structure and so have lower energy than otherwise. Regarded for many years as the explanation of these phases, the theory then went into the doldrums for a period, as some apparently serious faults in it were exposed. However, it was eventually shown that these faults stemmed from an overly simple representation of the theory. A rigorous reworking, in which

Jones' simple estimates were replaced by a powerful modern computation by Paxton, Methfessel, and Pettifor in 1997, confirmed the basic correctness of the principle underlying the theory.

## The Electronics Revolution

Before the electronics revolution could get under way there first had to be, of course, the electrical revolution: "electricity in every home." This revolution was ushered in by the development of long-range transmission of high-voltage current which required transformation down to domestic voltages. This was made possible by the invention of the soft magnetic silicon iron sheet. It was followed in the 1920s by the great invention of the tungsten-filament light bulb, with its enormous impact on everyday life—the fruit of some brilliant physical metallurgical research.

This first electronics step was a solid-state one, the cat's-whisker radio receiver with which our grandparents spent happy hours in the early 1920s, twiddling a fine wire over the surface of a galena crystal looking for a sensitive spot to give good reception. It was, of course, soon overtaken by valve radio, based on thermionics well understood as a consequence of the free-electron theory, as a process of evaporation of free electrons from the metal.

Semiconducting materials were first explained by Wilson in the 1930s as a variation on bandgap insulators in which the energy gap is so small—or, more generally speaking and important, streaked with impurity energy levels—that electrons can be thermally excited across the gap from one band to another. Practical applications remained limited at first, but in 1947 came the tremendous discovery of transistor action by Bardeen, Brattain, and Shockley. This opened the floodgates to the transformed modern world of solid-state electronics and all that has followed from it. Their original breakthrough has, of course, been reinforced subsequently by many supplementary inventions, most notably that of the integrated circuit, which can now consist of many millions of interconnected transistors formed on the surface of a silicon wafer. There are no signs of this feverishly active field slowing down, with both new materials such as gallium nitride and new devices such as quantum dots currently attracting great interest.

Another extremely active field at present is that of optoelectronics, spurred on by the introduction of optical-fiber telecommunications and by the rapidly increasing use of lasers. The production of continuous low-loss glass fibers, miles long, of extreme purity, free from defects, and with a carefully graded refractive

index from center to surface so as to hold in the traveling light signals without distortion, has been a triumph of modern materials science and technology. The same could be said of the semiconducting laser, a most sophisticated structure built up by molecular beam epitaxy, and optically active crystals.

Perhaps overshadowed by these electronic developments, but very impressive nevertheless, has been the continual improvement in magnetic materials. The scientific foundations have been laid down throughout the century, very fruitfully right from its beginning. Curie's great paper of 1895 on the temperature dependence of magnetic properties started things off, leading to the concept of a critical temperature, the "Curie point," which has inspired many developments in statistical mechanics. In 1905, Langevin tracked the microscopic basis of ferromagnetism down to individual molecules, possibly even single electrons, which anticipated Heisenberg's 1928 explanation in terms of the quantum exchange interaction between electrons. And in 1918, Weiss introduced the idea of domains, which explained how a bar of iron can exist in both magnetized and unmagnetized states.

The first permanent magnets were made by adding tungsten, chromium, and cobalt to iron, but the great breakthrough came in 1931, when Mishima in Japan marketed the alnico alloys, thus starting a series of developments and uses that continues to this day. Their effectiveness depends on the fine-particle principle. The magnetic softness of pure iron is due to the ease with which the boundaries between domains can move through the material. But these boundaries are rather thick—a few hundred atom spacings—and extremely fine particles cannot contain them. Such particles thus retain their full magnetization tenaciously. The alloying and heat treatment of alnico precipitates very fine rods of the magnetic phase from which the magnetic hardness ensues. More recently, the magnetic strength has been increased still further by adding rare-earth elements to form fine-grained structures of noncubic crystallinity.

A completely different line of magnetic development has been the introduction of nonmetallic magnets that combine their magnetic properties with useful insulating ones. The starting point here was Néel's discovery of antiferromagnetism and ferrimagnetism in the 1930s. Useful materials of this kind are the ferrites (mixed metal oxides) and the garnets. Immense amounts of fine particle iron oxide magnets are now used in video, audio recording tapes, and magnetic disc drive storage.

