

A CENTURY OF SUPERCONDUCTING TECHNOLOGY

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ABSTRACT

Cryogenic Engineering was the enabling technology by which Heike Kamerlingh Onnes discovered superconductivity in 1911. Thanks to years of careful development, Leiden had become the world centre for cryogenics and remained the only source of liquid helium for many years. Shortly afterwards, Kamerlingh Onnes speculated on the possibility of building a superconducting magnet, but was disappointed to find that superconductivity in the metals he had measured: mercury, tin and lead, was quenched by quite modest fields. Despite many advances in the theory, it was to be another 50 years before superconducting technology really got off the ground with the discovery, largely in the USA, of a new class of hard 'type 2' superconductors which could retain their superconductivity up to very high magnetic fields. Starting with small laboratory solenoids, a new industry was borne, which then expanded into larger scale applications like NMR spectroscopy, clinical MRI and large particle accelerators. The discovery of High Temperature Superconductivity promised a further expansion of the industry into new application areas, but this hope has yet to be fulfilled. Recently however the performance of HTS conductors has dramatically improved with the advent of oriented thin film YBCO tapes and it is hoped that these conductors will open up new applications for superconductivity, perhaps in electrical power engineering.

KEYWORDS: cryogenic, liquid helium, superconductivity, magnetic field, NMR, MRI, accelerator.

INTRODUCTION

This year we celebrate 100 years of superconductivity. Its discovery by Heike Kamerlingh Onnes was a classic example of new science being enabled by progress in technology – in this case cryogenic engineering. After describing some of that early technology and its role in the discovery of superconductivity, this review traces our

growing understanding of the superconducting state and how it has led to some spectacular applications in big science and a new global industry.

A NEW STATE OF MATTER

On May 8th 1911, at the physical laboratory of the University of Leiden, Professor Heike Kamerlingh Onnes wrote in his laboratory notebook '*kwik nagenoeg nul*', translated roughly as '*quick silver near enough zero*'. While measuring the resistivity of metals at very low temperatures, he had stumbled on a new and completely unexpected state of matter: superconductivity.

Cryogenic Technology

Although the discovery might seem like pure serendipity, it was actually the outcome of decades of systematic development work by Kamerlingh Onnes in cryogenic technology [1]. When he joined the university as Professor of Experimental Physics in 1882, he made it his mission to test the molecular gas theory of his chief, the great Johannes Diderick van der Waals. For this work, he needed to measure the 'permanent' gases over a wide range of temperature down to liquefaction. With the motto of 'through measurement to knowledge', he set about the task of building up a fully functioning cryogenics laboratory. At this time, very little of the required equipment was available to buy and it was necessary to build it in house. But technicians with the required skills were not available either, so from the time of his arrival at Leiden, Kamerlingh Onnes gave every encouragement to the in-house training of instrument makers [2]. By 1904, the Leiden school of instrument makers had grown to 32 students and these 'blue collar boys' were given a broad training in every aspect of laboratory technique, including glass blowing, forging, nickel plating, operating steam and gas engines, electric motors, generators and batteries, technical drawing etc. In 1901, the Society to Promote the Training of Instrument Makers was founded with Kamerlingh Onnes as its president, which he remained until his death. Here he used his influence to promote schemes for the financial support of students from poor backgrounds.

Typical of the technology development carried out by Kamerlingh Onnes and his blue collar boys was the modified Cailletet compressor. This machine, which uses a moving slug of mercury as a piston to compress the gas, was developed by Louis Paul Cailletet for the liquefaction of oxygen. The advantage of this arrangement is that it keeps the gas very clean and allows high compression ratios to be achieved because the 'piston' can go right into the head of the cylinder. However, Kamerlingh Onnes found many practical problems in using the compressor, notably the entry of air and contamination of the mercury by lubricant needed for the mechanical piston. Accordingly, he carried out a comprehensive upgrade, described in one of his Communications from the laboratory [3] and illustrated in Fig 1. The improved compressor was central to his subsequent work on liquefying hydrogen and helium.

The race to liquefy hydrogen was won by Dewar in 1898 [4], when he produced about 20cm³ of liquid before the jet was blocked by solids. Kamerlingh Onnes took much longer, partly because he was delayed for some years by a prohibition on the use of hydrogen by the Leiden municipality, fearful of an explosion, and partly because his style was to produce a 'cold factory' suitable for long term use. When it did arrive in 1906, the Leiden hydrogen liquefier was able to produce four liquid litres per hour continuously and economically. It would enable him to make comprehensive and detailed measurements at

low temperature and, in a couple of years' time, amass the large amount of liquid hydrogen needed to pre-cool his helium liquefier.

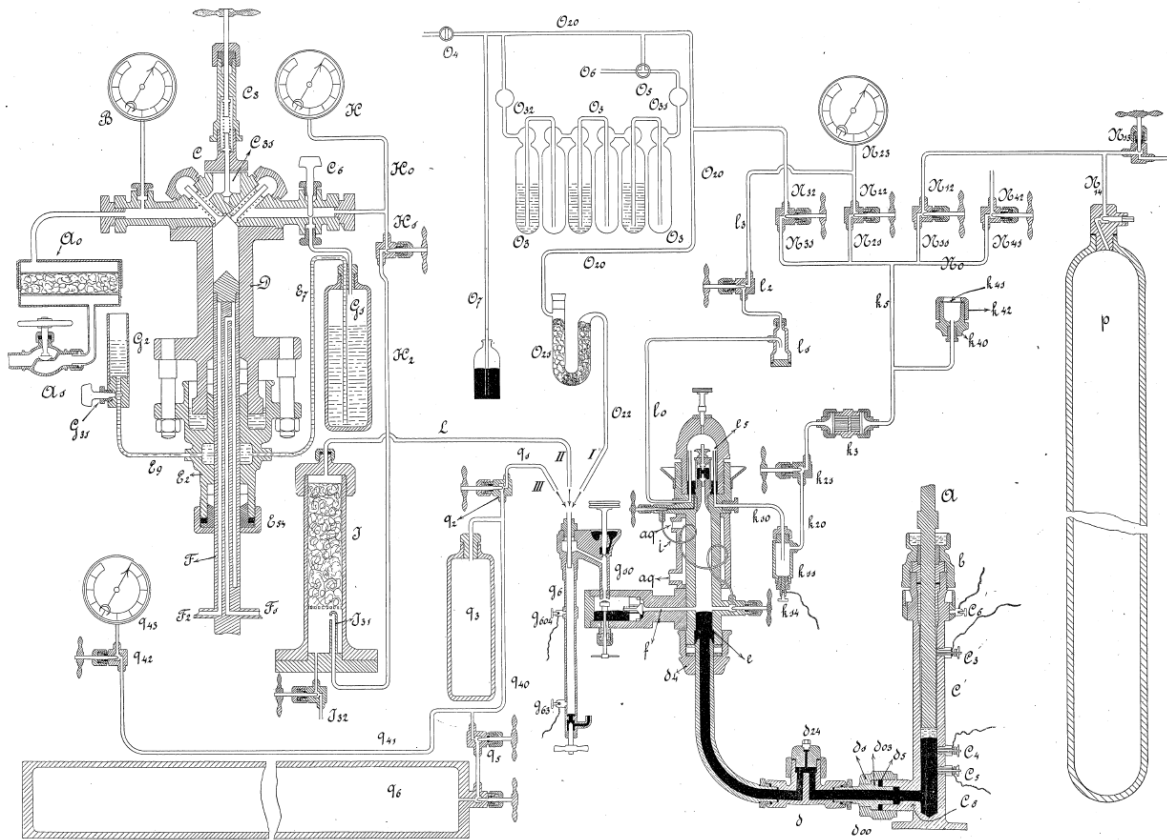


FIGURE 1. The improved Cailletet compressor system in which the original mercury piston has been replaced by a larger volume of mercury (shown black) moving up and down in a 'U' tube.

After making a detailed set of measurements on the isotherms of helium down to 56K and extrapolating to lower temperatures, Kamerlingh Onnes concluded [5] that the Boyle point for helium is ~23K (actually 23.2K) and the critical temperature is 5 – 6K (actually 5.2K). From this information, it was clear to him that helium could be liquefied by Joule Kelvin expansion with a regenerator after pre-cooling in pumped liquid hydrogen.

As with hydrogen, Kamerlingh Onnes decided to build a fully engineered liquefier, capable of continuous operation. An essential prerequisite was to obtain sufficient helium gas – about 360 litres, which he did by heating large quantities of Monazite sand, obtained from the USA via the good offices of his brother who worked in the government Office of Commercial Intelligence. He describes the laborious process of extracting and purifying the gas as '.....chiefly a matter of perseverance and care' [6]. In August 1908, the helium liquefier was ready. Helium gas, compressed to ~100 atm by the modified Cailletet compressor, was pre-cooled via a bath of pumped hydrogen boiling at 15K. Because there were not enough staff with the necessary skills to operate hydrogen and helium liquefiers simultaneously, a large quantity of hydrogen had to be liquefied and stored beforehand. After pre-cooling, the helium passed through a Hampson regenerator coil to the Joule Thompson valve. Nothing could be seen with a circulation pressure of 100 atm, but when this was reduced to 75 atm, the thermometer reading became 'remarkably constant with an indication of less than 5 degrees Kelvin'. Then the liquid surface was seen by reflection of light from below and once seen 'it remained in view like the edge of a knife against the glass wall'. Helium had been liquefied for the first time, Fig 2 shows the cold pot of the liquefier, which can still be seen at the Boerhaave Museum in Leiden.

