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THE NEW SUPERCONDUCTORS – A NEW INDUSTRIAL REVOLUTION?

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The discovery of superconductivity is a good example of how you can always expect the unexpected when working at the frontiers of experimental physics. Until 1986 the highest temperature for superconductivity had remained static at about $25K$, where it had been since the mid seventies. Since 1986 a new class of materials have been discovered that have raised the temperature to first $92K$, above the boiling point of liquid nitrogen at $77K$, and recently to above $125K$. It is the aim of this lecture to review the history of superconductivity, describe the physical attributes of a superconductor and the potential applications of the new high temperature superconductors.

History

The history of superconductivity is entwined with the history of low temperature physics research. By late last century, with the continuing improvements in refrigeration technology, scientists has succeeded in liquifying almost all the known gases. Michael Faraday, better known for his work on electromagnetism, had himself succeeded in the liquification of chlorine gas and gave the name 'fixed gases' to those that had so far defied liquification because of the extremely low temperatures required.

One of the pioneering laboratories for low temperature physics research was that of Prof. Kamerlingh Onnes, in Leiden, Holland. From early in the twentieth century, Onnes succeeded in making better and better refrigerators until eventually even the fixed gases could be made cold enough to condense into their liquid phase, or even sufficiently cold to freeze solid. This was typically accomplished by first cooling a compressed sample of the gas, then allowing the compressed gas to escape through a jet. As the gas expanded it cooled down even further, eventually to condense to a liquid. The ideal gas law describes this property of a gas

$$PV = NRT$$

where P is the gas pressure, V is the gas volume, N is the amount of gas in moles, R is the Rydberg constant and T is the temperature in Kelvin, K. Once a gas had been liquified, further cooling was possible by pumping away the gas vapour above the surface of the cold liquid. This simple description of the process ignores the sophistication of the actual apparatus employed for the experiments.

The last gas to be cooled enough to be liquified was helium which finally succumbed in 1908. Helium, which has the lowest boiling point of all gases, was an extremely difficult material to work with. It had been first discovered as a result of the observation of spectral lines in light from the Sun. Helium was obtained on Earth by heating the mineral ores of radioactive elements to drive off trapped gas formed from the alpha–decay of radioactive elements. The helium formed as the the result of the alpha particles combining with two electrons to make a helium gas atom.

One of the main rivals of Onnes was James Dewar, working in London. Dewar invented the vacuum flask for the storage of cold liquids, which now is named after him. Dewar

Gas	Boiling point	Freezing point	Date liquified
	(Room pressure values, in Kelvin)		
Ar	87.3	83.8	
N_2	77.4	63.2	1883
O_2	90.1	54.4	1877
Ne	27.1	24.6	
H_2	20.3	13.8	1898
He	4.2	*	1908

*He does not solidify at room pressure.

Boiling points of the 'fixed gases' and their date of first liquification. Subtract 273.15 to convert temperature in Kelvin (K) to Celsius ($^\circ C$).

also obtained supplies of helium gas from materials that were originally radioactive, but relied on an indirect process that involved the capture of gas bubbles from the mineral springs in the English town of Bath. Unfortunately for Dewar, these bubbles contained helium contaminated with the gas neon. This contributed to Dewar's lack of success with the liquification of helium.

Once Onnes had succeeded in cooling helium enough to liquify the gas, he embarked on a program of experiments to exploit the very low temperature of baths of liquid helium. At room pressure this is $4.2K$ which is about $-269°C$. At the time, a great deal of theoretical work was under way to try to explain the properties of solids by models based on the behavior of atoms. Thanks to experiments of Ernest Rutherford, the modern model of an atom as a small heavy nucleus surrounded by a cloud of electrons has just been introduced. Some of the heroic early developers of quantum mechanics had then tried to account for some of the properties of matter by use of models based on the Rutherford atom. The measurement of electrical resistance was regarded as an ideal way to probe the internal workings of a lump of matter comprised of atoms. The electric current of electrons passed though the solid, scattering from atom to atom. The scattering caused a resistance to the current flow could then be related to the effective size of the atoms. In warm solids, the size of the atoms is effectively larger than at low temperatures because the atoms vibrate with a larger amplitude compared to when they are cold. It was hypothesised that perhaps a very cold solid, with atoms almost frozen in place, may offer very little resistance to the current flow. The resistance was expected to show a gradual decrease with temperature, to perhaps even level out before absolute zero was reached.