## The Quiet Revolution

The polymer revolution crept up on us quietly and has spread universally, gradually replacing traditional materials by synthetics in innumerable familiar applications, in the household, in the clothes we wear, in rubbers, in paints and varnishes, even in dental fillings. It began with Baekelund's discovery of bakelite in 1909, produced from phenol and formaldehyde; from the 1920s onwards, many synthetic polymers were introduced with a wide variety of uses, leading to what is now a giant modern industry. In each of the recent decades of the century, the world production of synthetic plastics, resins, and fibers has increased fourfold. Notable among these are nylon, developed by Carothers in 1938, polythene (polyethylene) in the 1950s, perspex (polymethylmethacrylate, or PMMA ) for windows, and Teflon (polytetrafluorethylene, or PTFE).

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A beautiful theory, developed in the 1940s, by H.M. James and E. Guth, is the explanation of the extraordinary elasticity of rubber and other elastomers. These are slightly cross-linked polymers, with long lengths of crumpled molecular chain between successive cross-linked end points. The crumpling can fold, by thermal agitation, into a large variety of different shapes. However, if the end points are pulled apart, the allowed number of such shapes is reduced so that a penalty in configurational entropy has to be paid, the cost of which gives rubber its very weak elasticity. Entropy made tangible.

A striking and perhaps surprising application of synthetic polymers is in modern architecture, in particular, the use of Teflon in the form of extremely large membranes supported high by poles and cables to make semipermanent, tentlike structures. An early example is the Haj Terminal at Jeddah Airport in Saudi Arabia. More recent ones are at Denver International Airport in the United States, the Sony Center in Germany, and the Millennium Dome in London. Such constructions are very light and can be constructed on a vast

scale, covering, for example, an entire shopping arcade or sports arena. They will surely become a familiar feature of the new century.

## Strong Materials

The main use of bulk metals such as steel has, of course, been to make strong things, especially where tensile strength is required. The search through the past century for ever stronger and lighter materials has shown that useful strength is a subtle property. A glass shard will scratch brass, but not vice versa, which suggests that glass is the stronger material. But when dropped on a hard floor, it is the glass bowl that breaks, not the brass one. Such metals and alloys are "strong because they are weak." Their weakness stems from the ease with which dislocations can glide along slip planes through their crystal structure, which makes them ductile and protects them against brittle fracture.

Although first proposed in 1934, dislocations received little attention until after World War II, when there was an explosion of interest in crystal defects, both dislocations and point defects, which are important in photographic emulsions and in materials for nuclear reactors. A big advance occurred in 1956 with the observation of dislocations in the electron microscope. From then on, they ceased to be purely theoretical entities and became part of the observed microstructures of materials.

The development of strong materials faces a basic problem. Useful tensile strength is a combination of three properties: (1) plastic hardness (i.e., resistance to yielding), (2) elastic stiffness, and (3) toughness (i.e., resistance to crack failure). These properties are incompatible as a group of three, although it is easy to have just two of them: for example, (1) and (2) in brick, (1) and (3) in rubber, or (2) and (3) in copper. The challenge of materials science has been to start with two of these properties and to introduce the third without overly compromising the first two. The design of strong alloys, which follows the precipitation-hardening principle, starts with a basis metal that has (2) and (3) and then adds (1) by forming finely dispersed alloy precipitates that obstruct the movement of the dislocations. A favorable feature is that good hardening can be achieved from particles about 10–100 atomic spacings apart. This leaves most of the dislocation lines between obstacles lying in locally soft material, which is resistant to brittle cracking. In locally soft material, these sections of the dislocation lines cannot move forward except slightly because they are held back by the obstruct-

ed sections and by their general stiffness, which prevents them from looping between the obstacles.

The relentless search for ever stronger and lighter materials, especially those that remain strong at high temperatures (as required for aero-engines, for example) has led increasingly toward ceramics as a possible alternative to metals. They have many advantages. Some are very light and elastically stiff. Many have high melting points and remain strong when extremely hot. Moreover, at least some of them have excellent high-temperature oxidation and corrosion resistance. But they have one huge disadvantage: They are generally very brittle when cold.

Breakthroughs in solving this problem began in the 1950s. It was realized that brittleness is not the fatal quality; it is fragility, that is, ease of fracture. If a material can have a high resistance to cracking, then it does not matter that it is also brittle. The way to separate these two properties was discovered in the principle of the fiber composite. Strong fibers—which are brittle in that their structure precludes the presence of plastically weakening mobile dislocations—are densely embedded in a bonding matrix material, often a brittle epoxy resin. The principle is easily seen from a natural composite. Bend a bamboo cane to open up a sharp notch which has been scribed across it. Instead of cracking, even though it is brittle, its fibers at the tip of the notch simply spring apart, leaving the notch unable to continue as a crack. If an unnotched rod is pulled in tension, it can fail only by the long fibers dragging themselves through the enveloping matrix, which consumes much energy as friction, so that the material behaves toughly even though it is brittle. It is perhaps surprising that this principle was not recognized earlier in engineering-materials design, since Nature has made use of it for ages; even our biblical ancestors knew that bricks had to contain straw if they were to be strong.

