

## **The Potential Use of Gold in Superconductivity Related Applications**

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### **Abstract :**

Superconductivity is one of the most remarkable scientific phenomena ever investigated. It is the phenomenon whereby some materials exhibit zero resistance to the passage of an electric current when cooled to low temperatures, and requires a quantum mechanical explanation. Four Nobel prizes in physics have been awarded specifically on the subject of superconductivity, with many more enabled by superconducting technology. For example, particle beams are generated in accelerators and manipulated in “particle beam lines” in the “Big Physics” projects around the world eg. at CERN, Geneva, leading to major discoveries in fundamental particle physics. Similarly, at the JET Propulsion laboratory near Oxford, U.K, controlled nuclear fusion has been demonstrated, and magnetic containment of plasmas is key. In the chemical and biological sciences high field NMR spectroscopy has become indispensable for examining organic matter, revealing the mysteries of the workings of cells, genetics, and in the development of new polymers and pharmaceuticals.

With all these very advanced uses for superconducting magnets, it is easy to forget that superconductivity is big business, not just a scientific curiosity. MRI (Magnetic Resonance Imaging) superconducting magnets, the key component of high resolution body scanners, use approximately half of the world’s superconducting wire – the other half being mostly used in accelerator magnets. The MRI market is about 3 billion dollars per annum, and one MRI magnet uses 200km of wire. New applications for superconducting magnets are now appearing including “Catheter steering”, enabling much shorter timescales for life-saving brain tumour removals and “Functional MRI”, a whole new area in patient diagnostics.

Whilst the use of low temperature superconductors (LTS) is now well established commercially in superconducting magnets and niche electronic applications, the application of LTS in electric power distribution and transport has been very limited to date. It is now more than fifteen years since the so-called High Temperature Superconductor (HTS) materials were discovered: these can be operated at liquid nitrogen temperatures rather than liquid helium temperatures. However, materials processing and scale-up issues have prevented their widespread use, and in particular the required price/performance criteria are only beginning to be reached except in certain niche markets. BSCCO (Bismuth Strontium Calcium Copper Oxide) tapes up to one km long are now readily available, and have been demonstrated in high current cables for power distribution networks, but the general consensus is that 1) it is difficult to reduce the price much further because of the silver matrix required and 2) in applications where coils are required eg. motors, generators, transformers etc the properties of BSCCO are rather poor because of the critical current dependence on magnetic field. Magnetic fields are always associated with coils and windings, and such fields are of course fundamental to the operation of all electrical machines. YBCO (Yttrium Barium Copper Oxide) however, has good characteristics in field and for the last few years there has been intensive research and development costing several tens of millions of dollars worldwide into the scale-up of production of so-called “coated conductor”. This “second generation” tape can be produced by any of many different film deposition techniques, with more or less success for short lengths, but as yet it is unavailable in lengths more than a few tens of metres.

In the case of the first generation HTS conductor – ie. BSCCO tape – protection against thermal and electrical instabilities (localised hot spots and high electric field regions) is provided by embedding the superconducting fibres within a silver or silver alloy matrix which forms a tape. The process is called “PIT” or Powder-in-Tube technology. In the case of the second generation conductor – YBCO coated conductor – a film of YBCO is deposited on flexible metallic substrates – usually nickel alloy – with intervening buffer layers. The buffer layers are biaxially textured in themselves, via ion beam processes or variants, or they derive their texture from a textured

substrate produced by mechanical rolling followed by annealing and recrystallisation steps. The objective is to produce a biaxially textured YBCO film with as few high angle grain boundaries as possible, since these are known to reduce critical currents drastically. In order to give the required degrees of thermal and electrical protection a metallic overlayer is used. This so-called “shunt layer” is typically between 300nm and 3 microns thick in research samples, and will in the future depend on the application area, and the degree of protection demanded. This protective layer has other requirements and functions. For example, it must be resistant to oxidation at high temperatures which arises during processing steps and/or in service in an overload situation, and it must serve as a barrier to prevent ingress of moisture into the YBCO.

One of the aims of this paper is to consider the possible choices for this metallic “protection” layer. To date only silver and gold layers have been used in practical examples and there are excellent technical reasons for this choice involving key parameters such as the electrical and thermal conductivities, contact resistance, specific heat capacities, oxidation potential, lattice constant, coefficient of linear expansion etc. This paper will consider the likely relative importance of these parameters and indicate current gaps in our understanding.