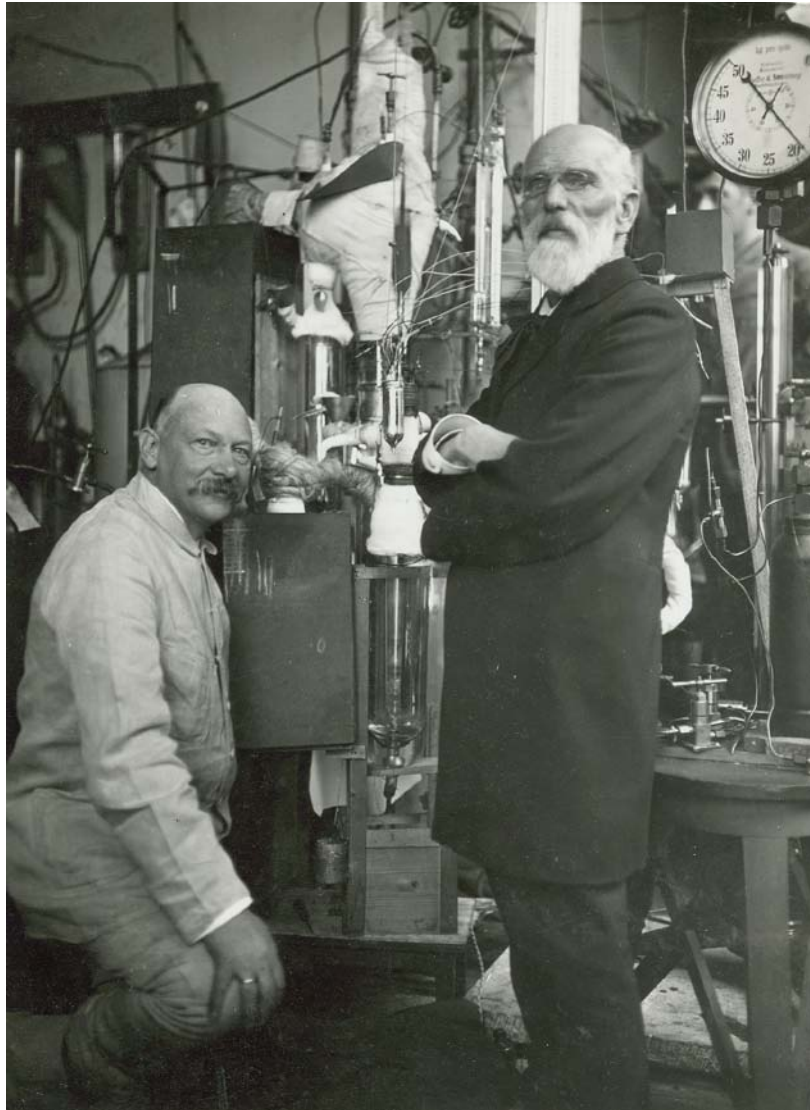


FIGURE 2. The first helium liquefier, with Kamerlingh Onnes (left) and Van der Waals. (photo Boerhaave Museum)

The resistivity of Metals

At the turn of the century, there were divergent views about how the resistivity of metals should behave as they approached absolute zero. The great Lord Kelvin believed that the electrons would be frozen in place and that the resistivity would consequently tend towards infinity, others expected it to fall to zero, and Matthiessen had predicted that it would fall to a constant value determined by the impurity level. Kamerlingh Onnes had already made measurements down to 14K in pumped liquid hydrogen and, with the advent of liquid helium, he resolved to extend them lower. His first attempt failed because of excessive boiling in the first cryostat, so characteristically he set about a complete redesign which produced the system shown in Fig 3(a), where helium from the liquefier is transferred into a cryostat in which the temperature may be regulated by pumping and is kept uniform by an ingenious stirring device.

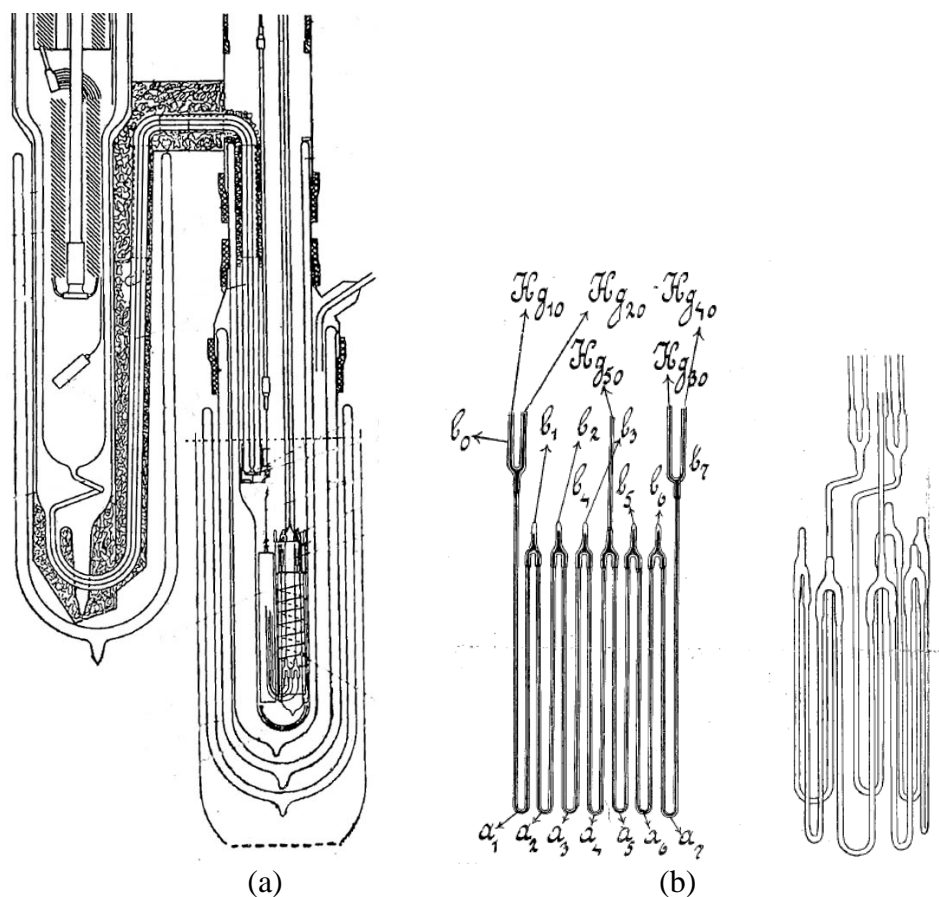


FIGURE 3. (a) Cryostat (on right) connected to the helium liquefier (on left), and (b) glass capillary tubes containing the mercury resistance sample, reproduced from [7].

The measured resistivities of gold and platinum seemed to become constant at low temperatures, as expected from Matthiessen's rule. To approach lower values, Kamerlingh Onnes needed purer materials than were readily available. At Leiden, they had good experience of purifying mercury by multiple distillation, so this was chosen, despite the added complication of needing to contain it in a glass capillary tube as shown in Fig 3(b).

On 8th April 1911, the mercury sample was cooled down to 4.2K and then the pressure was reduced to cool it further to ~3K. At 4.00 pm, Kamerlingh Onnes wrote in his notebook that the resistance was near enough zero [8]. Pumping continued to lower temperatures, after which he wrote "Just before reaching the lowest temperature (about 1.8K) the boiling suddenly stopped and was replaced by evaporation in which the liquid visibly shrank". The team had witnessed two different quantum condensations in the same afternoon! Further experiments showed that the disappearance of resistance as a function of temperature is abrupt and non linear, as shown in the plot published in December 1911, Fig 4. Two years later, in his Nobel prize lecture [9], Kamerlingh Onnes wrote "Thus the mercury at 4.2 has entered a new state which, owing to its particular electrical properties, can be called the state of superconductivity". It is interesting to note that the first 23 pages of his Nobel lecture are devoted to cryogenic technology, with superconductivity occupying only the last 7 pages – at heart he remained perhaps a true cryogenic engineer!

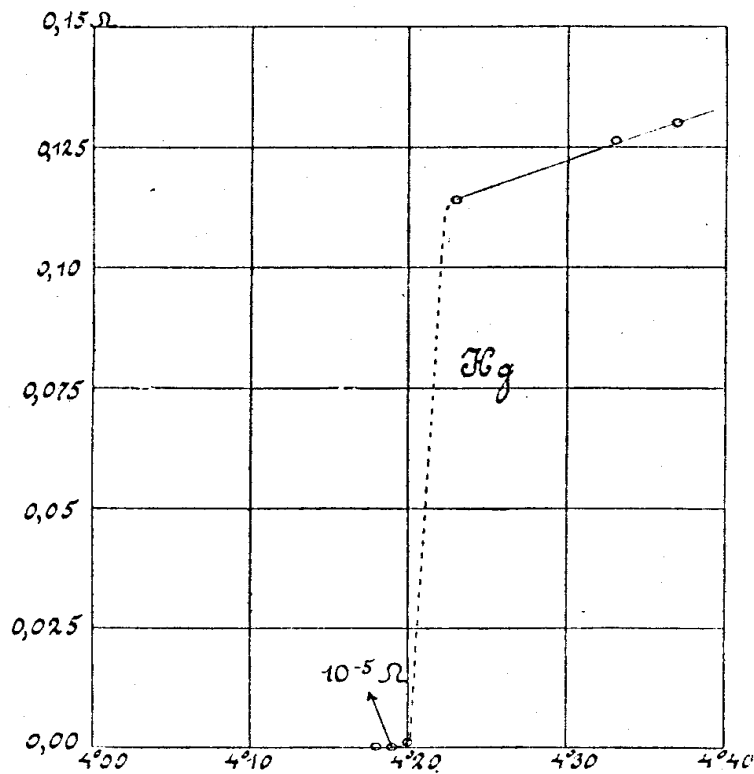


FIGURE 4. The sudden change with temperature in resistance of a mercury sample [10].

The experiments were extended to different materials, upon which lead and tin were also found to be superconducting. In addition, it was found that impure mercury, and even amalgam, behaved very much the same as high purity – so the original *raison d'être* for mercury turned out to be quite spurious! Lead wire was more convenient to work with than mercury in glass tubing, and enabled Kamerlingh Onnes to extend greatly the sensitivity of his resistance measurement by using the persistent current effect. A coil of lead wire with its terminals fused together was cooled in a field. The field was then removed, inducing a current in the coil which was monitored via its magnetic effect. From the observed decay rate of less than 1% per hour and the known inductance of the coil, it was calculated that the resistance was less than 2×10^{-11} of its room temperature value. At the suggestion of Paul Ehrenfest, who was visiting the laboratory, the experiment was repeated using a solid lead ring, with similar results. Ehrenfest wrote "It is uncanny to see the influence of these 'permanent' currents on a magnetic needle. You can feel almost tangibly how the ring of electrons in the wire turns around, around, around – slowly and almost without friction" [11]. Finally, in order to demonstrate conclusively that the magnetic field was coming from persistent currents, Kamerlingh Onnes set up another experiment with the lead coil and an ingenious arrangement whereby the closed circuit could be cut while carrying current under helium. Sure enough, the magnetic field disappeared when the wire was cut, verifying that it had indeed been caused by current flowing in the coil.

Before long Kamerlingh Onnes was speculating on the possibility of using his new discovery in technology. In a paper presented at the Third International Congress on Refrigeration at Washington and Chicago in 1913 [12] he writes "The solution of the problem of obtaining a field of 100,000 Gauss could then be obtained by a coil of say 30 cm in diameter and the cooling with a plant which could be realized in Leiden with a relatively modest financial support" – one can almost sense the research grant application

being drafted! Disappointment was quick to follow however with the discovery that superconductivity was quenched by the application of quite modest fields. In his Nobel acceptance speech, Kamerlingh Onnes writes stoically "Thus an unexpected difficulty in the production of magnetic field with coils without iron faced us. The discovery of the strange property which causes this made up for the difficulties involved". It was to be nearly half a century before his dream of superconducting magnets would become a reality.

