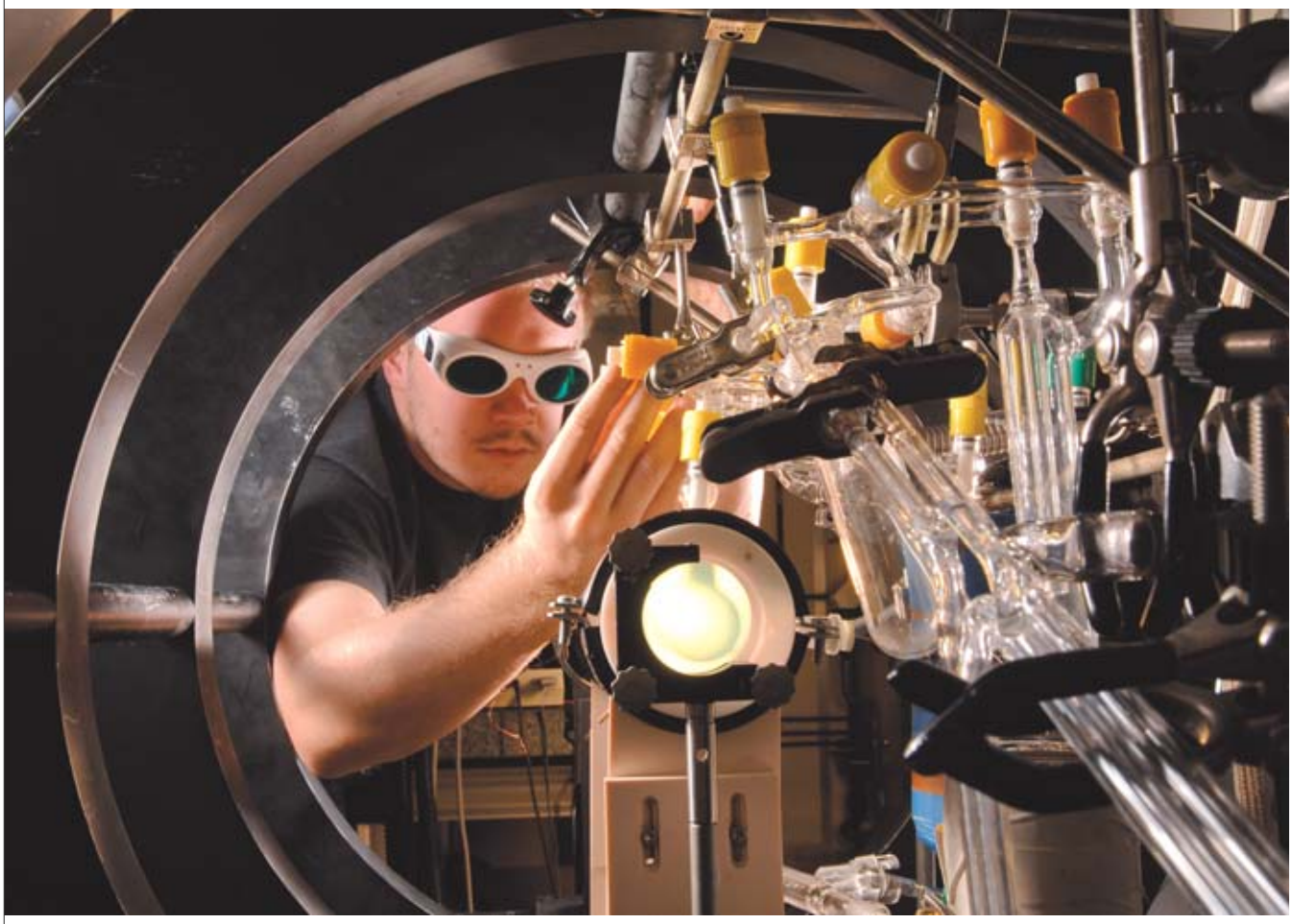
NMR, an **ever-advancing** spectroscopic technique

The CEA, spearheaded by the Saclay centre, has fostered the development of a strong nuclear magnetic resonance research culture aimed at constantly embracing new fields of application for this matter-focused analytical technique.



P. Stroppa/CEA

Building the CEA Saclay centre's optical pumping facility designed to polarise xenon-129. This technique can dramatically increase the sensitivity of NMR, by several orders of magnitude.

Nuclear magnetic resonance, or **NMR**, is a matter-focused analytical technique first developed over 60 years ago. Back in the early days of the CEA's Saclay centre (in the Essonne), Anatole Abragam was already making significant theoretical headway as a pioneer of this **spectroscopic** technique. Since then, the scope of application for NMR has continually expanded, and now embraces a huge range of diverse fields, from condensed matter physics right through to medical diagnostics and its flagship application: **magnetic resonance imaging** (**MRI**) (Focus C, ***The main methods of medical imaging***, p. 36).

The continuing history of NMR at the CEA is inextricably linked to these developments(1). Standout examples in the life sciences would include liquid-phase **protein** structure determination and the methods developed to gain insight into internal protein dynamics (see *NMR for protein analysis*, p. 52) or the medical applications championed under the **NeuroSpin** programme (see *Using imaging to understand the brain*, p. 38), plus the magnetic sensors for explosives detection in the field of security applications, and the nuclear science-driven studies on waste confinement matrices(2). Saclay is continuing to foster its now-traditional NMR-centred development culture aimed at constantly embracing new fields for NMR applications. In particular, one of the CEA's main research drives is to increase the NMR signal.

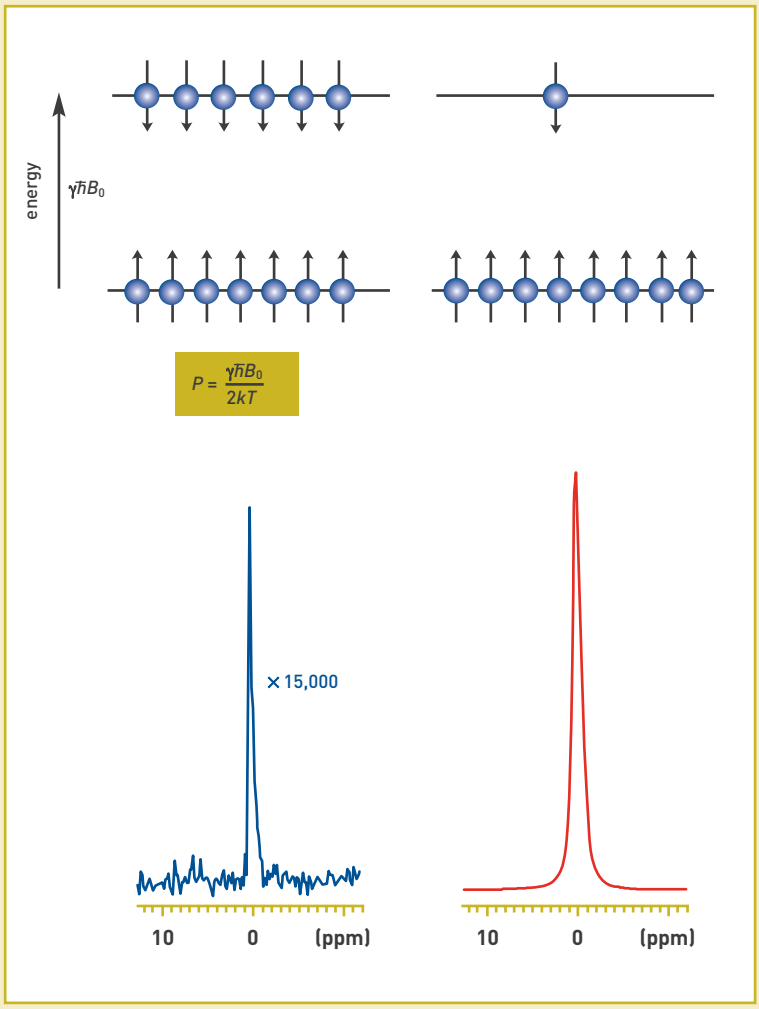
(1) See issue No. 1 of *Clefs CEA* (1986).

(2) Confinement matrix (for nuclear waste): a material like bitumen, cement or glass, that enfolds and helps confine **radionuclides**. When glass is used, the nuclides form an integral part of the matrix.