The other principle aim of this paper is to obtain an order of magnitude estimate, on the basis of market predictions and known requirements, of the total tonnage of the metal overlayer which will be used in the production of coated conductors for application areas in the future. This calculation is done in several different ways, assuming a layer of gold one to two microns thick on a one cm wide tape. Firstly, from the known usage of wire in the current major market for MRI magnets, it is possible to calculate the tonnage of metal overlayer which would be used if the new HTS coated conductor became a direct replacement for the existing LTS wire. For certain technical reasons this is not actually a very likely scenario but it is a useful starting point and is based on real current usage of superconducting wire today and only a 50% market penetration. The second method used here is to consider the production capacity of the BSCCO plants which have been set up to service the future requirements of the power industry. The largest US plant will be producing 20,000km per annum before 2010 and, if, as most workers in the field now acknowledge, this BSCCO capacity translates in the future to a similar coated conductor capacity, then it turns out that the tonnage of metal overlayer required worldwide will be rather similar to that calculated from the MRI wire replacement scenario above ie about 77 metric tonnes of gold. The third and final calculation method we have used in this paper is based on a number of market predictions of the growth of the use of HTS in various power applications made by various organisations worldwide. For the case of the US DOE 2001 forecast, the requirement is again 20,000km for the US power distribution industry alone by 2020, and this translates into ten times this amount for usage worldwide. Again, this is rather conservative and does not take into account the potential other major uses of coated conductor, in, for example, MagLev (Magnetically Levitated) trains, ships motors etc etc. So very conservatively we conclude that the annual tonnage of gold, if gold is indeed the material of choice for the protection layer, is certainly of the order of 100 Tonnes pa, and quite probably an order of magnitude more if further applications are realised. This excludes some relatively minor usage in electronic applications of both HTS and LTS superconducting materials which can conveniently be classed as “electronic uses” where the overall scenario is similar to that of mainstream electronic applications – ie bond wires, contacts, pcb’s etc.

In addition to these scenarios, we must add an extremely important recent development in coated conductors which may well accelerate volume applications. A recent international patent application, filed by 3-Cs Ltd., a small start-up company in the UK, considers the integrated manufacture of HTS power devices (including motors, generators, transformers, energy storage magnets and the like) in the form of essentially cylindrical modules which would be much easier to fabricate than long lengths of coated conductor. The essence of this invention is the use of thin film deposition and patterning techniques, originally devised for the semiconductor industry, but applied in three dimensions instead of two. Thus patterned layers are built up successively on a rotating cylindrical former and reel-to-reel winding processes are completely eliminated. Initial feasibility studies have given promising results and the new concepts are set to bring the market much closer. As for the conventional coated conductor approach, metallic overlayers are still required in the same proportion to protect the underlying YBCO layers and to enable low resistance contacts to be made.

## ***Introduction***

Superconductivity is no longer a scientific curiosity. For more than 40 years it has been a commercial reality – mainly in the form of superconducting magnets using so-called "Low Temperature Superconductors" (LTS) wires made of Nb:Sn or Nb:Ti alloys. Tens of thousands of superconducting magnets are now in daily use worldwide for high field NMR (Nuclear Magnetic Resonance) and MRI (Magnetic Resonance Imaging). Prior to these well-known applications superconducting magnets were mostly manufactured for the research community, starting with solid state physics investigations and continuing into the world of "Big Physics", where particle accelerators require beam-steering magnets producing enough field to guide the high speed particles around, for example, huge synchrotron rings. Nowadays there are even superconducting magnets which help surgeons to steer catheters within the human body in order to perform difficult operations – for example in the investigation and removal of brain tumours. Until recently, all these magnets have required liquid helium for cooling, or very sophisticated refrigerators, and their operating temperatures have been in the region 2 to 20K.