The early experiments were done with threads of frozen mercury immersed in baths of liquid helium. This was because mercury could be made extremely pure by repeated distillation. It was known that impurities in the material could significantly perturb the results. Careful measurements of the resistance of the frozen mercury threads as the temperature was lowered gave extraordinary results. Below $4.2K$, the resistance suddenly and unexpectedly dropped below the lowest level the apparatus could measure. The resistance appeared to completely vanish! The sudden drop was suggestive of a phase transition of the electrons into a new state. Onnes had discovered the first superconductor.

It is now known that the resistance of a superconductor is in fact identically zero, not just so low that it cannot be measured. In addition to mercury, several other pure metals were found to display superconductivity at room pressure, several more if the pressure was raised somewhat. It is interesting to note that none of the good electrical conductors at room

(Left) Predicted resistance of some metals at low temperatures. (Right) Experimental measurements of the resistance of mercury showing the transition to superconductivity below 4.2K.

temperature, such as copper, gold and silver, are superconductors. The temperature below which a material becomes a superconductor is known as the *critical temperature*, T_c.

The potential applications of a material that would conduct electricity with no resistance were obviously widespread. But it quickly became apparent that the pure metal superconductors had a serious limitation. This was that the superconductivity could be destroyed by a modest magnetic field. If the temperature was then lowered further, the superconductivity could be restored, requiring a higher field to destroy it once more. However, even at the lowest temperatures reached in the laboratory, close to absolute zero, the field required to destroy the superconductivity was still relatively weak. This field is called the *critical field*, H_c. The superconductivity could also be destroyed by passing too much current through the superconductor. The maximum current is called the *critical current*, usually expressed as a *critical current density*, J_c, with unit Amperes/cm^2.

Since most of the envisaged applications for superconductors involved strong magnetic fields, or large electric currents, for which the pure element superconductors were clearly unsuitable, searches continued for metal alloys and chemical compounds that would exhibit superconductivity that could withstand high magnetic fields and pass large electric currents. At the same time the search was on for a theory to explain the strange phenomenon.

At first it seemed that a superconductor was simply an exotic state of normal matter endowed with the property that it had no resistance to electric current. Consequently it was hoped that the phenomenon could be explained with classical theories derived from Maxwell's equations for electromagnetism. But it became clear that a superconductor was unlike anything that could be explained by classical theories. The main reason for this is the Meissner effect, discovered by Walther Meissner and Robert Ochsenfeld in 1933, although hints of it had been seen earlier by Onnes.

The periodic table showing the pure element superconductors with their critical temperature and their critical magnetic field. From Kittel.

If a material that simply has the property of zero resistance is placed in a magnetic field, eddy currents are generated as a result of the changing magnetic flux as a consequence of Faraday's Law of Induction. Since there is no resistance, the eddy currents never die away. These persistent eddy currents shield the interior of the material from the applied magnetic field. However, if the material is placed into a magnetic field while warm, above its critical temperature, the eddy currents induced will die away owing to resistive heating of the material in its normal state. This will allow the magnetic field to pierce the material. Now, simply cooling the material below its critical temperature does not result in a change in magnetic flux, so it was expected that the magnetic field would continue to pierce the material in its superconducting state. This was not observed. When a superconductor is cooled below its critical temperature, the applied field is *expelled* from the superconductor! This is now known as the Meissner effect.

Because of the Meissner effect, superconductors always exhibit perfect diamagnetism. A diamagnetic material is always repelled from a magnet because the magnetic field induces

A perfect conductor placed in a magnetic field and then cooled below its critical temperature when it becomes a conductor with zero resistance.