SUPERCONDUCTIVITY IN MAGNETIC FIELDS

Flux Exclusion

Around the quarter century point, in the 1930s, there were several important findings about the interaction between superconductors and magnetic field. In Berlin, Meissner and Ochsenfeld measured the field outside two cylindrical single crystals of tin as they were cooled in a magnetic field. They found that, as the cylinders were cooled through their critical temperature, all magnetic flux was suddenly expelled as in Fig. 5 - perfect diamagnetism [13]. The effect was completely reversible, showing that superconductivity is much more than a state of zero resistance, it is an equilibrium thermodynamic state which does not depend on the history of the superconductor.

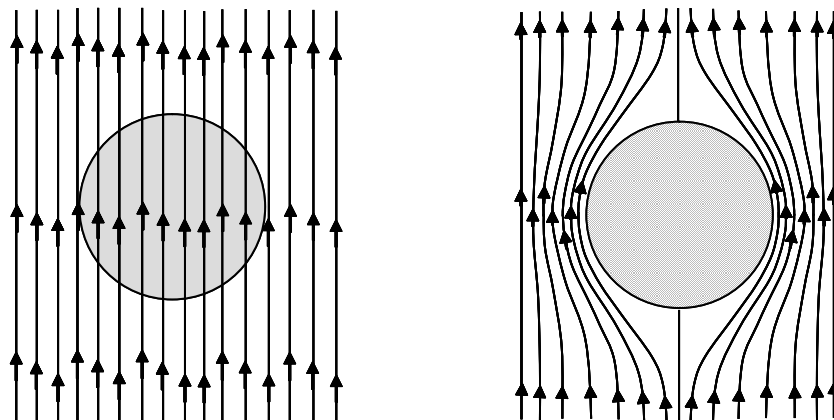


FIGURE 5. Meissner effect showing superconductor in field (a) above critical temperature and (b) below critical temperature.

Building on the Meissner effect, the brothers F and H London, while working in Oxford, realized that relationship with magnetic field is a more fundamental property of superconductivity than zero resistance [14]. The London equations describe how the electrons respond to magnet field in a cooperative way, screening the interior of the sample such that the magnetic field inside is always zero. At the surface of the superconductor, the field decays over a short distance, known as the London penetration depth, which is around $1\mu\text{m}$ and depends only on the density of the superconducting electrons. Later, F. London described superconductivity as a macroscopic quantum phenomenon and was the first to introduce the idea of a quantized fluxoid within the superconductor.

Higher Magnetic Fields

In Leiden, Keesom and de Haas found that some alloys could remain superconducting up to much higher fields, notably PbBi with a critical field at 4.2K of $\sim 1.7\text{T}$, considerably

higher than pure lead at 0.055T. Although they speculated that "If a solenoid were made of the saturated solution of bismuth in lead, we should be able to generate magnetic fields of 14,000 Gauss at the boiling point of liquid helium without development of heat and at 2K even fields of 19,000 Gauss" [15], there is no record of such a solenoid having been attempted.

Measurements on the alloys were confused by the fact that most samples comprised more than one phase so that their superconducting properties varied on a microscopic scale. Mendelssohn proposed the sponge model in which the superconductor was finely subdivided into regions of intrinsically different superconducting properties and this seemed to explain things quite well. However, L.V. Shubnikov, after working in Leiden with de Haas, went home to Kharkov, Ukraine, set up a cryogenics laboratory and started a comprehensive series of careful magnetic measurements on superconducting alloys [16]. He was careful to prepare homogeneous single crystals of the alloys and verify that there were no second phases by X-ray analysis – so no chance of sponge behaviour. What he found was that at low fields the alloys displayed Meissner diamagnetism, just like the pure metals. As the field was increased however there came a point where it entered the superconductor, without quenching superconductivity, and the sample remained superconducting up to much higher fields before finally becoming resistive. Looking at alloys of different compositions such as PbTl, he found that as the percentage of Tl was increased, the field at which flux entered the sample decreased but the field at which the sample was driven resistive increased. In fact he had identified all the features of Type 1 and Type 2 superconductivity. Type 1 materials, such as the pure metals Hg, Pb, Sn, exclude the field totally, but this process of flux exclusion raises their free energy such that, above a fairly low level of field, it becomes energetically favourable for them to switch to the resistive state and admit the field. Type 2 materials are able to admit the field while still remaining superconducting; in this way they are able to 'relieve the magnetic pressure' and remain superconducting up to much higher fields.

Sadly, Shubnikov's huge contribution went largely unrecognized at the time, although it was published in Ukraine and known about in the West. He was imprisoned in 1938 and 'disappeared'; after the war it emerged that he had been murdered by the authorities.

Understanding Superconductivity

In 1957 in USA, Bardeen, Cooper and Schrieffer published their famous paper which finally solved the mystery of superconductivity. They showed how the electrons could condense into Cooper pairs, which were attracted to each other via interaction with the lattice phonons. Although the momentum of individual electrons may be changed by scattering, the momentum of the pair remains unchanged, i.e. the scattering offers zero resistance to current flow [17].

Whereas BCS had built up their solution from quantum mechanics, Ginzburg and Landau, working in the USSR, took a macroscopic phenomenological view of the superconducting phase transition. Later, they were joined by Abrikosov who showed that, in a type 2 superconductor, it becomes energetically favourable for magnetic flux to enter the material in the form of fluxoids, each carrying one quantum unit of flux $\phi_0 = h / 2e = 2 \times 10^{-15} \text{Vs}$. The boundary between type 1 and type 2 behaviour is governed by the relative magnitudes of the London penetration depth and the coherence length, which is the shortest distance over which the superconducting wave function can change. Finally, Gor'kov showed how this theory was completely compatible with the BCS theory [18].

SUPERCONDUCTING MAGNETS

In 1954, George Yntema made the first superconducting magnet because he wanted to achieve temperatures below 1K by the adiabatic demagnetization of a paramagnetic salt. He chose to use niobium wire, having found the properties in the classic book "Superconductivity" by D Shoenberg. Fortunately he did not read the section in which Shoenberg explained how superconducting magnets were not feasible because at high fields, according to the sponge model, the regions of wire available for carrying current fell to a very small fraction of the total. Instead, he just bought some fine niobium wire, wound it around an iron 'C' core as shown in Fig 6 – and it worked! [19]. Although the magnet only made a field of 0.7T and did not create much of a stir at the time, Yntema did make one very important observation – the critical current of the niobium wire in field was greatly increased by cold working and reduced by annealing

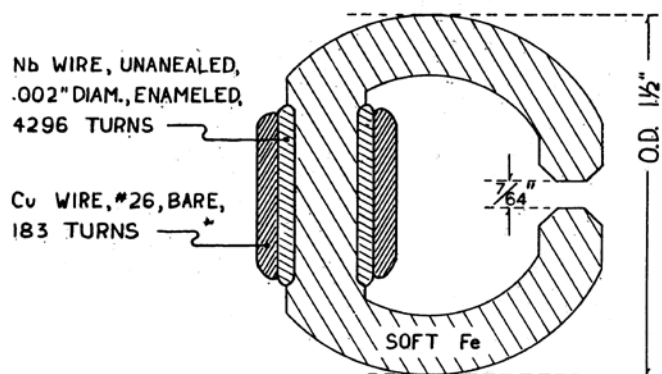


FIGURE 6. The first superconducting magnet made by G. Yntema in 1954 [19].

High Field Materials

In the late 1950's, several new materials were discovered, most of them based on niobium, which had strong type 2 characteristics and were able to carry high current densities in high fields. Much of this work was reported at the International Conference on High Magnetic Fields, held in MIT in 1961 [20], exactly 50 years after Kamerlingh Onnes's discovery. There was a real buzz at this conference, with chalkboards in the lobby to display new results as they came in and extra sessions being added on the final Saturday to accommodate further contributions. The best superconducting properties were described for Nb_3Sn , a brittle intermetallic compound discovered in 1954 by Bernd Matthias, who was probably involved in the discovery of more high field superconductors than anyone else. J. Kunzler had developed a way of making this brittle material into long lengths of wire and measurements in pulsed fields were reported at the conference showing that it could carry substantial currents up the fields of nearly 20T. Niobium zirconium had much lower performance, but it was the only ductile material reported at this time. It was already becoming clear that the current carrying capacity was strongly dependent on the microstructure and several workers published data on the effect of cold work and precipitation heat treatment on critical current density in NbZr. Niobium titanium was developed some time later by John Hulm's group at Westinghouse, and also at Atomics International. Despite having a slightly lower critical temperature than NbZr, it had better current density at high field and was easier to process in contact with copper

– a crucial factor in the later production of filamentary composite wires. NbTi has since become the standard work horse of the superconducting magnet industry with production running at several thousand tonnes per year. Fig 7 summarizes the properties of the main high field superconductors known in the 1970s.

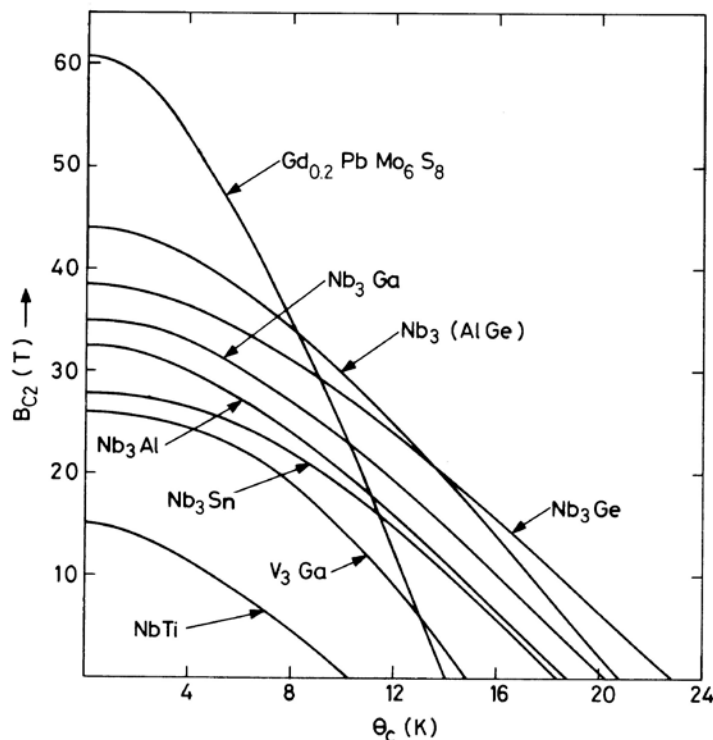


FIGURE 7. Critical properties of metallic superconductors known in the 1970s.