Nuclear polarisation

When half-integer **spin nuclei** are plunged into a **magnetic field**, their **magnetic moments** align either parallel or antiparallel to the field, thus creating two levels of energy. Given the weak energy involved, in thermodynamic equilibrium conditions the distribution of populations in these two states obeys a Boltzmann law (diagram at left). The nuclear **polarisation** P, which is a dimensionless quantity representing the relative between-population difference between the two states, is proportional to the amplitude of the static magnetic field B_0 and inversely proportional to the absolute temperature T of the sample. k is the Boltzmann constant ($k \approx 1.38 \cdot 10^{-23}$ J/K), which can be interpreted as the constant of proportionality linking the temperature of a system to its thermal energy, while $\hbar$, the Planck constant, corresponds to the quantum of energy ($\hbar \approx 1.05 \cdot 10^{-34}$ J·s) and γ is the gyromagnetic ratio of the nucleus, i.e. its sensitivity to the magnetic field. It represents the coefficient of proportionality between its spin angular momentum and its nuclear magnetic moment. Thus, the polarisation in currently-available **superconducting magnets** is, at around 10^{-5}, generally extremely weak.

When the polarisation of system with strong population differentials can be efficiently transferred towards nuclear magnetic moments, the species is defined as being "hyperpolarised" (diagram at right). One method of hyperpolarisation is called **optical pumping**. **Rare gases** can be optically pumped to dramatically increase signal strength, as illustrated in side-by-side spectra from the same ^{129}Xe sample (at left, heated ^{129}Xe spectrum obtained through 15 hours compiled, and at right, hyperpolarised ^{129}Xe after a 1 second acquisition time).

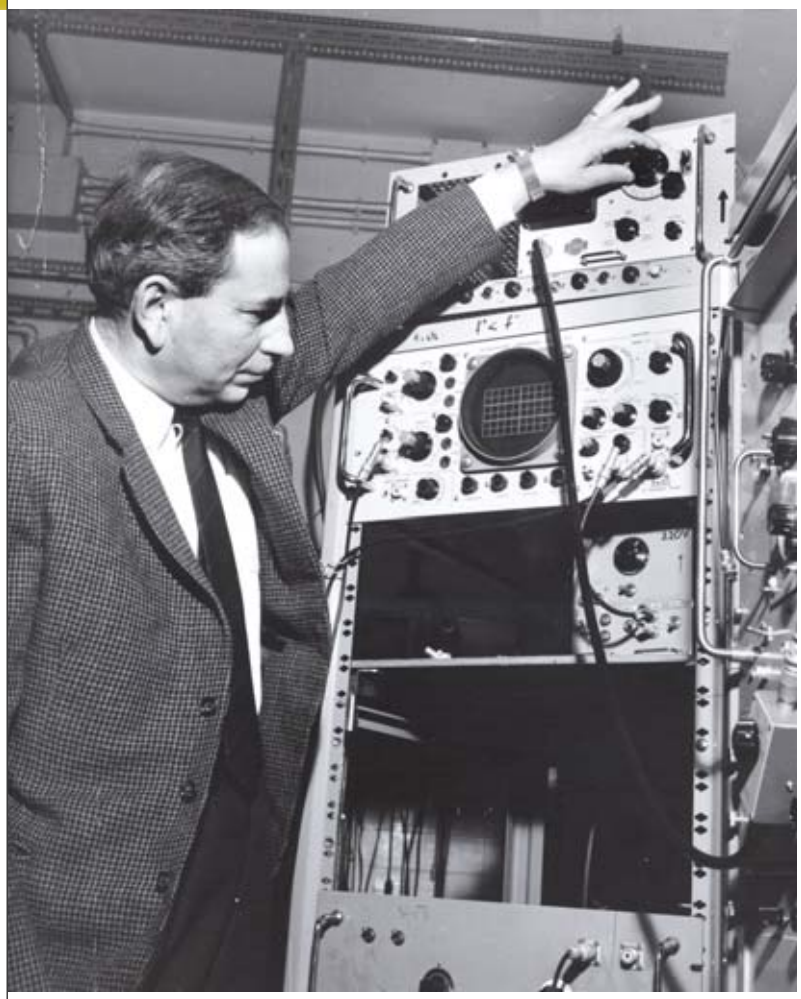


This work hinges on two core research thrusts: to increase nuclear spin **polarisation**, and to improve detection sensitivity.

How to gain in sensitivity?

Certain types of **atomic nuclei** share a unique feature: an intrinsic **magnetic moment**, whose properties obey the laws of **quantum** mechanics. Their projection along a **magnetic field** cannot vary continuously, but only take on a few well-known values. In fact, NMR analysis focuses on a macroscopic sample, therefore working at a fundamental scale of the overall nuclear **magnetisation**, which is the sum of the contributions from each of these microscopic 'compasses'. The greatest strength of this spectroscopic technique stems from the very weak energy levels employed. Indeed, to excite these nuclear magnetic moments only needs waves roughly the same as those used in the FM radio band (or in mobile phones for the strongest magnetic fields). NMR is therefore a unique method for probing the very heart of physical matter, which it does non-invasively: the disturbances are minimal, as typically 10,000 times weaker than **thermal agitation**. However, the flip-side of the extremely low energy employed is that even in the strongest magnetic fields, it still requires around 100,000 nuclei before there is a difference in population states able to give rise to a signal. This is the root of the main weakness in NMR: its low sensitivity (see Box).

So-called "brute force" methods, based on increasing the static magnetic field and/or decreasing temperature, were developed in an attempt to increase nuclear spin polarisation, but they quickly reached their limits. A while back, the scientific community realised that it was possible to create far more polarised nuclear systems that by brute force methods. These approaches consist in transferring the polarisation of systems like **electrons** or **photons** prepared in a more strongly ordered state towards nuclear magnetic moments. Saclay has been following in this tradition for a number of years, through research led by Anatole Abragam and Maurice Goldman on nuclear magnetic order. It is also under this same research thrust that an **optical pumping** experiment was set up at Saclay ten years ago, with the aim of transferring the angular momentum of a light beam towards the nuclear magnetic moments of the **rare gas** xenon. Within minutes, the nuclear polarisation is multiplied by several orders of magnitude compared to thermodynamic equilibrium condi-



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Anatole Abragam and Maurice Goldman pioneered NMR research at the CEA with their work on nuclear magnetic ordering. The photo features Anatole Abragam.

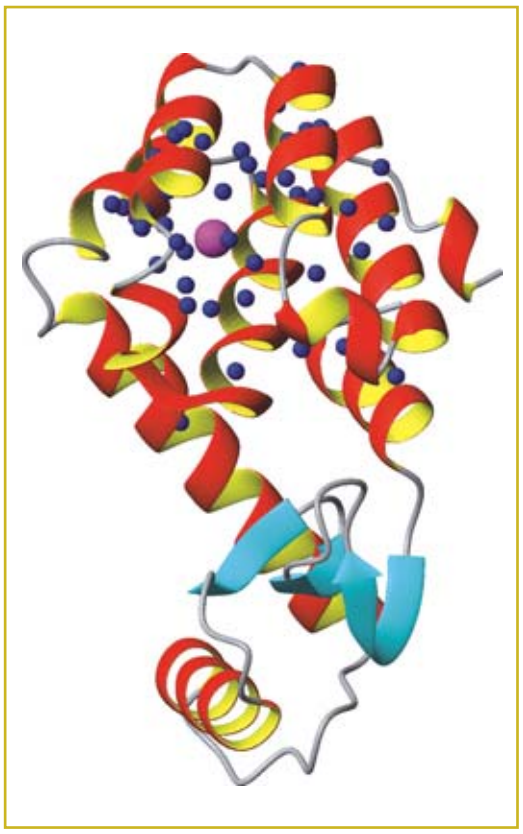

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Figure 1.
Example of a protein whose hydrophobic cavity could be probed (blue spheres corresponding to NMR-detected atomic nuclei of hydrogen) due to the fact that xenon (violet-coloured sphere) tends to localise there.

tions. When the rare gas used only has two levels of magnetic moment energy, this 'hyperpolarisation' can only be maintained for a few hours. Hyperpolarised rare gases (^{3}**He**, ^{129}Xe) can find many applications, mainly in imaging.