A true superconductor placed in a magnetic field while in its normal state and then cooled below its critical temperature when it expels the magnetic field showing the Meissner effect. Adapted from Dahl.

magnetic dipoles of the opposite orientation. In a normal diamagnetic material, such as the metal bismuth, this effect is always very weak and is associated with induced dipole moments of individual atoms. This is a *microscopic* effect. This is not the case with a superconductor, the Meissner effect results from currents induced in a surface layer of the superconductor, a *macroscopic* effect. These surface currents allow the external field to penetrate into the bulk of the superconductor a small amount and act to shield most of the material from the external field so that it retains its superconducting properties.

Theory of Superconductivity

Owing to the Meissner effect, superconductors could not easily be described by normal theories of electromagnetism. A successful theory of superconductivity had to wait nearly 40 years from the first discovery and required the full development of quantum theory applied to model the structure of solid matter comprised of many atoms. This turned out to be a very difficult task!

In 1957, John Bardeen, Leon N. Cooper and J. Robert Schrieffer published was has now become known as the BCS theory of superconductivity. To understand this theory, it is first necessary to look at how electrons behave in metals.

Each metal atom in a lump of metal contributes, typically, one of its outer shell electrons to roam essentially free around the entire lump. These free electrons carry the electric current through a metal because they are free to move in and out of the lump under the influence of an electric field provided by, for example, a battery. Resistance to the current flow is a result of electrons scattering from the positive metal ions.

In an ordinary lump of metal, cooled to absolute zero, each free electron would like to occupy the lowest possible energy level. However, because electrons obey the Pauli exclusion principle, they cannot all crowd down into the lowest energy levels available. This is in the same way that electrons that pack into the space surrounding a nucleus must go into successively higher and higher energy levels, and hence build up the periodic table of the elements. This ensures each electron is in a unique state as required by the exclusion principle. Thus in a metal some electrons are forced into high energy levels, with the consequence that they can have a large kinetic energy.

However, the BCS theory says that some electrons can have their physical properties drastically altered so that they no longer have to obey the exclusion principle. They proposed that this happens when two electrons become bound together to form a new particle. The mechanism for this is quite simple to understand. When an electron travels through the crystal lattice of a metal, the electric field of the negatively charged electron can pull on the positive ions of the host lattice. When the positive ions move minutely towards the traveling electron this causes a transitory concentration of positive charge behind the electron. This small concentration of positive charge can then exert an attractive force on a second passing electron. Thus the two electrons can be said to be bound together as a result of a perturbation of the crystal lattice. Any perturbation of a crystal lattice follows the rules of quantum mechanics and the energy and momentum involved in the perturbation have discrete values. Each allowed perturbed state is called a *phonon*, with a specific energy and momentum. Consequently the two electrons can be thought of as interacting via the exchange of a phonon of the lattice.

This bound pair of electrons now effectively constitutes a new particle called a *Cooper pair*. It is this Cooper pair which can travel through the solid without scattering, and hence without resistance. A simple way of seeing why is to consider that any scattering event causes the first electron to loose energy and momentum by creating a phonon in the lattice which will be compensated when the second electron absorbs the phonon, therefore the net energy and momentum of the Cooper pair is unchanged. A more sophisticated picture is that all Cooper pairs are able to condense together into the same energy state and hence form a giant 'electron molecule'. This entire condensed state is able to propagate through the crystal without scattering because it is energetically unfavourable for it to do so.

The two electrons that make up a Cooper pair are physically quite far apart, from hundreds to thousands of Angstroms, much further than the lattice spacing in the host crystal lattice, typically one Angstrom. The characteristic separation of the electrons in a Cooper pair, called the *coherence length*, ζ.

This pairing mechanism is extremely weak, it is easily disrupted by thermal agitation of the lattice. This is why superconductivity is only seen at low temperatures. Furthermore, the penetration of an external magnetic field the surface of a superconductor has a *characteristic* *depth*, λ. When the spacing of the Cooper pairs, ζ, is equal to or greater than λ, then the superconductivity can be destroyed instantly when an external magnetic field exceeds the critical field. The induced surface currents are unable to shield the bulk of the material from the external field which then causes the material to return to its normal state.