Understanding Current Density

Although the effect of microstructure on current density was known experimentally, it was not explained by the sponge model and a proper understanding could only be gained by reference to the earlier work of Ginzburg, Landau, Abrikosov and Gor'kov (GLAG), which was still largely unknown in the West. With the accumulation of experimental data and theoretical work, particularly by Goodman [21], it became clear that the field does penetrate type 2 superconductors in the form of quantized fluxoids and these were actually visualized by Träuble and Essmann using a magnetic decoration technique [22]. Left to their own devices in a single crystal, the fluxoids form themselves into a uniform triangular lattice. A uniform density of fluxoids obviously means a uniform average field, which implies zero current density. To get a useful current density within the volume, the fluxoids must be forced to adopt a non uniform distribution by pinning them to defects in the crystal and, as already explained at this conference [23], a whole new materials technology has grown up to optimize the pinning force and hence the critical current density.

Unfortunately, the achievement of good flux pinning does have a down side. If the flux lines interact strongly with the material then motion of flux through the material is a viscous process which dissipates energy. Thus, although type 2 superconductors have zero loss under dc conditions, when the field changes and consequently the fluxoids move, they dissipate energy – an ac loss.

Making Magnets that Work

It is a tribute to the dynamism of US industry that, while the new results were being announced at the MIT conference, one could already buy commercial supplies of NbZr superconducting wire – and many researchers did. What they found was that, although some very small magnets worked more or less as expected from the performance of the wire as measured on short samples in a magnetic field, most magnets fell far short of expectations. In addition, the magnets exhibited 'training': an effect whereby the performance of the magnet improved a bit after several attempts to energize it. Prospects for real applications still seemed to be far away.

Cures for degraded magnet performance came to be known as *stabilization* and the first was devised at the Avco Everett Laboratory in Boston by Stekly and Zar, who wanted to build a large magnet for an MHD power generator. They joined the superconducting wire to a copper conductor along its entire length and arranged for the copper to be well cooled by heat transfer to the liquid helium bath [24]. In normal operating conditions, all the current flows in the superconductor, but if any disturbance hits the superconductor and raises its temperature above critical, the current switches to the copper and generates Ohmic heat which is transferred to the helium. If the heat transfer is sufficient, the conductor cools down again, current transfers back to the superconductor and operation resumes. Stekly and Zar called the technique cryostatic stabilization and characterized the stability by a parameter α , which is the ratio between Ohmic heating and heat transfer at a given temperature; if $\alpha < 1$, the conductor is stable, if $\alpha > 1$, it is unstable. Cryostatic stabilization has worked well and made it possible to design large magnet systems in the safe and certain knowledge that they will work. In effect, one is building a cryogenic magnet, which would even work without any superconductor, but of course at the cost of an enormous cryogenic power loss. Cooling may be provided by natural convection through channels in the magnet winding or by forced flow circulation along the conductor as in the cable in conduit conductor (CICC) sketched in Fig 8. The CICC principle has been used in many large systems and will be adopted for the world's largest project, ITER, the thermonuclear fusion prototype reactor currently under construction in Cadarache, France.

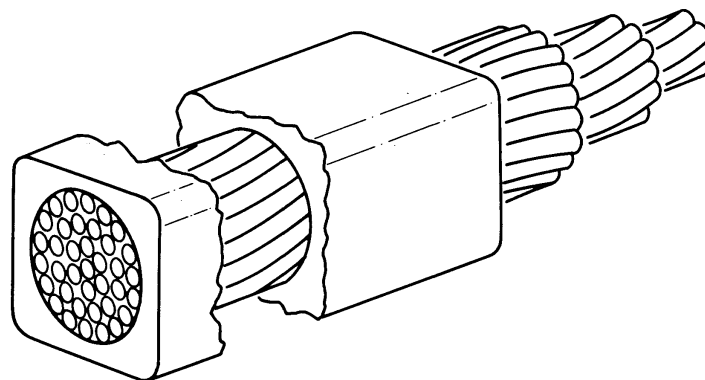


FIGURE 8. Sketch of a cable in conduit conductor CICC.

Cryostatic stabilization works well, but comes with a cost – the large volumes of copper and cooling needed, which effectively dilute the current density down to a level which would make the use of superconductivity in many applications awkward, clumsy and hopelessly uneconomic. Such applications include MRI, particle accelerators, NMR and high field magnets for research – in fact most of the present day market. To achieve reliable performance in these applications, it was necessary to eliminate the disturbances which were degrading the magnet performance. The most important of these disturbances turned out to be *flux jumping*: a phenomenon afflicting all Type 2 superconductors capable

of high current density when they are immersed in a magnetic field. Fig 9 sketches the currents and field profile inside a superconducting slab to which an increasing field is applied. The slab responds by setting up screening currents which reduce the field within the slab. Note that these are not the same as London surface currents - they flow throughout the bulk of the slab and they depend on history; if the field is reduced as in Fig 9(b), they reverse in direction to oppose the change, just like eddy currents. This picture is known as the Bean critical state model after its originator C.P. Bean.

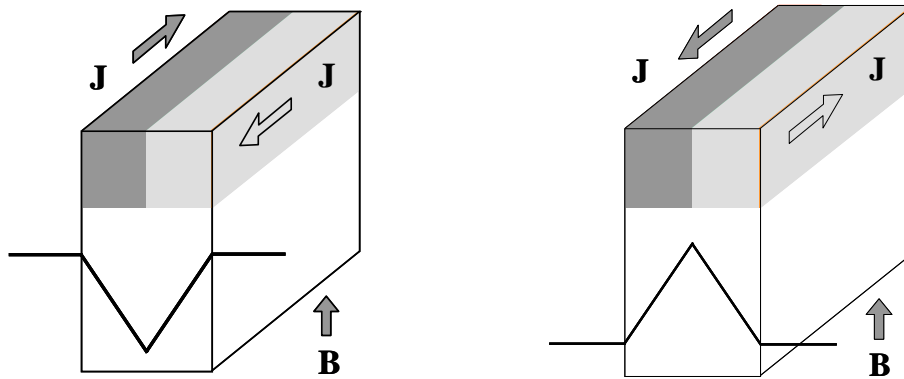


FIGURE 9. Screening currents induced by (a) rising and (b) falling field.

Flux jumping comes about because the critical current density falls with increasing temperature and because fluxoid motion dissipates heat. Fig 10(a) sketches the change in field pattern and hence the flux motion $\Delta\phi$ if the critical density of the screening currents falls by ΔJ_c . This flux motion generates heat ΔQ and raises the temperature $\Delta\theta$, which brings a reduction in screening current density and hence a further change in field pattern. Thus we have a feedback loop as sketched in Fig 10(b) and the feedback is positive, meaning instability. Microscopic fluctuations in any of the factors around the loop can trigger an avalanche which grows without limit - a flux jump - and which may quench superconductivity in the magnet. Stability can be restored by weakening any of the links around the feedback loop; the usual way is to divide the superconductor into fine filaments as sketched in Fig 10(c) and thereby reduce the flux change for a given change in current density. This condition on filament size is known as the *adiabatic stability criterion*.

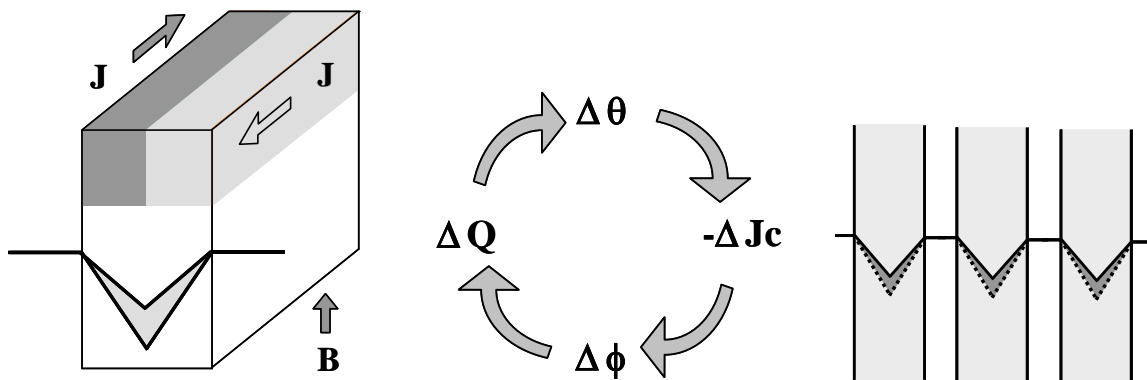


FIGURE 10(a). Flux motion caused by change in current density (b) feedback loop (c) fine subdivision.

If the superconductor is in contact with a good normal conductor such as copper, similar arguments may be made in terms of the relative speeds of magnetic and thermal diffusion to give a criterion on the maximum distance between any part of the

superconductor and the copper. This condition is known as the *dynamic stability criterion*. Filamentary composite wires are almost always made with superconducting filaments embedded in a matrix of copper. In this situation, both adiabatic and dynamic stability criteria apply. For NbTi in copper, coincidentally both criteria give the same condition: the NbTi filaments should be less than $\sim 50\mu\text{m}$ in diameter. To de-couple the filaments in changing fields, it is necessary to twist the wire like a rope [25]. Since the early 1970s, all superconducting wires have been made in this format, with filament counts ranging from ~ 50 to $\sim 50,000$.

APPLICATIONS OF SUPERCONDUCTIVITY

Big Science

This year also marks the centenary of Rutherford's first experiments on nuclear structure, and we should recognize that one of the strongest drivers for superconducting technology in the 1970s was the high energy physics community, which saw it as a way of building more powerful accelerators using less energy and without the need for more real estate. The most powerful accelerator for reaching the highest energies is the synchrotron, where the magnetic field must be ramped up in synchronism with the increasing particle beam energy. Ramping the field of a superconducting magnet produces flux motion in the superconductor which causes ac loss and could create a serious cryogenic problem. Fortunately the ac loss is reduced by fine filamentation; in fact it is simply proportional to filament diameter, so the finer the better and so wires for accelerators are made with filaments in the range 5 to $10\mu\text{m}$ – much smaller than needed for stability.

An important consideration in synchrotrons, where the particle beam must be steered around a ring magnets several km in diameter with a precision of just a few mm, is that every magnet must produce exactly the same field. Every magnet must therefore carry exactly the same current, and the best way of achieving this is to connect them all in series. On ramping, each magnet develops an inductive voltage across its terminals and these add around the series connected ring of magnets. If the magnet is wound from many turns of thin wire, the inductance will be high and so will the voltage. It turns out that, to keep the ramping voltage down to manageable level, magnet conductors must operate at many thousands of Amps, much higher than the critical current of a single wire. Synchrotron magnet conductors therefore comprise 30 – 50 wires in parallel and the wires must be fully transposed to ensure that they all carry the same current. Various configurations of twisted and woven wires were tried, but eventually the Rutherford cable shown in Fig 11 emerged as the preferred type and has been used in every superconducting synchrotron to date.