Hyperpolarisation is also the focus of physics research, since in contrast to the environments conventionally studied, systems that are highly concentrated and strongly polarised are no longer governed simply by the laws of classical NMR, as nonlinear phenomena start to manifest. In more specific terms, a distant **dipolar** field produced by the strong magnetisation influences the spectra of each nucleus in several different ways: changes in **resonance** frequencies and line shapes, and even the appearance of **chaotic** maser(3) phenomena, which give an intense signal without having to excite the nuclear magnetic moments, i.e. without having to perturb the state populations via a **radiofrequency** pulse. These phenomena, which increase with increasing magnetic fields and detection sensitivity, are being studied through a research project backed by the French National Research Agency, the **ANR**, under its 'white programme'. This project should lead to two outcomes. On one hand, it should provide deeper insight into the ability of these systems to adopt chaotic behaviour patterns due to nonlinear phenomena, whereas if NMR has developed it is wholly due to the linearity of the magnetisation response to excitation and to resonant frequencies being linearly proportional to the magnetisation. On the other hand, the research conducted should provide an environment conducive to developing new modes of magnetisation transfer stretching the gain in sensitivity to all the nucleus types used.

(3) Maser (Molecular Amplification by Stimulated Emission of Radiation): a device that produces coherent **electromagnetic waves** through stimulated emission. The twin of laser for low-energies.

NMR as a local probe

As well as being laser-polarisable, xenon has another important advantage for use in NMR. Its electron cloud is highly sensitive to its immediate environment, lending it remarkable properties as a local probe. These properties yield a spectral signature that is highly varied, i.e. that covers a very wide range of spectral frequencies. This can be exploited in studies on porous materials, where the chemical shift of confined xenon can be related to pore size. It is also possible to combine the fact that xenon tends to localise to hydrophobic zones with the sensitivity gain obtained through a preliminary optical pumping step, and thereby use the dissolved rare gas as a probe for liquid-phase biological **molecules**, especially the hydrophobic cavities of proteins (Figure 1). This novel approach, engineered at the CEA, has been twinned with a method based on **single-crystal X-ray diffraction**. The NMR-based method, although more difficult to deploy, ultimately offers a more multi-faceted vision, as it combines the structural aspect with dynamic and thermodynamic information on the interaction between xenon and protein.

Finally, the properties of xenon can be used to engineer novel MRI biosensors. This research thrust aims to develop a molecular imaging system for early disease detection, and is backed by the ANR though a *biological physicochemistry* project (a partnership between the CEA's Physical sciences and Life sciences Divisions). The idea is to carry polarised xenon to certain biological receptors using host molecules with exceptionally high affinity for xenon. *Cryptophanes* have emerged as excellent candidates for the role. These cage compounds are chemically modified to render them soluble in biological media and then functionalised to incorporate biological target recognition 'antennae'. This strategy brings a number of advantages. Over and above the enhanced sensitivity of a noiseless imaging system that is also highly specific since it has frequency selectivity guaranteeing that only the encapsulated xenon will be imaged, the strategy also boasts another advantage in that polarised xenon can be reintroduced long after the cage has been injected. Furthermore, the exchange occurring between the inside and outside of the cage can be exploited to further increase detection sensitivity via frequency-selective pulsing techniques, as the cage is regularly reloaded with hyperpolarised xenon. The biosensor concept has been validated *in vitro* on a system engineered with a cryptophane and a **DNA** strand capable of recognizing **micromolar** concentrations of a complementary DNA strand in solution (Figure 2). Research designed to extend this approach is currently underway. One aim is to develop a range of cages triggering different chemical shifts of the encapsulated xenon, which would pave the way to *multiplexed MRI*, while another is to employ the approach for small-animal *in vivo* imaging (working with NeuroSpin).

Improving the signal strength of overall nuclear magnetisation

The second research thrust – to increase the sensitivity of NMR – consists in designing and improving systems for detecting overall nuclear magnetisation. The CEA proposed to develop ultra-sensitive, magnetic force-driven **cantilevers** for surface analysis, and is currently exploring the idea. There is also a thriving research drive into optical detection of magnetic resonance, such as based on observing the nuclear magnetisation-induced rotation of laser polarisation. Lastly, it is possible to increase signal strength with the conventional method, which consists in measuring the induction induced by **precession** of the overall nuclear magnetisation in a **coil** whose axis is perpendicular to the direction of the static magnetic field, by adapting the coil size to the sample size. This is because signal-to-noise ratio per mass unit of coil is inversely proportional to coil volume. In the last few years, this approach has been employed to analyse fluid samples of just a few nanolitres

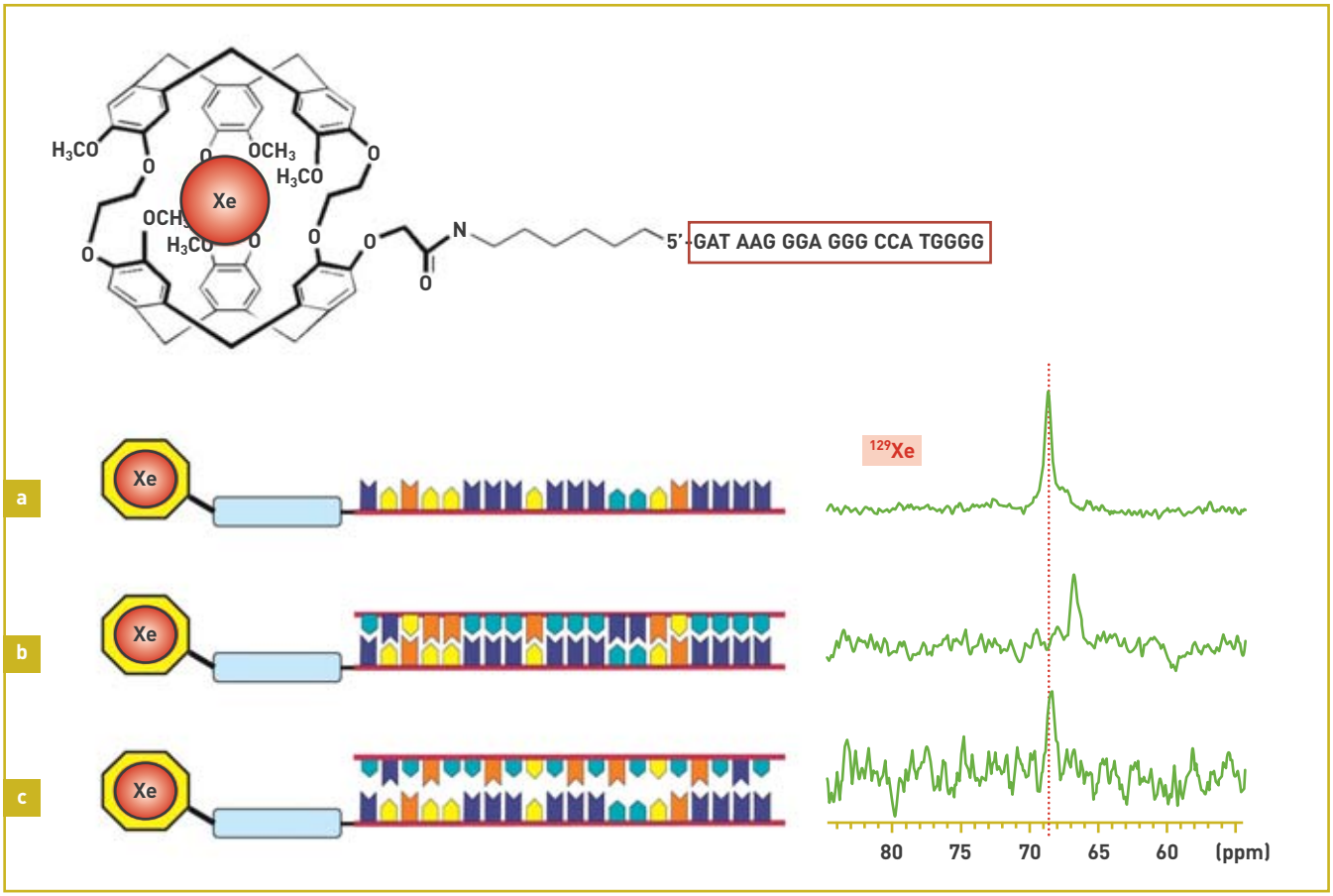


Figure 2.
The biosensor concept has been validated *in vitro* on a system engineered with a cryptophane encapsulating polarised xenon and a DNA strand (shown in a) and capable of recognizing the presence (shown in b) or absence (shown in c) of a complementary DNA strand in solution, concentrations way below those conventionally used in NMR. The change in the spectral signature of xenon gives a strong indication of the molecular recognition ability of this kind of system.