For an effective superconductor for industrial applications it is necessary to find a material with $\lambda > \zeta$. Such materials were soon discovered. Usually they consisted of metal alloys or compounds. They displayed all the characteristics of the elemental superconductors, except that instead of the complete loss of superconductivity above a critical field, they allowed the selective penetration of the external field into the bulk of the material by the formation of *magnetic vorticies* consisting of domains of normal material surrounded by superconducting material. The bulk of the material continues to be shielded from the magnetic field. If the external field is raised still higher, the size and number of the magnetic vorticies increase, until eventually there are no superconducting regions left and the material returns to its normal state. Materials which allow the penetration of external magnetic fields while retaining their superconducting properties are known as type II superconductors. The original elemental superconductors are type I. The exceptions to this are niobium and vanadium which are both type II superconductors.

The magnitude of the magnetisation (induced magnetic field) of a type I (left) and type II (right) superconductor as a function of the strength of an external magnetic field. Adapted from Kittel.

The type II superconductors are characterised by a lower critical field, H_{c1}, when the external field first begins to pierce the material and form the magnetic vorticies. As the external field increases in strength the ratio of the volumes of superconducting material to normal material inside the vorticies decreases, until at an upper critical field, H_{c2}, the material is entirely normal.

Until 1986, all practical applications of superconductors exploited type II superconductors with large H_{c2} values which could therefore retain their superconducting properties to produce usefully strong magnetic fields or carry usefully large currents without resistance. Some examples are the metal alloys NbTi and Nb_3Sn. Successful application of these materials to produce strong magnetic fields needed careful attention to the processing steps used to produce the alloys. It was necessary to introduce lattice dislocations or other defects which act to pin the magnetic vorticies in place. Free movement of the vorticies in more perfect material leads to heat dissipation with the consequent danger of the material returning to its normal state.

After 1986, the picture changed dramatically with the discovery of the new high temperature *ceramic* superconductors.

The new high temperature superconductors

In 1986 J. Georg Bednorz and K. Alex Müller were studying ceramic compounds with a chemical structure that put them in the class known as perovskites. They already had experience with the material $SrTiO_3$ which is well known for is extremely high dielectric constant, indicating that relatively weak external electric fields could produce a large polarization of the crystal lattice. Bednorz and Müller chose to investigate a class of perovskites composed of lanthanum, barium, copper and oxygen (La–Ba–Cu–O). They chose these materials because the Cu atoms existed in the compound in a state of a fractional average valence greater than 2. In this situation it was suspected that electrons could interact strongly with the Cu and O atoms in the lattice. History shows that they were correct. Superconductivity was discovered in the La–Ba–Cu–O system with critical temperatures as high as $40K$, remarkable for a superconductor, astounding for a ceramic!

Paul Chu then investigated the pressure dependence of the critical temperature in the La–Ba–Cu–O compounds and found that T_c decreased as the pressure increased. He therefore sought ways to naturally increase the pressure in the lattice by the substitution of smaller atoms for the less important La and Ba atoms. He soon discovered that substitution of the smaller yttrium ion for the larger lanthanum ion produced a material with a T_c around $90K$. The compound was $Y_1Ba_2Cu_3O_{7-\delta}$, dubbed *ibco*. Again the Cu has an average valence grater than 2. This material has a seemingly impossibly high critical temperature and people began to question whether the BCS theory could account for the superconductivity mechanism in these new materials. However subsequent research has revealed than in all of the new materials, planes of Cu–O bonds permeate that crystals along which the Cooper pairs of electrons form by the exchange of phonons as usual.

Since Chu's discovery, further work has pushed T_c higher, rising through $110K$ for compounds of Bi–Sr–Ca–Cu–O, dubbed *bisco*. At present (mid 1994) the record is around $125K$ for the compound $Tl_2Ba_2CaCu_3O_{10}$.