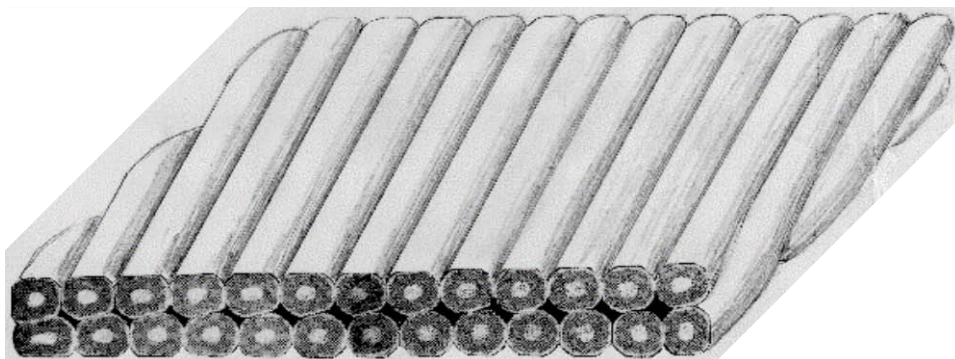


FIGURE 11. Rutherford cable for use in synchrotron magnets; each wire is fully transposed with respect to every other wire, so they all take the same current.

In the mid 1960s the group at Rutherford Laboratory began a plan to upgrade their aging synchrotron Nimrod with superconducting magnets. This work was then merged with work at Karlsruhe and Saclay laboratories to form GESSS (Group for European Superconducting Synchrotron Studies) with the objective of building the SPS at CERN as superconducting machine. Although many advances in filamentary wires, cables and magnet technology were achieved, the group failed in its objective, the SPS went ahead as a conventional machine and the focus for superconducting synchrotron development moved across the Atlantic. The 400GeV synchrotron at Fermilab became operational in 1972 and was the most powerful machine in the world but, even as it was being commissioned, there already were plans for an 'energy doubler'. After a lot of prototypes and development of some new techniques for producing superconducting magnets with the required precision on an industrial scale, the energy doubler renamed Tevatron was commissioned in 1984. Shown in Fig 12, with a peak field of 4.2T, it produced a beam energy of 950GeV and ran for many years [26].

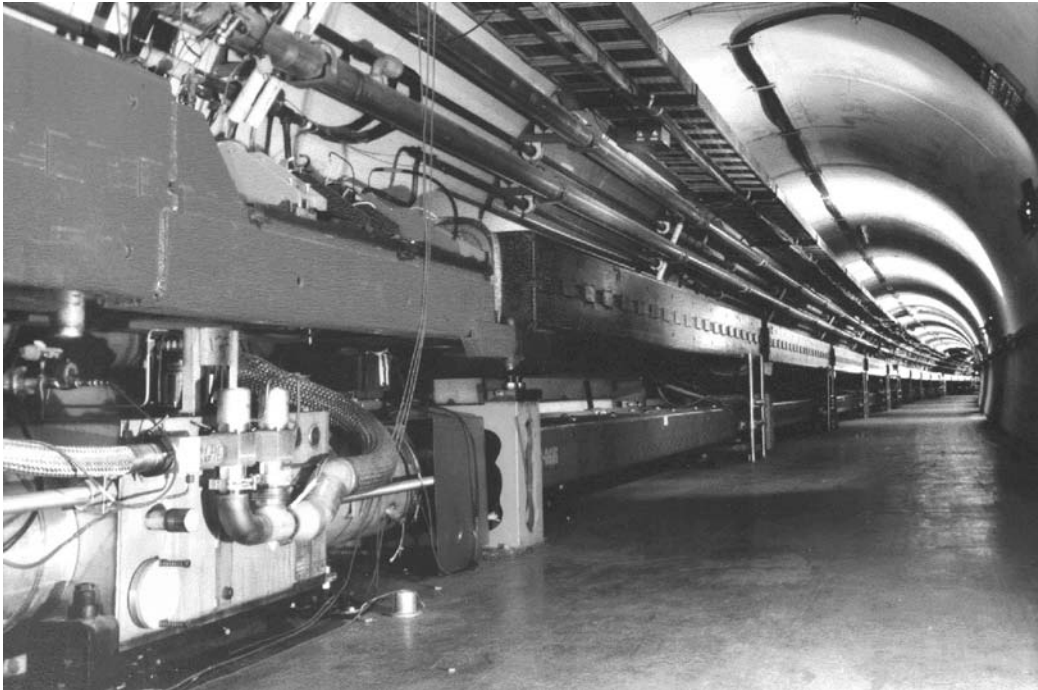


FIGURE 12. The Tevatron, showing the conventional magnet ring with the more compact superconducting ring installed underneath it (photo Fermilab).

Presently being commissioned in Geneva, the Large Hadron Collider LHC is the largest synchrotron yet and the largest cryogenic system in the world. It uses 120 tonnes of subcooled superfluid helium to cool the 27km circumference underground ring down to a working temperature of 1.8K, thereby allowing the NbTi magnets to achieve a peak field of 8.4T, producing a proton beam energy of 7TeV [27]. In fact there are two beams circulating in opposite directions and colliding in four huge underground caverns, where four very large experiments and two smaller ones are located. To accommodate the contra-rotating beams a novel design has been developed with two magnets of opposite polarity contained in the same iron yoke and the same cryostat. As well as the magnets, the rf system is also superconducting, with cavities made from pure copper with a thin niobium coating and operating at 4.5K. Fig 13 shows the LHC tunnel, some 100 metres below the surface in Geneva.



FIGURE 13. The LHC tunnel, with cutaway representation of a dipole magnet in the foreground (photo CERN).

Aimed at developing a sustainable long term solution to the world's ever growing energy needs, the international tokamak reactor experiment ITER [28], currently under construction in Cadarache, France, will surpass even the LHC in size, complexity and technological challenge. The burning plasma will be confined by a ring of 18 toroidal field coils producing a maximum field of 11.8T in an aperture 16m tall by 9m wide; each coil weighs 360 tonnes – about the same as a Boeing 747 at takeoff. As with the synchrotron, the ac losses must be controlled by dividing the Nb_3Sn superconductor into micron sized filaments – a requirement which does not sit easily with the enormous scale of the structure. It has been solved by using a massive CICC containing more than 1000 multifilamentary wires carrying a total current of 68kA in a 40mm diameter conduit, cooled by forced flow supercritical helium at 4.5K. Fig 15 shows a visualization of the final torus, together with some of those who are starting to build it.

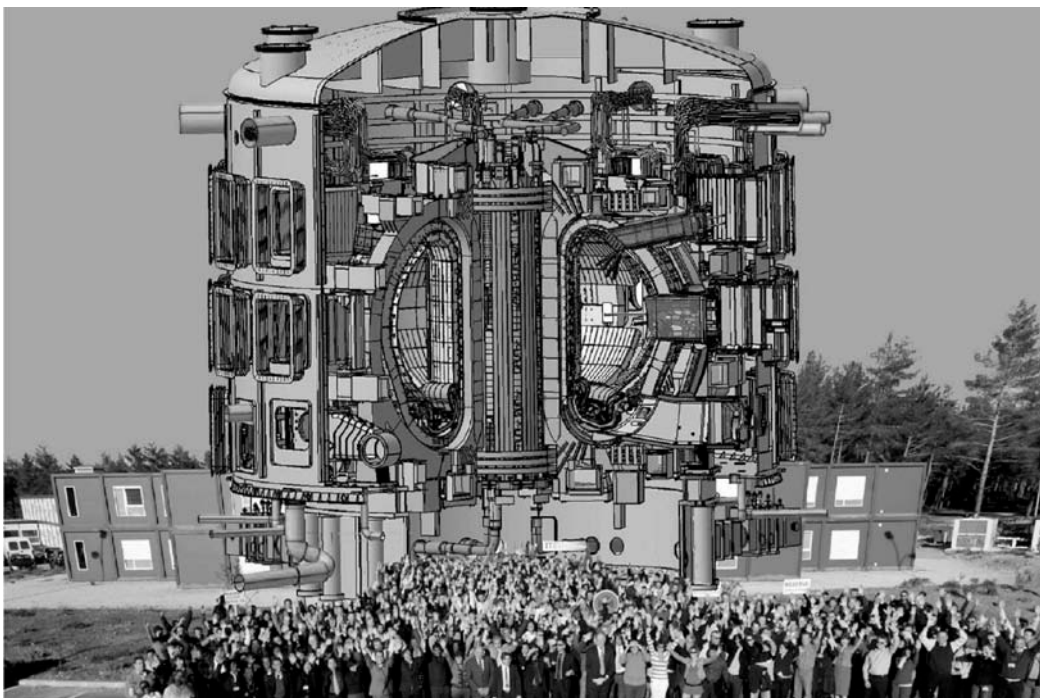


FIGURE 14. Impression of the complete ITER torus (courtesy of ITER)

A NEW INDUSTRY

Among the delegates at the 1961 MIT Conference were Martin and Audrey Wood, a husband and wife team who had recently spun off a small magnet company from Oxford University in UK. Excited by all they had heard in Boston, they made a decision en route for home that they would order one pound of NbZr wire from the Wah Chang Corporation, noting that at the time it cost more than one pound of gold [29]. Martin made a small solenoid from the wire; Fig 15 shows him testing it at the University Clarendon Laboratory and he was delighted to find that it produced 4T. Not all the early magnets were so successful, but the company grew steadily through the 1960s, making a variety of 'one-off' research magnets, whose performance reliability improved when filamentary NbTi wire became commercially available in the 1970s.

For sustained commercial growth, products are better than projects and the first product made its appearance in 1966 when the company delivered a Nuclear Magnetic Resonance NMR spectroscopy magnet. NMR spectroscopy uses the precession frequency of nuclei in a magnetic field to gain detailed information about the molecular structure surrounding the atom of that nucleus. It is a dream application for superconductivity because the sensitivity and resolution of the spectrometer increase strongly with field, and also because persistent current operation produces a temporal stability thousands of times better than the best power supply, giving an immediate advantage over conventional iron magnets on both counts. NMR spectroscopy has now established itself as a powerful routine tool for use across a wide range of research, notably chemistry and biology.