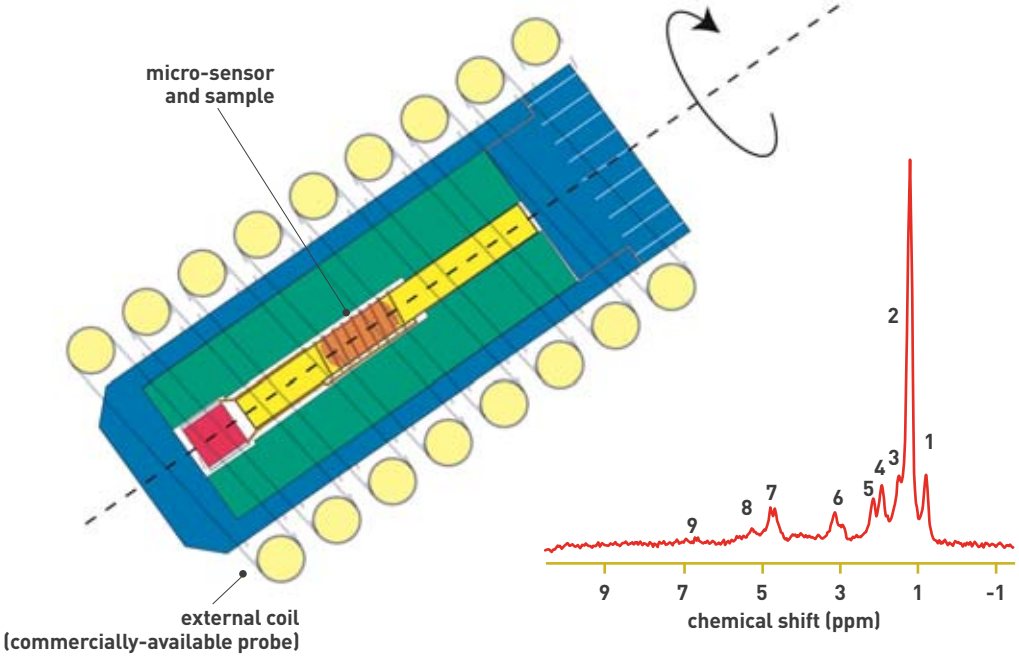
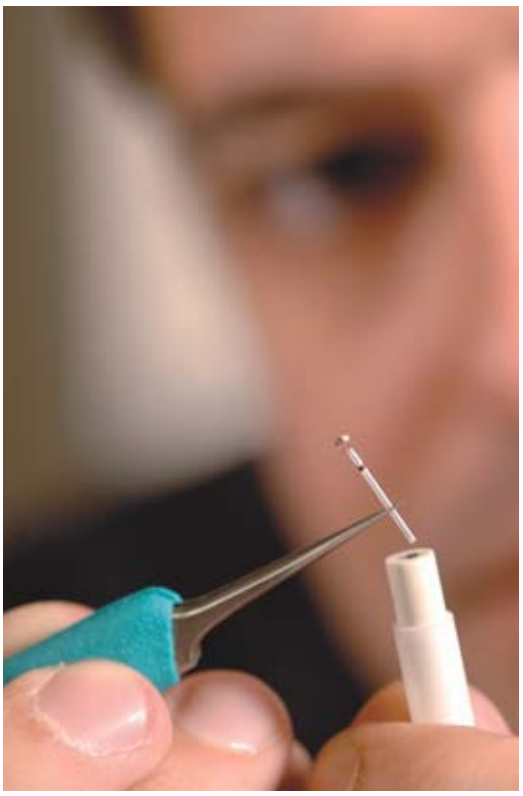


Figure 3.
MACS (magic-angle coil spinning) system developed at the CEA, employing a solenoidal microcoil placed around the solid-state sample, and inductively coupled to a static coil. Fast-spinning the set-up at the 'magic angle' of 54.7° from the axis of the static magnetic field can generate a one-order-of-magnitude gain in sensitivity.

(10^{-9} L) in size. Until now, these breakthroughs could not be extended to solid samples, since they lack molecule diffusion and thereby give very wide and uninformative spectra. In solid state, the nuclear magnetic moments measured are dependent on their orientation in relation to the static field of the molecule containing these nuclei. It is however possible to obtain a similar **spectral resolution** to liquids by fast-spinning the sample at the 'magic' angle of 54.7° from the axis of the static magnetic field, but the mechanical stresses involved mean coil-to-sample distance has to increase, which drives sensitivity down. In 2007, a CEA research team proposed an elegant solution to this problem, involving a **solenoidal** microcoil (micro-sensor) placed close round the sample, and magic-angle-spinning the whole set-up (Figure 3). The microcoil is **inductively** coupled to an external coil that stays static. This microcoil acts as a relay between sample and **spectrometer**, playing a role in the nuclear magnetisation excitations as well as in detecting precession. This magic-angle coil spinning (MACS) approach uses commercially available probes and spectrometers but boasts one order of magnitude-better sensitivity. It is doubly useful for studying **radioactive** matter, since the protection and security barriers that induce sensitivity loss can be placed outside the microcoil.

There is little doubt that different combinations of these building blocks designed to increase the sensitivity of NMR will pave the way to new fields of application for NMR.



P. Stroppa/CEA

Microcoil deployed in the MACS system. This innovative solution, based on rotating microcoils, promises to drive significant leaps forward in NMR.

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Saclay Institute of Matter and Radiation (IRAMIS)
Physical Sciences Division
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FOCUS C

The main methods of medical imaging

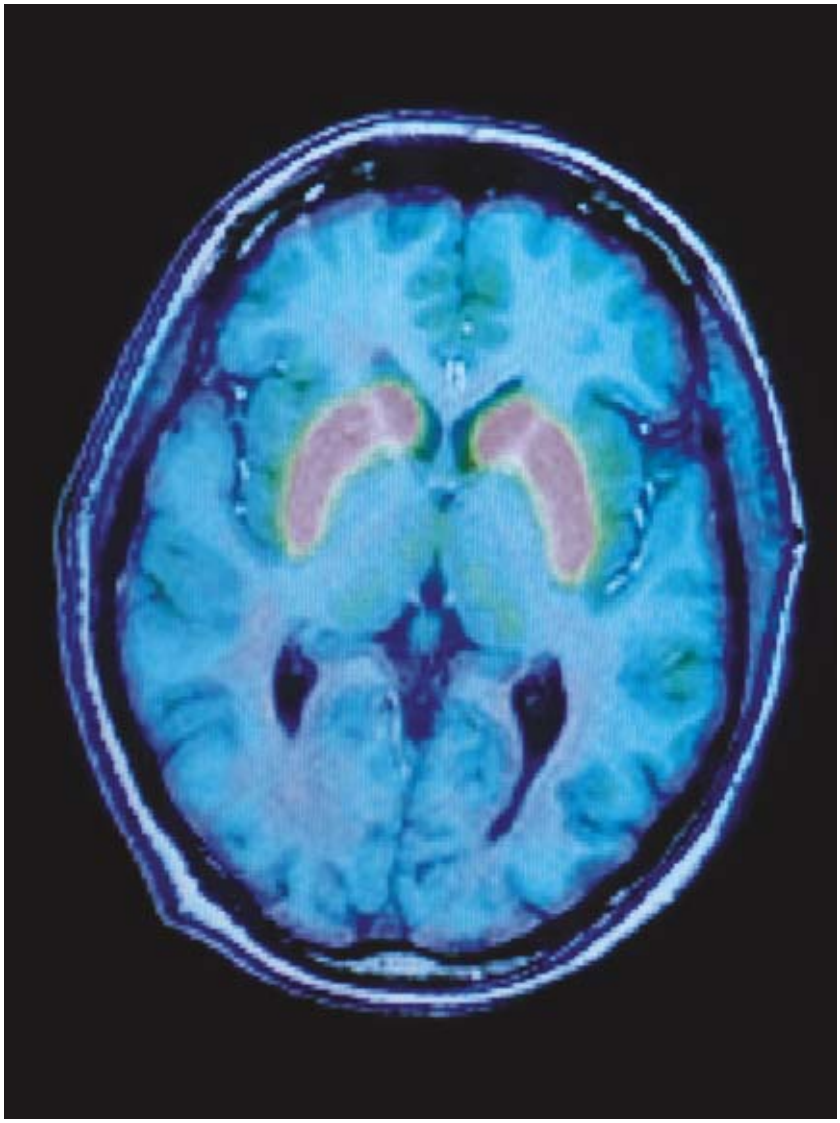
Medical imaging is a unique, non-invasive set of techniques that make it possible to visualise biological processes actually within living organisms themselves. It is a key means for providing insight into physiology and pathology, and ultimately for disease diagnosis, prognosis and therapy. Imaging is therefore the first-choice investigative tool in several branches of medicine and biology.