All of these new high temperature superconductors are type II superconductors, but with several additional properties. The most significant of these is that the coherence length is very short compared to the older metallic superconductors. The consequence of this is that the material forms copious numbers of vorticies when the magnetic field pierces the superconductor for strengths above the lower critical field. Furthermore, at temperatures close to, but below, the critical temperature, these vorticies can move around under the influence of electric currents passing through the material. This is very undesirable because this can cause the return of resistance, even though the material is still physically a superconductor. Indeed, under some conditions, the resistance can rise to above that of copper at the same temperature!

The remarkable recent pace in superconductivity discoveries. Adapted from Bednorz and Müller.

Coherence lengths and penetration depths for superconductors

Material	Coherence length, ζ	Penetration depth, λ
Low temperature Type I superconductor	$\zeta > \lambda$	
Low temperature Type II superconductor	50 – 300 Å	100 – 1000 Å
High temperature Type II superconductor	10 – 30 Å	1,000 – 100,000 Å

Fortunately the magnetic vorticies may be trapped and frozen at defects in the crystals, or other irregularities. Many people are seeking ways of processing the new materials to enhance this trapping effect. One possible method is to selectively damage the material by the implantation of high energy ions.

A second serious problem is the phenomenon of *weak links*. These occur when the supercurrents of Cooper pairs must jump from grain to grain within the superconducting material. Each jump occurs as a result of the ability of particles to 'tunnel' through forbidden gaps, provided the gap is not too wide. However the tunneling process is delicate and can be easily disrupted. The new superconductors are particularly susceptible to this type of disruption which can severely limit the critical current in the material. The effect can be minimised be further cooling of the material, or by careful processing techniques that reduce the number of jumps required to get through the material.

Potential Industrial Applications

Potential applications for the new high temperature superconductors fall into two categories: The first involves the use of the material to make microelectronic devices, the second involves the use of the material to generate strong magnetic fields.

At first glance, it might be thought useful to wire up the various components of a computer with superconducting wire. This would surely allow the computer to operate faster with less wasted heat than at present. This is true, but it turns out that ordinary metals, when cooled to liquid nitrogen temperatures do this job almost as well, making superconductivity unnecessary. However it is possible to make superconducting microelectronic devices that exploit properties of Cooper pairs bestowed upon them by quantum mechanics. Just as the Cooper pairs must tunnel from one grain to another in a bulk sample of superconductor, they can also tunnel thought deliberately introduced insulating barriers. The tunneling process can be strongly affected by the presence of external perturbations, such as extremely weak magnetic fields. It turns out that a superconducting loop , containing two insulating barriers, will transmit a current that depends very sensitively on the strength of any magnetic fields threading the loop. This is the basis of an extremely sensitive way of measuring weak magnetic fields. Indeed, such a device, known as a Superconducting Interference Device (SQUID) may be used to measure the strength of the magnetic field from the human brain! SQUIDS based on the new superconductors are now on the market and are much cheaper to operate that previous designs that required liquid helium cooling. SQUIDS may also be used in make accurate maps of the Earth's magnetic field which are useful in prospecting for new mineral deposits.

Superconducting junctions involving a thin insulating layer can also form the basis of microelectronic devices that perform extremely quickly compared to conventional room temperature electronics. IBM once investigated the possibility of making a very fast computer based on the conventional superconductors, but gave up the effort before such a machine reached the market. As yet, the new superconductors do not seem to have been applied in this area.

By far the most exciting applications of the new superconductors is the possibility of the generation of extremely strong magnetic fields. Since the supercurrents persist indefinitely, such magnets can operate without drawing any power, except for the power required to keep them cool. Numerous applications have been proposed. One of the most exciting of these is to use the Meissner effect for magnetic levitation of trains. Such a frictionless train could be capable of very high speed travel. Numerous practical difficulties have prevented these trains from entering service. Most of these are related to the need to generate extremely strong magnetic fields that would invariably destroy the superconductivity of the new materials. Several prototypes have been constructed using the old cold superconductors.