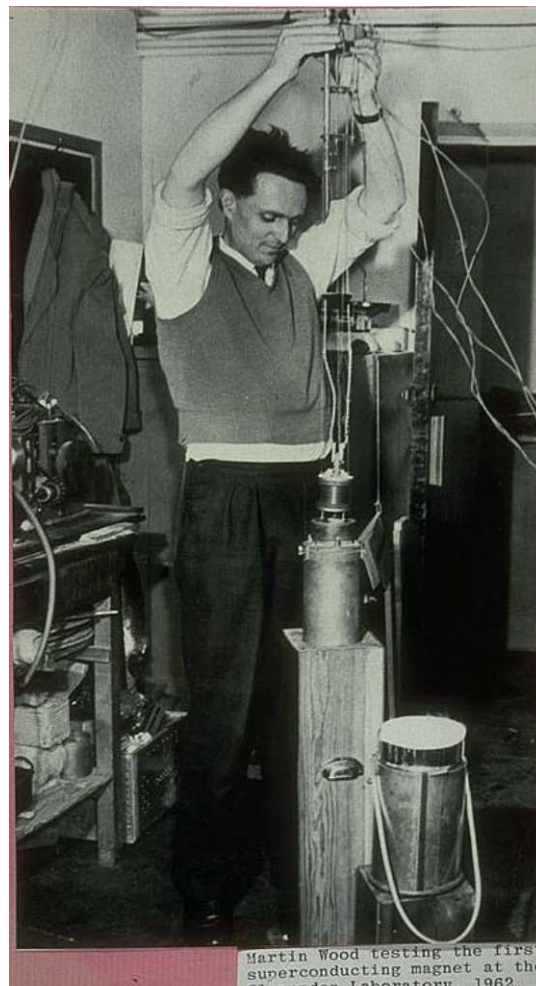


FIGURE 15. Martin Wood testing the first Oxford Instruments magnet in 1962.

NMR spectroscopy looks at the chemistry of a small sample $\sim 1 \text{ cm}^3$, it is averaged over the whole sample and contains no spatial information. By means of slight variations in the field over a sample, different volumes may be brought into resonance at different times. Making use of spin decay times and spin echo effects it is possible, by the sequential imposition of field gradients in three orthogonal directions to get enough spatial information to build up a pixel map of proton density in the sample. This is the basis of magnetic resonance imaging MRI, which has become a major diagnostic technique in clinical medicine. Although fields at the low end of the 0.5 – 3 T required can be produced by conventional electromagnets or even permanent magnets, the advantages of superconductivity in terms of low power demand, light weight, compact size etc. mean that it is used in most systems now operating. The world's first superconducting MRI system shown in Fig 16 was built by Oxford Instruments in 1979 [29]; since that first prototype, the world annual production has risen to ~ 3500 units. For most members of the public, it will be their only contact with superconductivity or cryogenics – Fig 17.

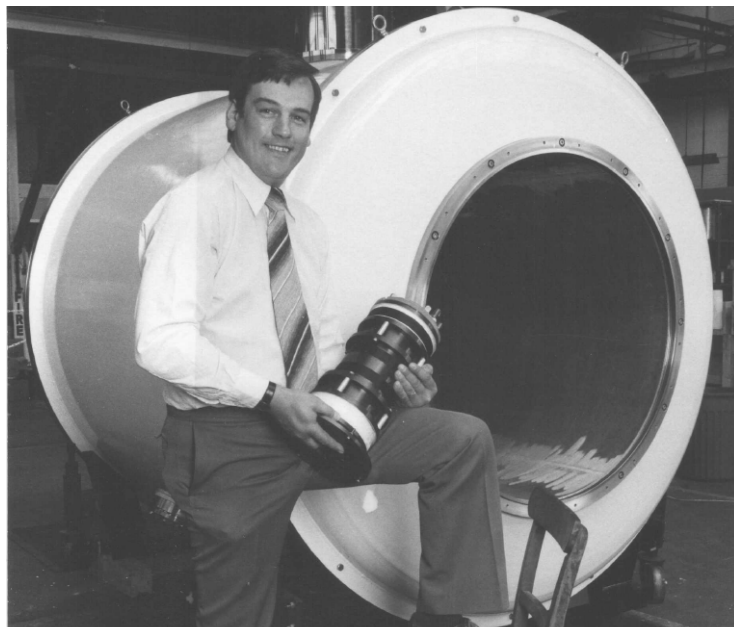


FIGURE 16. The world's first superconducting MRI magnet (photo Oxford Instruments)



FIGURE 17. A modern MRI system (photo Siemens)

Market Size

Fig 18 plots the world markets for all superconducting products using data from the Consortium of European Companies determined to Use Superconductivity, CONECTUS [30]. The overwhelming dominance of MRI may be clearly seen, followed by research and big science. There is some indication of growth in large scale industrial applications such as power engineering, and magnetic separation but, despite many fascinating developments, the market impact of superconducting electronics continues to be a rather small.

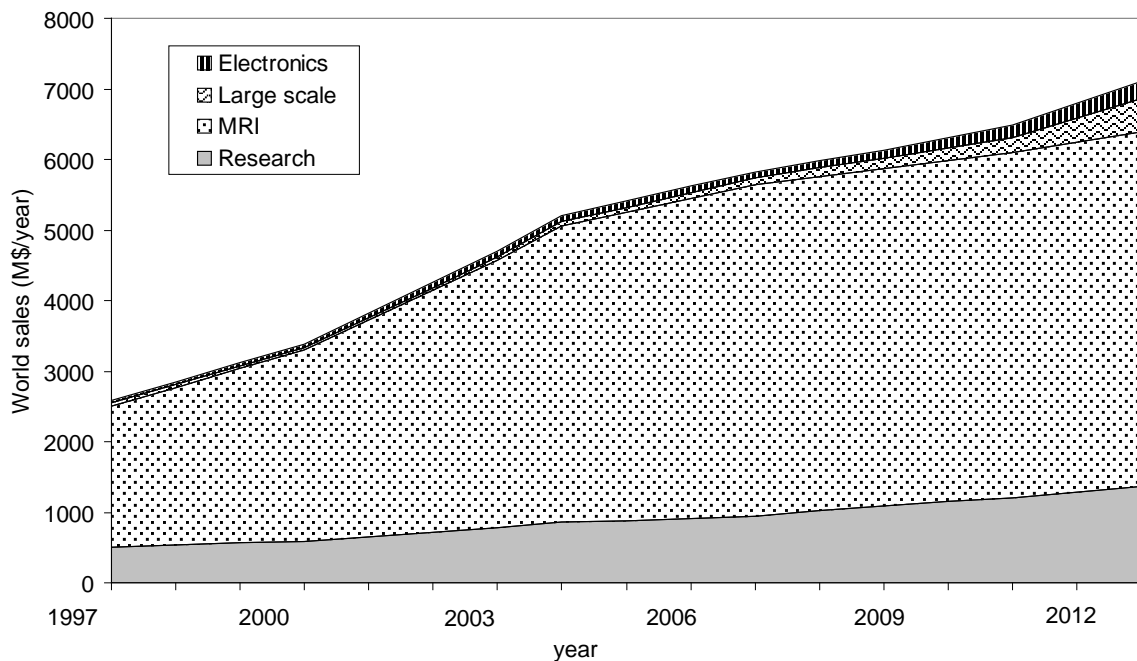


FIGURE 18. World markets for all superconducting systems (CONECTUS)

HIGH TEMPERATURE SUPERCONDUCTIVITY

In 1986, exactly at the $\frac{3}{4}$ century point, our community was galvanized by the discovery of superconductivity at much higher temperatures. Just one year on from their discovery by Bednorz and Müller, critical temperatures had topped 100K. Many of these results were reported at the legendary New York meeting of the American Physical Society in March 1987, where the session lasted until 3.15 am – the 'Woodstock of Physics'. Fig 19 illustrates this spectacular jump in critical temperatures.

Not only did the new superconductors have high critical temperatures, they also had high critical fields and the prospects for exploitation seemed very rosy. These are difficult materials to produce and handle and it took some time before wires became available, but when people tried to put current through these wires in magnetic fields it became clear that there were two fundamental problems: flux flow and grain boundary mismatch.

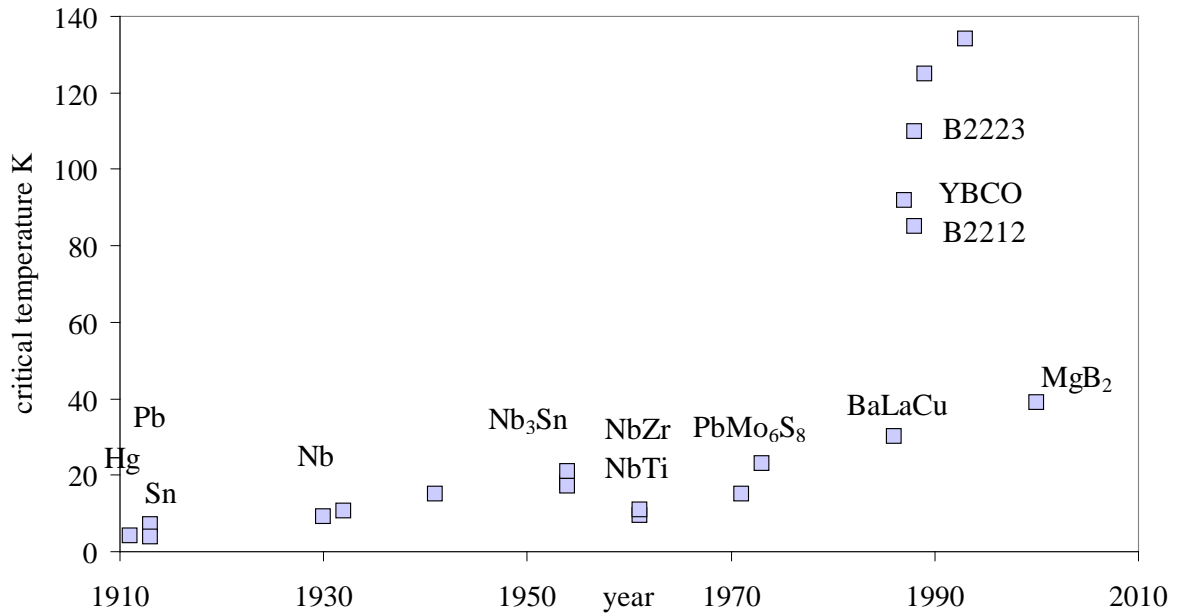


FIGURE 19. A century of critical temperatures

In the low temperature type 2 superconductors, there is a fairly sharp boundary between the fluxoids being pinned securely in the material and the total loss of superconductivity. In high temperature superconductors HTS, the boundary is more diffuse. At low temperatures and fields, the fluxoids are securely pinned and current is carried without loss. With increasing temperature or field a new region is entered where, when current (a flux gradient) is imposed, the fluxoids break free and flow across the superconductor, dissipating energy and producing a resistance. The material is still superconducting, but resistive to current flow – no use for engineering. As shown in Fig 20(a), the boundary between flux pinning and flux flow is called the irreversibility line. Fig 20(b) shows the irreversibility lines for the common HTS materials plotting actual field against reduced critical temperature. It may be seen that things start to go wrong at quite modest fields.