The first strong composite to become generally available was, of course, fiberglass, in the 1950s. Fiberglass is a tough constructional material made from brittle glass fibers in a brittle resin, used for boat hulls, car bodies, and many other things. Some 10 years later, carbon fiber appeared—very light, very stiff, and now used widely in sporting goods and aircraft structures. Still under development today are ceramic fibers such as silicon carbide, which hold promise for use in the hottest parts of aero-engines. Fibers are also beginning to make possible "smart" materials that are able to signal and thus give early warning of deterioration in their mechanical condition or other local features of their surrounding structure, useful in such structures as an aircraft wing or a bridge.

## Conclusion

In the materials world, the century has gone out in style: smart materials, quantum wires and dots, diamond films and coatings, glassy alloys, and shape-memory alloys being only a few of its latest innovations. The subject itself has also sprung many recent surprises: high-temperature oxide superconductors, carbon fullerenes, and quasicrystals with their strange five-fold symmetry, to name but a few. It is, of course, impossible to predict the next ones. What can be safely predicted, however, by simple extrapolation, is that there will be many.

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It is perhaps more possible to predict the main line of materials development in the coming century. Almost certainly, we will see more materials for biomedical uses. We have already had an early experience of this in the dentist's chair, where the traditional mercury amalgam fillings have largely given way to polymeric ones. A light-sensitive polymer is pasted into the cavity and then hardened by exposure to blue light for about a minute. The newer versions of this bind well onto the tooth. A great orthopedic advance occurred about 40 years ago with the replacement of an arthritic hip with an artificial joint. The alloy ball head and its supporting alloy spike are sealed into the medullary cavity with PMMA cement, which is then hardened in situ. The ball head rotates in a polyethylene cup cemented into the pelvis. Probably 1 million people have now benefited from this replacement. A problem is the slow deterioration of the adjacent bone tissue. This can be minimized by having the stem deform mechanically like bone. Imitation bonelike material is now being developed that has similar mechanical properties to real bone, but possesses much greater fracture toughness.

The coming century will see a vast extension of such technologies, extending as far as organ replacement. At a more humble level, we look forward to the tube of biomedical "glue" which we simply squeeze on to a cut to seal and heal it.

Finally, as the new millennium gets under way, what in the materials world will be seen as the outstanding feature of the century just past? Despite the cornucopia of exciting new materials it has provided, I think it will be remembered mainly for something else: It was the century when we understood materials, scientifically, for the first time—what they are and how they perform. Two advances have been outstanding in making this possible: x-ray analysis, which showed us where the atoms are inside materials; and quantum mechanics, which explained how they interact and produce the bulk properties of matter.

FOR FURTHER READING: To go more deeply into the above topics the reader may wish to consult the following books: Lillian Hoddeson, Ernest Braun, Jürgen Teichmann, and Spencer Weart, eds., *Out of the Crystal Maze: Chapters from the History of Solid-State Physics*, (Oxford University Press, New York, 1992); *The Beginnings of Solid-State Physics: A Symposium organized by Sir Nevill Mott* (The Royal Society, London, 1980); Robert Cahn, *The Coming of Materials Science* (Pergamon, Oxford, in press); and Herbert Morawetz, *Polymers: The Origin and Growth of a Science* (Dover Publications, New York, 1995).

*Alan Cottrell received his BSc degree in 1939 from the University of Birmingham, followed by a PhD degree in 1942. He was a lecturer in metallurgy at the University of Birmingham from 1943 to 1949, professor from 1949 to 1955, followed by three years as deputy head of the Metallurgy Division of the Atomic Energy Research Establishment. His posts at the University of Cambridge include Goldsmiths' professor of metallurgy (1958–1965), Fellow of Christ's College (1958–1970), Master of Jesus College (1974–1986), and vice-chancellor (1977–1979). As Master of Jesus College, he introduced its first female students. He held a number of scientific advisory posts with the British government, including deputy chief and chief scientific advisor (studies) to the Ministry of Defense, deputy and later chief scientific advisor to Her Majesty's government, and numerous other scientific advisory posts. He is a foreign honorary member of the American Academy of Arts and Sciences, a foreign associate of the national Academy of Sciences and the national Academy of Engineering, and a Fellow of ASM International and the Royal Swedish Academy of Sciences. Cottrell has also been chosen to receive the 1997 Copley Medal, which is the highest award that the Royal Society in London can bestow. He received the 1996 Von Hippel Award, which is the Materials Research Society's highest honor. He was knighted by Queen Elizabeth in 1971.*