Another promising application is in the use of superconducting magnets to produce the strong magnetic fields used in hospital magnetic resonance imaging machines. A magnet that used liquid nitrogen as a coolant would be much cheaper to operate than the present magnets which use liquid helium.

Other interesting applications include Magnetic Energy Storage (MES) and magnetic propulsion for ships. In MES, large electric currents are stored in vast underground superconducting coils. The current is induced in the coil during times of off peak power generation and then tapped out again as needed. The coils need to be very strong because of the enormous forces generated by the magnetic field of the stored current. Despite this disadvantage MES has the advantage that the electric current can be recovered from the coil with close to 100% efficiency. In magnetic propulsion for ships, sea water is drawn in through a duct where is passed through a very strong magnetic field at right–angles to the direction of water flow. An electric current is then run through the sea water at right–angles to both the magnetic field and the flow direction. This results in a magnetic force on the water which expels it from the ship, providing propulsion. Prototypes for both of these applications have been constructed using the old superconductors, but practical implementation is still a long way off.

Superconductivity in Australia

A very large consortium of industry, CSIRO and Universities is presently involved in the research needed to develop the new superconductors to make them useful (see table on next page). The consortium is focusing on the Bi–Sr–Ca–Cu–O system because it shows the most promise for high magnetic fields/high current applications. This is because the material forms a planar crystal structure that makes it less vulnerable to weak links compared to $Y_1Ba_2Cu_3O_{7-\delta}$. There are two compounds of greatest interest. These are $Bi_2Sr_2CaCu_2O_{8+y}$ (2212), $T_c = 80K$, and $Bi_2Sr_2Ca_2Cu_3O_{8+y}$ (2223), $T_c = 110K$. In practice the higher temperature material is preferred and it has been found that the addition of lead increases the volume fraction of this phase when the material is grown from the starting material. The superconductors based on thallium have higher critical temperatures that this material, but the presence of thallium makes them very toxic to work with and therefore are not being investigated intensively at this time.

Current densities and operating magnetic fields for possible applications of the new high temperature superconductors.

The Australian High Temperature Superconductor Materials Laboratory.
Headed by Prof S.X. Dou, University of Wollongong
Participating and Supporting Organisations

Universities

University of Wollongong
University of Queensland
RMIT
University of Technology, Sydney
University of New South Wales
Monash University
University of Melbourne
Australian National University
Griffith University
Curtin University
ADFA

Industry

Metal Manufactures Ltd
Electricity Supply Association of Australia Ltd.
Asian and Pacific Resource Ltd.

Government

CSIRO, Division of Applied Physics
Australian Nuclear Science and Technology Organisation (ANSTO)

To produce the material in a form suitable for use in high field magnets or for power transmission it is necessary to make wires or tapes. To do this, starting materials are made into a powder and placed in a tube of silver. This tube is then drawn down into a wire which is rolled flat to form a tape. Heat treatment then promotes the growth of the 2223 phase inside the tape. The resulting tape is reasonably flexible and can be fabricated into useful shapes. Research is presently under way aimed at increasing the upper critical field and the critical current density of these tapes. A measure of the present state of the art is shown in the figure on the previous page which shows the required current density as a function of magnetic field for several envisaged applications for the new materials.

Clearly the new superconductors are not yet ready to trigger a new industrial revolution. There are still many problems to be overcome before the critical current density can be increased, the problems of flux pinning and weak links reduced and the severe mechanical problems of working with a material that is a ceramic are solved. Despite this, one of the most significant things about the new superconductors is that they work at all! Nobody expected the BCS mechanism to function at such (relatively) high temperatures. In many laboratories world wide there are tantalising hints that superconductors with even higher critical temperatures may be possible, perhaps as high as $200K$. However so far nobody has been able to obtain reproducible results at that temperature. It is hard to imagine that a material that was sufficiently 'flexible' to allow electrons to bond via the exchange of phonons at high temperature could possibly hold itself together without falling apart at the slightest perturbation. Despite this, it would be nice to think that such materials exist, or that there was some unusual compound waiting to be discovered with a critical temperature warmer than room temperature!

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