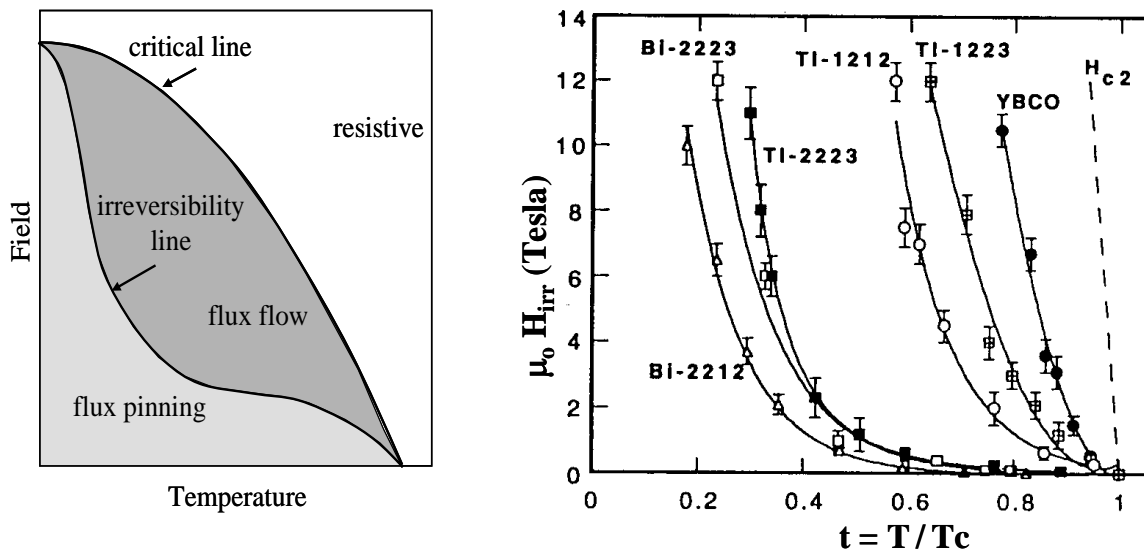


FIGURE 20. Irreversibility in fields HTS (a) boundary between flux pinning and flux flow (b) irreversibility field of common materials plotted against fraction of critical temperature [31].

Problems for current flow at grain boundaries come about because HTS materials are very directional and their coherence length is short. The definitive experiment on grain boundaries was done by Dimos et al [32] and is illustrated in Fig 22. A thin film of YBCO was deposited on an insulating substrate and, in the region of a grain boundary three bridges were etched away – one on the grain boundary and one on each of the grains. Critical currents were measured for each of the intact grains and across the boundary between them. The experiment was repeated for many bicrystals with different angles between the crystal planes on each side of the grain boundary and, as shown in Fig 21, it was found that the critical current across the grain boundary fell rapidly as the mismatch angle between the crystal planes increased.

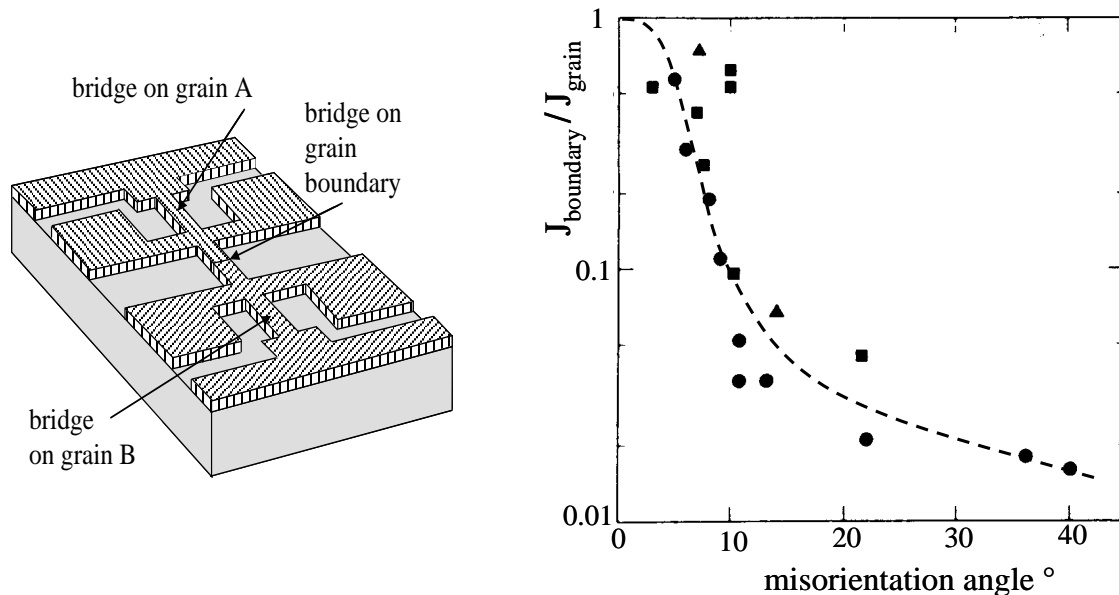


FIGURE 21. Measurement of the critical current between grains as a function of the angular mismatch between crystal planes on either side of the grain boundary [31].

The clear conclusion from Dimos's experiment is that any technologically useful conductor must have all its grains aligned to within a few degrees from one end to the other – almost a single crystal a km long! Early on it was found that $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ (B2212) and $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ (B2223) have a tendency to align naturally when they are processed in contact with silver, and the first technical wires and tapes were based on these materials. Unfortunately however, as shown in Fig 20, these materials have some of the lowest irreversibility fields. They will carry high currents in high fields at low temperatures and high currents in low fields at high temperatures, so are fine for example in power transmission cables at high temperature or high field inserts at low temperature. But to achieve the goal of currents in high fields and high temperatures needs a different material. From Fig 20, it seems that $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (YBCO) is a good candidate, but unfortunately it shows little inclination to align and must be strongly persuaded.

The task of producing a YBCO conductor with uniform grain alignment over its entire length was a formidable challenge which has occupied a decade of intense development work, but we now have a solution. The trick lies in producing a substrate with rather similar lattice parameters to YBCO which is itself aligned. YBCO deposited onto this substrate will then follow the same alignment. The aligned substrate may be produced by precision rolling of nickel or nickel alloys [33] or by ion beam assisted vacuum deposition in which the assisting ion beam is directed at a 'magic angle' to the substrate [34]. The YBCO layer is put down by vacuum deposition, by metal organic

chemical vapour deposition MOCVD [35] or by liquid phase metal organic deposition MOD [36]. Fig 22 shows one of the more successful results of this development work, the YBCO coated conductor of Superpower [37]. This tape can now be produced in km lengths, with a minimum critical current at any point in the length $> 280\text{A}$ per cm width (in self field at 77K). Some anisotropy of current carrying capacity according to the field direction remains, but this has been greatly improved over earlier tapes by doping with Zr.

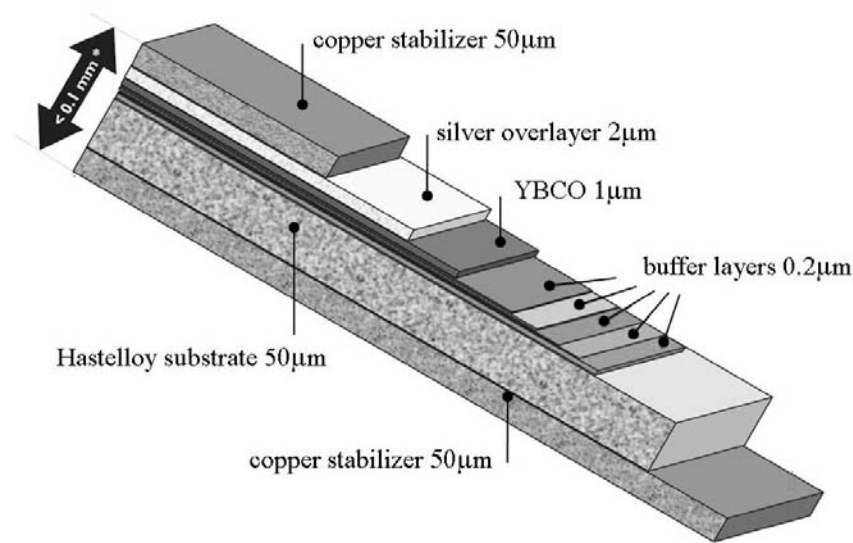


FIGURE 22. Aligned coated YBCO tape by Superpower [37]

The Future

After a quarter century of first rate work in materials science and technology, we now have HTS conductors which are able to fulfil all their earlier promise: high current in high field at high temperatures. So the \$64,000 question is: where will they find their first large commercial application? Will they displace one of the older materials from an existing application or will they open up an entirely new application?

As already shown in the CONECTUS survey, today's largest application by far is MRI – so can HTS succeed here? Operation at higher temperature would surely reduce running costs and enable the cryostat to be simplified, perhaps enabling a dry system and thereby eliminating the cost of liquid containment with its potential hazard of over pressurization. MRI is now a highly competitive business and designers are always on the lookout for every cost reduction. However, because modern cryogenics are so efficient, the cost of cryogenics in the operating budget of an MRI installation comes somewhere near the bottom of a long list. Reducing this cost will make a difference, but not a large one. Simplifying the cryostat could be a more important contribution, but only if it can be achieved without increasing the cost. Unfortunately, cost is presently the Achilles heel of HTS conductors – a problem which is only exacerbated by the remarkable cheapness of NbTi. A typical NbTi 'wire in channel' conductor for a MRI system at 2T and 4.2K costs about a dollar per kA metre. With much higher performance, Nb₃Sn wire for use in a high field 12T magnet at 4.2K can be had for ~ \$5 per kA metre. Everyday copper cable for house wiring is much more expensive at ~\$20 per kA metre, but HTS is dearer still. B2212 wire costs ~ \$100 per kA metre at 12T, but only when it is cooled to 4K. For high temperature operation, coated YBCO tape costs ~\$400 per kA metre at 77K in self field [37]. Given that superconductor is already the largest single cost component in a present day MRI magnet, it is clear that HTS needs to achieve some very substantial cost

reductions before it can break into this market. Lower costs should be achieved with MgB_2 conductor, albeit with much lower performance than YBCO, but even here the cost reduction has a long way to go.

Given the remarkable ability of modern cryogenics to minimize ambient heat leaks, perhaps HTS could compete more strongly in areas where a large part of the refrigeration load comes from dissipation at low temperature rather than heat leakage from room temperature – such as 50/60Hz power engineering. It has long been hoped that a technology which abolishes Ohm's law would find its place in power engineering and strong efforts were made in the 1970s and '80s to develop transformers, generators, motors, cables etc. using low temperature superconductors. They generally worked well, but none of them went on to commercial application, largely because of the perceived fragility of helium cryogenics and because the refrigeration power load was not much less than the saving in resistive power of the conventional machine. HTS has a clear advantage here; the ideal coefficient of performance of a 77K refrigerator is 25 times greater than a 4.2K refrigerator.