Medical imaging started with X-ray radiation and then developed further with the discovery of artificial radioactivity and the allied screening techniques. The next leaps forward, first to Nuclear Magnetic Resonance (NMR) and then to superconducting magnets, led to technological breakthroughs in Magnetic Resonance Imaging (MRI).

One of the key dynamic human brain imaging methods is Electroencephalography (EEG) which uses electrodes fitted on the scalp to measure the electrical activity produced by the brain through synaptic currents generated in neurons. EEG gives information on the time-locked neurophysiological activity of the brain, and in particular the cerebral cortex. This information is used in neurology for diagnostics, or in cognitive neuroscience for research.

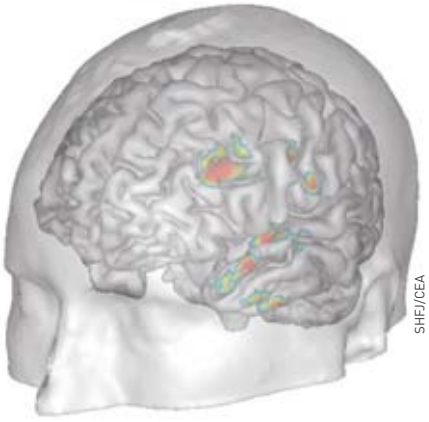
Magnetoencephalography (MEG) records the magnetic fields produced by the currents generated by neurons in the brain, using sensors fitted close to the head. MEG is employed in clinical settings by neurologists, especially when the focus is on epilepsy, and for cognitive neuroscience research. MEG can also be used to study developmental disorders like dyslexia, psychiatric disorders like schizophrenia and neurodegenerative disorders like Parkinson's and Alzheimer's.

Positron Emission Tomography (PET) consists in intravenously administering a tracer molecule labelled with a radioactive isotope and using external detection techniques to track how a normal or diseased organ functions. Radioactive tracers present the same physico-chemical properties as their non-radioactive counterparts, with the exception that they are able to emit radiation. This means that they act as a marker that is followed, using appropriate detection methods, to track the previously-labelled molecule's kinetics through the body. The data gathered is then analysed and transformed using a mathematical model to generate a screen image showing where the radiotracer settles in the body. PET is a widespread technique in physiological or pathophysiological studies on cognition and behaviour and is commonly used to study central nervous system disorders



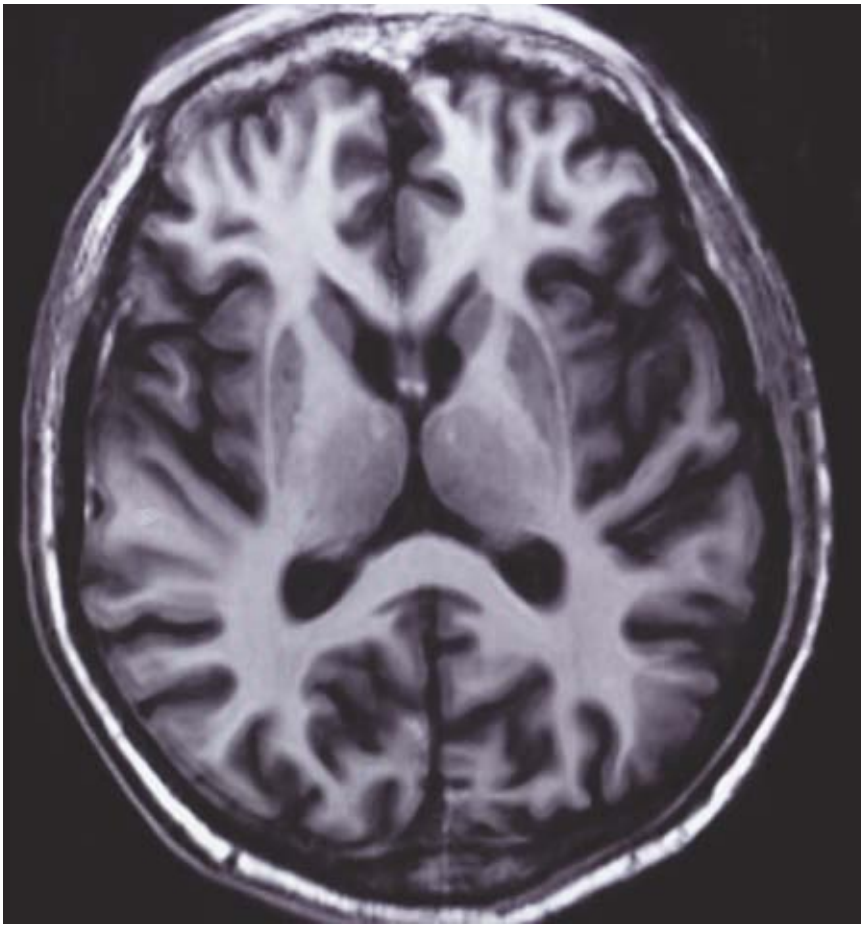
P. Stroppa/CEA

A PET image. The PET camera detects the positrons emitted by radioactive tracers previously injected into the living subject, and 3D images of the target organ are reconstructed by computer analysis.



SHFJ/CEA

Melancholic depression. PET images measuring regional energy activities merged with the aMRI image of the patient's brain. Areas of hypoactivation are individually detected.



P. Stroppa/CEA

Image acquired through the SHFJ's 3-T MRI system at Orsay (Essonne). This technique provides extremely high-precision analysis of infectious or inflammatory lesions, brain vessel damage, and tumours.

such as epilepsy, cerebral ischaemia, stroke, and neurodegenerative disorders (Parkinson's disease, Huntington's disease).

Magnetic Resonance Imaging (MRI) is a non-invasive *in vivo* imaging method. MRI is capable of studying 'soft' tissue such as the brain, bone marrow, or muscle, for example. It can be used to map anatomic structure (anatomical MRI, or aMRI), monitor organ function (functional MRI, fMRI) and track various processes of metabolism (Magnetic Resonance Spectroscopy, MRS). After its first developments in 1946, MRI uses the physical phenomenon of NMR that exploits the magnetic properties of atomic nuclei. Certain nuclei, such as the hydrogen nuclei for example, have a weak magnetic moment, or spin. NMR works by detecting variations in the magnetisation of atomic nuclei in response to an extremely powerful magnetic field and electromagnetic wave-driven excitation. When an electromagnetic wave is applied at the right frequency, i.e. the *resonance frequency*, these nuclei change alignment and emit signals as they return to their initial position. Technological advances in computing and magnetic fields have taken NMR from condensed matter physics on to chemical analysis and then structural biology, and more recently into medical imaging.

Anatomical MRI. MRI makes it possible to visually display all body organs. The resonance, under a very-high magnetic field, of water molecules, which are naturally abundant in most biological tissues, is used to generate cross-sectional images detailing brain structures (grey matter, white matter) down to the millimetre and even less. Radiologists use 'anatomical' imaging to detect and localize brain lesions.

Functional MRI. The recent acceleration in data acquisition and processing has led to the advent of 'functional' MRI, which is able to show neural activity in different brain regions. Indeed, speaking, reading, moving or thinking all activate certain areas in the brain. This neuronal activation triggers a local increase in blood flow in the brain regions concerned. Although it cannot directly detect neuronal activity, fMRI is able to detect the local, transient increase in blood flow that neuronal activity causes, which it does by gauging the magnetization of the haemoglobin contained in red blood cells.

Diffusion MRI (dMRI). Diffusion MRI is a powerful tool for measuring the movements of water molecules at the microscopic scale, thereby providing a precise architecture of the neuronal tissue and its variations. It offers a more direct method of measuring than other conventionally used imaging techniques. Diffusion MRI makes it possible to investigate tissue structure at a much finer scale than the millimetre scale offered by MRI image resolution, with the added advantage of being much faster.

This array of medical imaging technologies is rounded off by nuclear magnetic resonance spectroscopy (MRS), a non-invasive method of gaining biochemical and metabolic information on the central nervous system. MRS, which is based on the same principles as MRI, can be used to provide precise quantitative data on dozens of different molecules.

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dMRI can diagnose certain pathologies very early on and provide images of the connective fiber clusters (white matter) that network the various brain regions together.

Superconductivity and superconductors

P. Stroppa/CEA

One of the main fields of application of superconductivity is medical imaging. This is the 3-tesla magnetic resonance imager at the SHFJ hospital in Orsay (Essonne).

Some historical background

Trains "flying" above the track using magnetic levitation, electricity storage finally resolved using giant magnetic coils, electrotechnical instruments and electric power transmission cables with no joule losses, magnetic fields that can be used to explore the human body and deliver even higher resolution images. People have been marvelling at the potential uses of superconductivity since 1911 when Dutch physicist Heike Kammerlingh-Onnes first discovered the extraordinary property exhibited by superconducting materials; their electrical resistance drops to zero below a certain critical temperature (which varies with their isotopic mass). This discovery won him the Nobel Prize in Physics in 1913.

Apart from zero electrical resistance and optimal electrical conductivity, the superconductors discovered by Kammerlingh-Onnes (later named type I superconductors) possess another remarkable property manifested by the Meissner effect, discovered in 1933 by German physicists Walter Meissner and Robert Ochsenfeld. If we ignore the London penetration depth[1], superconductors can be said to exhibit perfect diamagnetism, i.e. the superconducting material fully expulses its internal magnetic field up to a certain critical field value whereas, in theory, the magnetic field of a material with perfect conduction of electricity should equal that of the externally applied field.

Herein lies the second obstacle that continues to hamper superconductor applications: superconductivity is lost at above a critical magnetic field strength. For many years physicists thought there was only one type of superconductivity and that the magnetic anomalies observed in some samples were due solely to the presence of impurities. In the 1950s, however, Russian physicists Vitaly L. Ginzburg and Lev Davidovitch Landau came up with the theory that there were actually two types of superconductors.

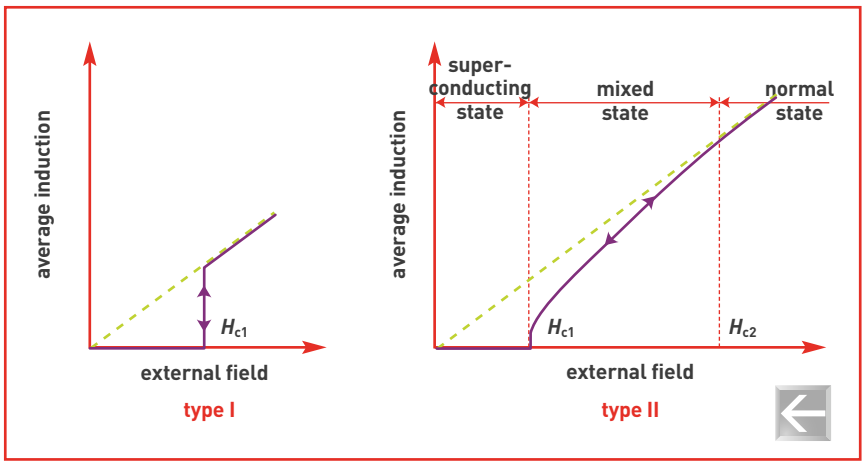
In 1957, the Russian-American physicist Alexei A. Abrikosov finally confirmed type II superconductivity. Type II superconductors exhibit a completely different type of magnetisation characterised by a mixed state that allows them to retain their superconducting state even in intense magnetic fields. This means they are not subject to the Meissner effect. In 2003, Abrikosov, Ginzburg and the Anglo-American physicist Anthony J. Leggett were awarded the Nobel Prize in Physics for their research into superconductors.

It was also in 1957 that American physicists John Bardeen, Leon N. Cooper and John R. Schrieffer published their theory of superconductivity, which won them the 1972 Nobel Prize in Physics. This BCS theory (named after the first letter of their surnames) postulates that electrons move through a conductor as Cooper pairs (two electrons with opposite spin). These pairs act like spin-zero bosons and condense into a single quantum state via a phonon interaction, which

(1) In 1935, Fritz and Heinz London proposed another explanation for the Meissner effect by claiming that the magnetic field decreases with depth from the surface of a superconducting material over a characteristic length λ_L known as the penetration depth.

is also a quantized mode of vibration. It is this electron-phonon interaction that underpins **resistivity** and superconductivity. **Ions** move in response to the ultrafast passage of an electron (10^6 m/s), thereby creating an area of positive electrical charge which is held after the passage of the electron. This attracts another electron that pairs up with the first electron thereby resisting the **Coulomb repulsion** but not **thermal agitation**, which explains why temperature has such an adverse effect on superconductivity.

The BCS theory, which applies to '**conventional**' **superconductors**, did not however provide for the appearance of superconductivity at fairly high temperatures, i.e. higher than the temperature of liquid nitrogen (77 **K**, i.e. – 196 °C), and *a fortiori* at ambient temperature. This 77 K threshold was reached by using compounds such as Y-Ba-Cu-O (current records stand at around 165 K, at high pressure, and 138 K, i.e. – 135 °C, at standard pressure). German physicist Johannes Georg Bednorz and Swiss physicist Karl Alexander Müller were awarded the Nobel Prize in Physics in 1987 for their work on **unconventional superconductors**. They discovered a lanthanum-based copper oxide **perovskite** material that exhibited superconducting properties at a temperature of 35 K (- 238 °C). By replacing lanthanum with yttrium, particularly in $YBa_2Cu_3O_7$, they were able to significantly raise the critical temperature thus developing the cuprate family of superconductors. Although these are highly effective superconductors, the fact that they are ceramics makes them difficult to use in electrotechnical applications. All **high-critical-temperature superconductors** are type II superconductors.



(taken from Lavoisier, *"Matériaux supraconducteurs"*)

Figure 1.
Average induction in type I and type II superconductors under an externally applied magnetic field.

The strange magnetic properties of type II superconductors

In the presence of a magnetic field, type II superconductors exhibit perfect diamagnetism up to certain field H_{c1} just like type I superconductors. Beyond H_{c1}, however, type II superconductors enter a mixed state that allows partial field penetration up to H_{c2} (Figure 1), thereby permitting a material to be superconducting under a high magnetic field.

This mixed state resembles an array of normal-state cores that start to fill the superconducting material at H_{c1} and over. Each region contains a flux quantum ($2.07 \cdot 10^{-15}$ **weber**) and is surrounded by a vortex of superconducting currents (Figure 2). When the magnetic field increases, the network densifies until it completely fills the superconducting material at H_{c2}.

The distinction between the two types of superconductivity is coupled to the concepts of coherence length ξ and penetration depth λ_L, which characterise the interface between a normal region and a superconducting region. ξ represents the spatial variation of the superconducting state (i.e. the density of the superconducting electrons) and λ_L the London penetration depth of the magnetic field. It is the ratio of these two characteristic lengths, known as the *Ginzburg-Landau parameter* and written as κ ($\kappa = \lambda_L/\xi$), that determines which type of superconductivity is involved. If $\kappa < \sqrt{2}/2$, the superconductor is type I, and if $\kappa > \sqrt{2}/2$, the superconductor is type II.

At the interface, the penetration of the magnetic field, as defined by λ_L, corresponds to an increase in free energy in the superconducting material, while the formation of the superconducting state, characterised by the coherence length, is related to a decline in free energy. The interface's energy balance varies with the ratio κ. In type II superconductors, the

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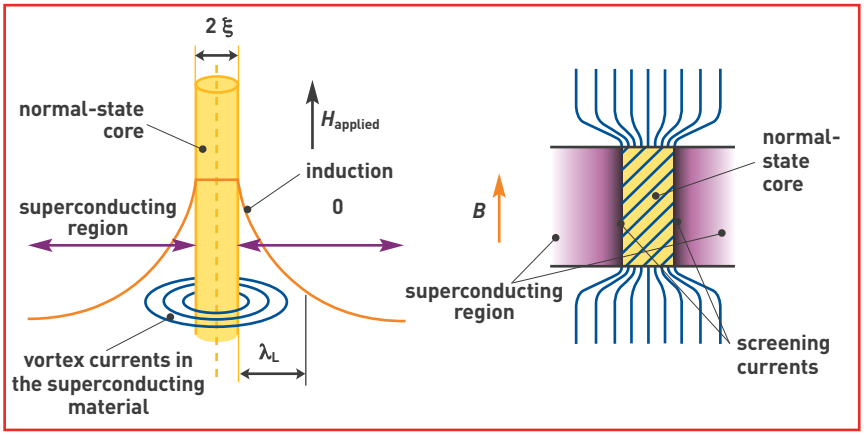

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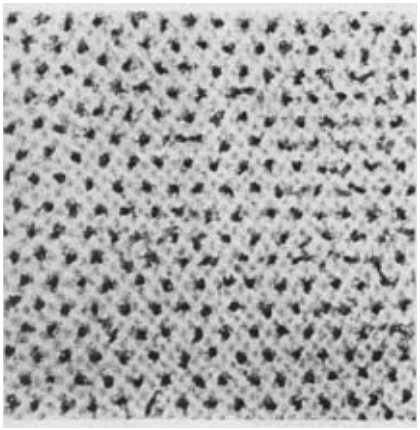
Figure 2.
Diagram of a vortex illustrating penetration depth and coherence length.