For HTS to hold on to its cryogenic advantage however, it must not incur ac losses which are too large. For large changes in field, ac loss power is proportional to the width of superconductor perpendicular to the changing field. Early LTS machines used NbTi wire with filaments of $\sim 10\mu\text{m}$ diameter, but some prototypes were made using wires with sub micron sized filaments. So for a HTS machine to incur the same refrigeration power demand, the filament size must be no more than $25\times$ greater, i.e. $\frac{1}{4}$ mm or even $25\mu\text{m}$. With a layer thickness of $\sim 1\mu\text{m}$, coated tapes are fine where the changing field can be kept parallel to the tape, e.g. power transmission cables. But in electromagnetic machines like motors, generators and transformers, there are always places where the field is broadside on to the tape. Here, it will be essential for the tape to be subdivided and, although a promising start has been made, more work is needed to produce a subdivided tape in which all the current paths are correctly transposed.

CLOSING REMARK

Looking back on the century as depicted in Fig 23, it does seem that the major milestones have come at roughly 25 year intervals - so are we now due for another milestone? For sure LHC has been a major event, but it is founded on a technology which is now approaching middle age. Which of the more recent developments will turn into a major application remains for the future to decide.

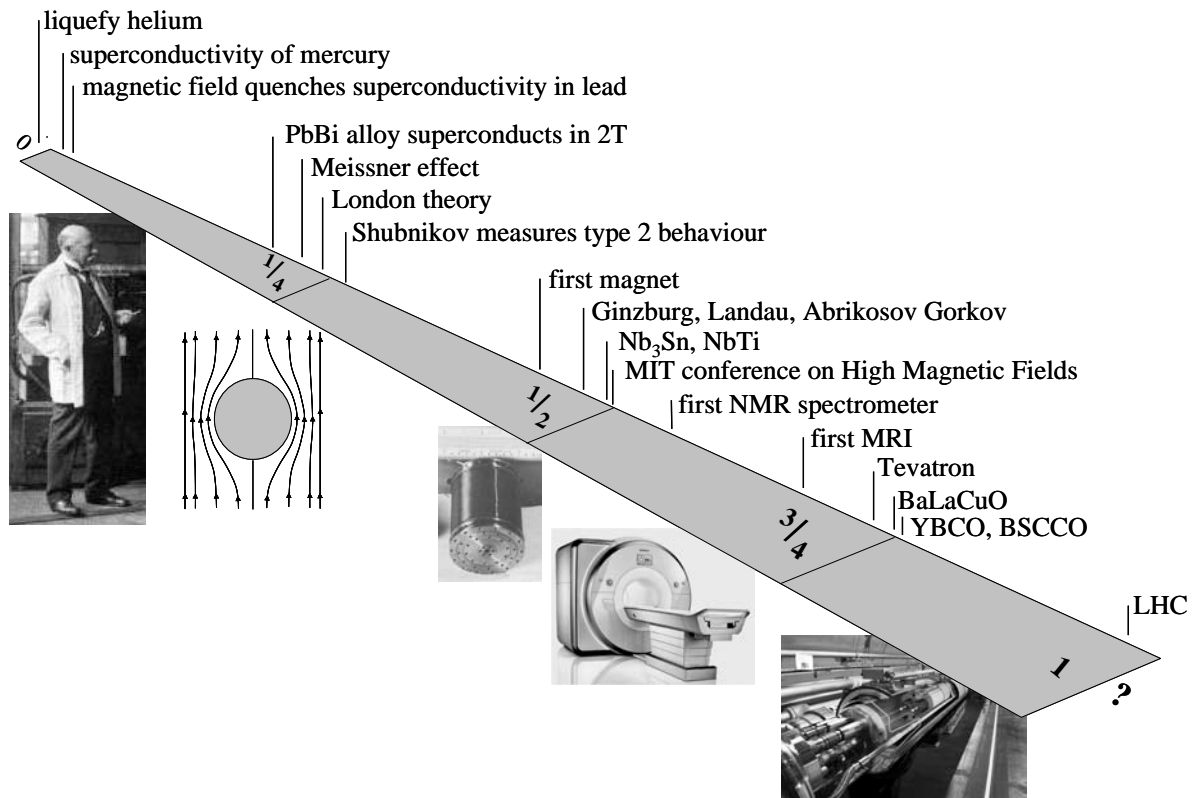


FIGURE 23. Timeline of the century.

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REFERENCES

1. Van Delft, D. "Heike Kamerlingh Onnes and the Road to Liquid Helium", in '100 Years of Superconductivity', pub Museum Boerhaave, Leiden 2011, also available at www.ewh.ieee.org/tc/csc/europe/newsforum/Contents16.html.
2. Van Delft, D. "Freezing Physics: Heike Kamerlingh Onnes and the quest for cold", pub Edita 2008, ISBN 9789069845197, also available as a free download from www.knaw.nl/Content/Internet_KNAW/publicaties/pdf/20071021.pdf
3. Kamerlingh Onnes H. Communications from the Physical Laboratory at the University of Leiden No 54 (1900) *.
4. Dewar J, Proc Royal Soc London, **63**, pp 63 (1898).
5. Kamerlingh Onnes H. Communications from the Physical Laboratory at the University of Leiden No 102a (1907) *.
6. Kamerlingh Onnes H. Communications from the Physical Laboratory at the University of Leiden No 108 (1908) *.
7. Kamerlingh Onnes H. Communications from the Physical Laboratory at the University of Leiden No 123 (1911) *.
8. Kes, P. "Kamerlingh Onnes's Notebooks and the Discovery of Superconductivity", in '100 Years of Superconductivity', pub Museum Boerhaave, Leiden 2011, also available at www.ewh.ieee.org/tc/csc/europe/newsforum/Contents16.html

9. Kamerlingh Onnes H. "Investigations into the properties of substances at low temperatures which have led, amongst other things, to the preparation of liquid helium. Nobel Lecture, 11th Dec 1913, available for download at http://nobelprize.org/nobel_prizes/physics/laureates/1913/
10. Kamerlingh Onnes H. "On the sudden rate at which the resistance of mercury disappears" Communications from the Physical Laboratory at the University of Leiden No 124g (1911) *.
11. de Bruyn Ouboter, R. "Superconductivity: discoveries during the early years of low temperature research at Leiden". IEEE Trans Magnetics MAGNET-23, pp355 (1987).
12. Kamerlingh Onnes H. "Report on researches at the Leiden cryogenic laboratory between the second and third International Congress of Refrigeration". Communications from the Physical Laboratory at the University of Leiden Suppl 34 (1913).
13. Dahl, P. " Superconductivity: Its Historical Roots and Development from Mercury to the Ceramic Oxides" pub American Institute of Physics, ISBN 13: 9780883188484 (1997)
14. London, F. "Superfluids Vol 1, Macroscopic Theory of Superconductivity" , Dover Publications, New York 1960
15. Keesom, W.H. and de Haas, W.J. "The influence of magnetic field on supraconductors". Communications from the Physical Laboratory at the University of Leiden No 208b (1930).
16. Shepelev, A.G. "The Discovery of Type 2 Superconductors (Shubnikov Phase)" Chapter 2 in "Superconductor" ed A.M Luiz, pub Intech, ISBN 978-953-307-107-7, also available for free download at <http://www.intechopen.com/books/show/title/superconductor>
17. Blundell, S. "Superconductivity, a very short introduction", pub Oxford (2009) ISBN 978-0-19-954090-7.
18. Waldram, J.R. "Superconductivity of metals and cuprates", Institute of Physics Publishing (2009) ISBN 0-85274-337-8.
19. Yntema, G. "Niobium superconducting magnets", IEEE Trans MAG-23, No 2 pp390, (1987)
20. Kolm, H, Lax, B. Bitter, F. & Mills, R. "High Magnetic Fields", pub MIT Press and Wiley (1962)
21. Goodman, B.B. "Type 2 Superconductors", Rep Prog Phys **39** part 2 pp445 (1966).
22. Essman, U. and Träuble, H. "The direct observation of individual flux lines in type 2 superconductors". Phys Lett **24A**, pp526 (1967).
23. Freyhardt, H.C. "How superconductors became practical: a walk through the history and science of flux pinning". paper PL2A-03 at this conference.
24. Stekly, Z.J.J. & Zar, J.L. "Stable superconducting coils", IEEE Trans Nucl Science NS-12 (1965).
25. Smith P.F. Wilson M.N. Walters, C.R. Lewin J.D. "Experiment and theoretical studies of filamentary superconducting composites", British Jnl Physics D **3**, pp1517 (1970).
26. Edwards, H.T. "The Tevatron energy doubler" Ann. Rev. Nucl. Part Sci **35**, pp605 (1985).
27. Evans, L. and Bryant, P. "LHC Machine" JINST **3** SO8001 (2008) available for free download at <http://iopscience.iop.org/1748-0221>
28. Aymar, R. et al "Overview of ITER-FEAT: the future international burning plasma experiment" Nucl. Fusion **41**, pp1301. See also www.iter.org.
29. Wood, A. "Magnetic venture: the story of Oxford Instruments", pub Oxford University Press, ISBN 0-19-924108-2 (2001)
30. Consortium of European Companies determined to Use Superconductivity at www.conectus.org.
31. Johnson, J. D. et al: Research Review 1994, Cambridge University IRC in Superconductivity pp167.
32. Dimos, D. et al "Orientation dependence of grain boundary critical currents in YBa₂Cu₃O_{7-δ} bicrystals". Phys. Rev. Lett. **61**, pp219 (1988)
33. Goyal, A. et al "High critical current density superconducting tapes by epitaxial deposition of YBCO thick films on biaxially textured metals", Appl. Phys. Lett. **69**, (12) pp1795 (1996)
34. Iijima, Y. et al " In-plane aligned YBa₂Cu₃O_{7-x} thin films deposited on polycrystalline metallic substrates", **60** pp769 (1992).
35. Selvamanickam, V. et al " High-current Y-Ba-Cu-O coated conductor using metal organic chemical-vapor deposition and ion-beam-assisted deposition" IEEE Trans App Superconductivity, **11** (1) pp 3379 (2001).
36. Araki, T. Hirabayashi, I. "Review of a chemical approach to YBa₂Cu₃O_{7-x} coated superconductors - metal organic deposition using trifluoroacetates". Superconductor Sci. Tech. **16** R71 (2003)
37. Selvamanickam, V. et al "Progress in Research and Development of IBAD-MOCVD Based Superconducting Wires" at 2010 Applied Superconductivity Conference, to be published in IEEE Trans App Superconductivity, **21** (3) (2011).

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