U. Essmann and H. Träuble

Magnetic pattern on the surface of a superconductor in mixed state.

material		ξ (μm) 0 K	λ_L (μm) 0 K	κ	T_c (K)	$\mu_0 \cdot H_{c1}$ (teslas) 0 K	$\mu_0 \cdot H_{c2}$ (teslas) 0 K
type I	Al	1.36	0.05	0.04	1.18	0.010 5	
	Pb	0.083	0.037	0.5	7.18	0.080 3	
type II	NbTi	0.005	0.3	60	9.25	0.01	14
	Nb_3Sn	0.003 6	0.065	18	18	0.017	25.5
	YBaCuO	plane 0.003 axis *c* 0.000 6	plane 0.8 axis *c* 0.2	≈ 300	93		140

Table.
Characteristics of some type I and type II superconductors. $\mu_0 \cdot H_{c1}$ and $\mu_0 \cdot H_{c2}$ represent **magnetic inductions**, where μ_0 is the **magnetic permeability** of a vacuum (and of the material in this particular case).

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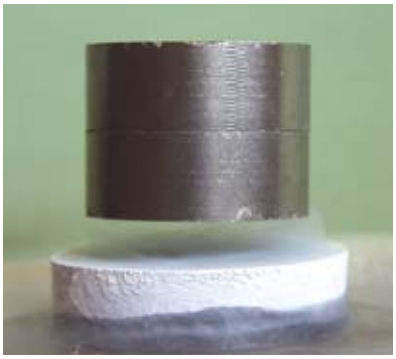
mixed state therefore results from the creation of a large number of interfaces, with each interface corresponding to a negative energy balance conducive to superconductivity above the H_{c1} field (Table).

Potential avenues for application

Type I superconductivity does not present any great potential for new areas of application. Unfortunately, the critical temperature that limits superconductivity applications is very low in the two superconducting materials that currently offer real-world applications i.e. **niobium-titanium, NbTi** (9.2 K) - the first superconducting cables in niobium-titanium alloy were developed in the early 1960s - and **niobium-tin, Nb_3Sn** (18 K). These materials have to be cooled to the temperature of liquid **helium** (4.2 K)[2] in order to activate their superconducting properties. This temperature was the first important milestone towards achieving superconductivity at ambient temperature, which is the ultimate goal.

Type II superconductors can withstand very strong magnetic fields, and are also able to carry extraordinarily high current densities, up to another critical value that varies with the magnetic field (Figure 3). This fact heralded the development of the first superconducting **magnets**. The current densities that can be generated under these conditions are huge in comparison with what can be achieved with domestic or industrial electrotechnical applications (around 10 A/mm²).

Since the 1970s, the CEA has been focusing its research on the production of large-scale intense **permanent** magnetic fields (**magnetic confinement** of **fusion plasmas**, particle physics, medical imaging). In fact, these are the predominant applications of type II superconductors, mainly NbTi[3], where superconductivity significantly cuts down on electric power consumption despite the **cryogenic** efficiency of the facilities - in fact, one watt dissipated at 4.2 K requires a minimum consumption of 300 W at ambient temperature in the largest industrial power plants. While researchers the world over still dream of developing superconducting materials that function at room temperature, it would seem that applied superconductivity will still have to rely on the use of very low temperature cooling for the foreseeable future.


LEG Grenoble

The discovery of high-critical-temperature superconductivity made it possible to see how superconductivity manifests in the open air in the form of a magnet floating above a pellet of liquid-nitrogen cooled YBaCuO, which is now a famous example of the effect.

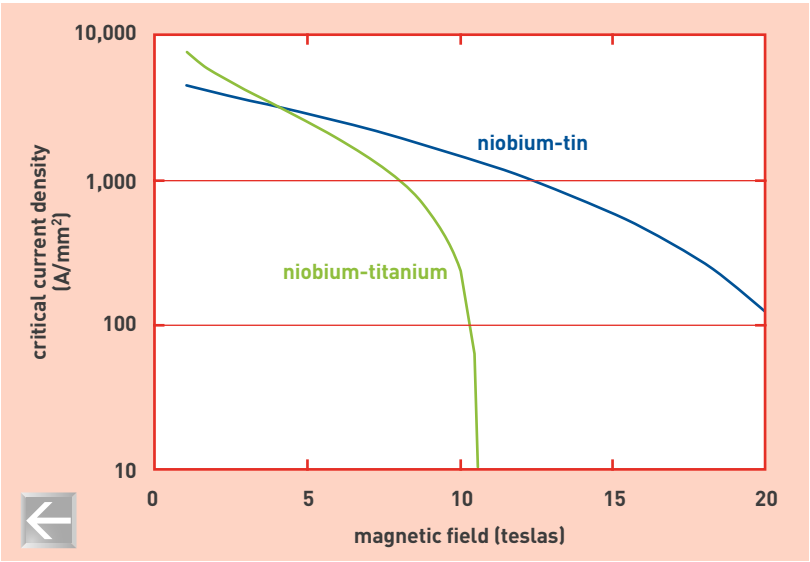


Figure 3.
Characteristic critical current densities in relation to a 4.2-K magnetic field for the two superconducting materials most widely used, particularly in the manufacture of superconducting magnets.

(2) The history of superconductivity actually goes as far back as William Ramsay who, in 1895, was the first person to isolate helium. Indeed, where would the science of superconductivity be today if it wasn't for helium which is the key component of the ultra-low cooling process? Note also that Kammerlingh-Onnes finally succeeded in producing liquid helium in 1908 following unsuccessful attempts by James Dewar in the late 19th century, thus paving the way to the discovery of superconductivity.

(3) Produced in quantities of around 1,500 to 2,000 tons per year.

The different types of magnetism

The origins of magnetism lie in the properties of electrons as explained by the laws of quantum physics. Part of an electron's magnetic properties (*spin magnetism*) results from its quantum-mechanical spin state, while another part results from the orbital motion of electrons around an atom's nucleus (*orbital magnetism*) and from the magnetism of the nucleus itself (nuclear magnetism). This is put to use, in particular, for nuclear magnetic resonance imaging in the medical field. Magnetism is therefore produced by electric charges in motion. The force acting on these charges, called the Lorentz force, demonstrates the presence of a magnetic field.

Electrons have an intrinsic magnetic dipole moment (the magnetic quantum state being the Bohr *magneton*), which can be pictured as an electron's rotational motion of spin around itself in one direction or another, oriented either upwards or downwards. The *spin quantum number* (one of the four numbers that 'quantifies' the properties of an electron) equals 1/2 (+ 1/2 or - 1/2). A pair of electrons can only occupy the same *orbital* if they have opposite magnetic dipole moments.

Each atom acts like a tiny magnet carrying an intrinsic magnetic dipole moment. A nucleus (the neutron and proton individually have a half-integer spin) will have a half-integer spin if it has an odd atomic mass number; zero spin if the atomic mass number and charge are even, and an integer spin if the atomic mass number is even and the charge odd.

On a larger scale, several magnetic moments can together form magnetic domains in which all these moments are aligned in the same direction. These spatial regions are separated by domain walls. When grouped together, these domains can themselves form a macroscopic-scale magnet (Figure E1).

The type of magnetism that comes into play is determined by how these elementary constituents are ordered, and is generally associated with three main categories of material: *ferromagnetic*, *paramagnetic* and *diamagnetic*.

Any material that is not diamagnetic is by definition paramagnetic provided that its magnetic susceptibility is positive. However, ferromagnetic materials have particularly high magnetic susceptibility and therefore form a separate category.

1. Ferromagnetic materials are formed of tiny domains inside which atoms exhibiting parallel magnetisation tend to align themselves in the direction of an external magnetic field like elementary dipoles. In fact, the magnetic moments of each atom can align themselves spontaneously within these domains, even in the absence of an external magnetic field. Applying an external field triggers domain wall movement that tends to strengthen the applied field. If this field exceeds a certain value, the domain most closely oriented with the direction of the applied field will tend to grow at the expense of the other domains, eventually occupying the material's whole volume. If the field diminishes, the domain walls will move, but not symmetrically as the walls cannot fully reverse back to their original positions. This results in remanent magnetisation, which is an important feature of naturally occurring magnetite, or of magnets themselves.

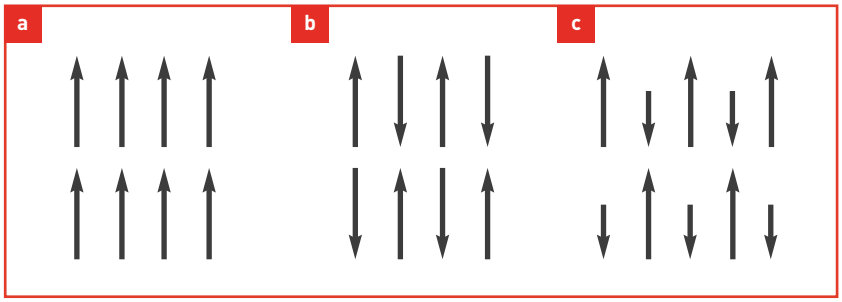


Figure E1.
Intrinsic magnetic dipole moments have parallel alignment in ferromagnetic materials (a), anti-parallel alignment but zero magnetisation in antiferromagnetic materials (b), and anti-parallel alignment with unequal moments in ferrimagnetic materials (c).

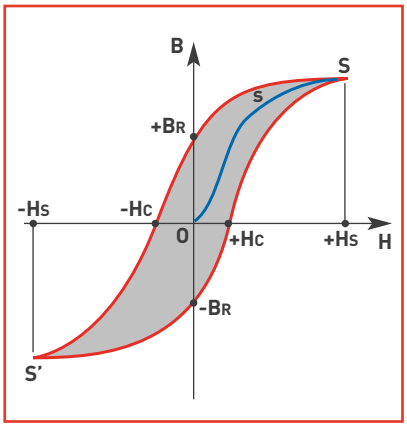


Figure E2.
The induction B of a magnetic material by a coil is not proportional to its magnetic excitation (*field H*). While the initial magnetisation forms an OsS-type curve, shown in blue in the figure, it reaches saturation at point s. Only a partial induction is retained if the field approaches zero; this remanent induction can only be cancelled out by reversing the magnetic field to a "coercive" field value. This hysteresis loop illustrates the losses due to "friction" between the magnetic domains shown on the area bounded by the magnetisation and demagnetisation curves.

The whole process forms a hysteresis loop, i.e. when the induced field is plotted against the applied field it traces out a *hysteresis curve* or *loop* where the surface area represents the amount of energy lost during the irreversible part of the process (Figure E2). In order to cancel out the induced field, a coercive field has to be applied: the materials used to make artificial permanent magnets have a high coercivity.

Ferromagnetic materials generally have a zero total magnetic moment as the domains are all oriented in different directions. This ferromagnetism disappears above a certain temperature, which is known as the Curie Temperature or Curie point.

The magnetic properties of a given material stem from the way the electrons in the metallic cores of a material or of a transition metal complex collectively couple their spins as this results in all their spin moments being aligned in the same direction.

Materials whose atoms are widely distributed throughout their crystal structure tend to better align these elementary magnets via a coupling effect. This category of materials, which is characterised by a very high positive magnetic

Stoiber Productions, München

A Transrapid train using magnetic levitation arriving at the Long Yang bus station in Shanghai (China). This German-built high-speed, monorail train was commissioned in 2004 to service the rail link to Pudong international airport.

susceptibility, includes iron, cobalt and nickel and their **alloys**, steels in particular, and some of their compounds, and, to a lesser extent, some **rare earth** metals and alloys with large crystal lattices, and certain combinations of elements that do not themselves belong to this category. In **ferrimagnetic** materials, the magnetic domains group into an anti-parallel alignment but retain a non-zero magnetic moment even in the absence of an external field. Examples include magnetite, ilmenite and iron oxides. Ferrimagnetism is a feature of materials containing two types of atoms that behave as tiny magnets with magnetic moments of unequal magnitude and anti-parallel alignment. **Antiferromagnetism** occurs when the sum of a material's parallel and anti-parallel moments is zero (e.g. chromium or haematite). In fact, when atoms are in a close configuration, the most stable magnetic arrangement is an anti-parallel alignment as each magnet balances out its neighbour so to speak (Figure E1).

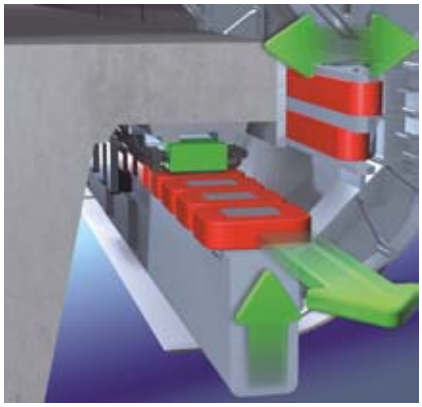
2. **Paramagnetic** materials behave in a similar way to ferromagnetic materials, although to a far lesser degree (they have a positive but very weak magnetic susceptibility of around 10^{-3}). Each atom in a paramagnetic material has a non-zero magnetic moment. In the presence of an external magnetic field, the magnetic moments align up, thus amplifying this field. However, this effect decreases as temperature rises since the thermal agitation disrupts the alignment of the elementary dipoles. Paramagnetic materials lose their magnetisation as soon as they are released from the magnetic field. Most metals, including alloys comprising ferromagnetic elements are paramagnetic, as are certain minerals such as pegmatite.

3. **Diamagnetic** materials exhibit a negative and an extremely weak magnetic susceptibility of around 10^{-5}. The magnetisation induced by a magnetic field acts in the opposite direction to this field and tends to head away from **field lines** towards areas of lower field strengths. A perfect diamagnetic material would offer maximum resistance to an external magnetic field and exhibit zero **permeability**. Metals such as silver, gold, copper, mercury or lead, plus quartz, graphite, the noble gases and the majority of organic compounds are all diamagnetic materials.

In fact, all materials exhibit diamagnetic properties to a greater or lesser extent, resulting from changes in the orbital motion of electrons around atoms in response to an external magnetic field, an effect that disappears once the external field is removed. As Michael Faraday showed all that time ago, all substances can be "magnetised" to a greater or lesser degree provided that they are placed within a sufficiently intense magnetic field.

Electromagnetism

It was the Danish physicist Hans Christian Ørsted, professor at the University of Copenhagen, who, in 1820, was first to discover the relationship between the hitherto separate fields of **electricity** and **magnetism**. Ørsted showed that a compass needle was deflected when an electric current passed through a wire, before Faraday had formulated the physical law that carries his name: the magnetic field produced is proportional to the intensity of the current. **Magnetostatics** is the study of static magnetic fields, i.e. fields which do not vary with time.



Close-up of the magnets used to guide and power the train.

Magnetic and **electric fields** together form the two components of **electromagnetism**. **Electromagnetic waves** can move freely through space, and also through most materials at pretty much every frequency band (radio waves, microwaves, infrared, visible light, ultraviolet light, X-rays and gamma rays). **Electromagnetic fields** therefore combine electric and magnetic **force fields** that may be natural (the Earth's magnetic field) or man-made (low frequencies such as electric power transmission lines and cables, or higher frequencies such as radio waves (including cell phones) or television.

Mathematically speaking, the basic laws of electromagnetism can be summarised in the four **Maxwell equations** (or **Maxwell-Lorentz equations**) which can be used to provide a coherent description of all electromagnetic phenomena from electrostatics and magnetostatics to electromagnetic wave propagation. James Clerk Maxwell set out these laws in 1873, thirty-two years before Albert Einstein incorporated the theory of electromagnetism in his *special theory of relativity*, which explained the incompatibilities with the laws of classical physics.