Since the discovery of high temperature superconductivity (HTS), which resulted in the possibility of operating superconducting devices at much higher temperatures (typically 77K, the temperature at which nitrogen liquifies) the number of potential applications has increased enormously, and the technology is poised to reach far beyond the existing magnet applications and into new areas such as power generation, distribution and transport. Worldwide, tens of millions of dollars are now being spent in R&D on new forms of conductor to address these new application areas because of the potential benefits in energy efficiency (and consequent reduction in atmospheric pollution), reduced weight and size, and enormous current densities possible compared with copper-based conductors operating at room temperature. These very high current densities are possible because there is zero electrical resistance below the critical temperature and thus there is no Joule heating. Joule heating within electrical machines is obviously wasted energy and is equivalent to friction in mechanical systems, but the problems are more severe than that. Resistive or Joule heating can lead to thermal runaway and premature failure of components.

As we shall show, gold has a part to play in the new superconductors, known as "coated conductors" based on YBCO films deposited on buffered nickel alloy substrates. This is partly because of its high thermal and electrical conductivity, high specific heat capacity, resistance to oxidation and general compatibility with high temperature processes. Moreover, its lattice match and thermal expansion match to the underlying superconducting YBCO layer are excellent and results in some new possibilities currently being examined.

We begin with a brief review of the history and background of low temperature superconductivity, and its scientific importance and commercial exploitation before moving on to consider high temperature superconductivity and its likely impact in the 21st century. The detailed explanation of superconductivity is beyond the scope of this paper, and indeed high temperature superconductivity is still not fully understood. However, it is necessary to have some background on the major observations, effects and explanations in order to understand the present state of development and to comment on existing applications before making predictions about future applications. It helps to have a physical picture in mind whereby pairs of electrons can move through the crystal lattice without actually bumping into the lattice and losing energy through scattering mechanisms. This behaviour is possible because of "polarons" ie lattice perturbations which couple the pairs of electrons and allow them to move unobstructed by the lattice.

## ***History and background of Superconductivity***

Superconductivity was discovered in 1911 by the Dutch physicist, Prof. Kammerling Onnes (1), while he was carrying out experiments on the conductivity of metals at very low temperatures at the University of Leiden. He had first succeeded in liquifying helium in 1908, and in 1913 he was awarded the Nobel prize for his low temperature investigations into the properties of metals. In 1911 it was already known that conductivity was dependent on the amount of scattering of the electrons at imperfections in the lattice – in particular, impurities and lattice vibrations. Such low temperatures, around 4.2K, had never been reached before, and he first started investigating the electrical resistance of platinum and gold, probably on the basis that they were very pure and did not have significant oxide layers to affect the voltage measurements. Normal behaviour was observed, with resistance gradually decreasing with temperature, as expected. Then he moved on to investigating very pure mercury and to his amazement he observed zero voltage drop across a capillary tube containing a thread of solidified mercury as the sample was

cooled in the region of 4.2K. Figure 1 shows his plot of resistivity as a function of temperature, with its sharp transition.

The temperature at which such a sudden decrease in resistance is observed for a superconductor is called the "critical temperature" and written  $T_c$ . Below  $T_c$ , it is also observed that as the current is increased beyond a critical value, the zero resistance behaviour disappears and the superconductor behaves as a normal metal. There is thus a specific critical current  $I_c$  for a superconductor at any temperature below  $T_c$  - see Figure 2 - and lowering the temperature enables an increase in  $I_c$ . Sharp transitions such as these must have prompted at least some physicists to think in terms of "quantum phenomena" which only a few years before had provided explanations for the photoelectric effect and the "ultra-violet catastrophe". In both of these cases, sharp cut-offs in the relationships between physical parameters had been observed and could not be explained using classical physics. Quantum theory was in its infancy and Planck's constant was a key parameter. A satisfactory theoretical explanation for superconductivity, however, did not emerge until the 1950's by which time solid state theory was well developed and the role of electron-phonon interactions was much better understood.

At first this discovery of superconductivity produced tremendous excitement as people realised the implications of zero electrical resistance for all electrical machines and power transmission cables. Omnes even performed an experiment whereby a current flowed in a loop of lead wire for over a year without any power supply and without significant current loss. This was the first demonstration of a "persistent current" - which is key to the operation of today's high-field NMR spectrometers. However, it was soon established that, at least for the superconductors investigated at that time, there also exists a "critical magnetic field" above which superconductivity completely vanishes (Figure 3), and that this critical field was too low for the superconductors to have any practical significance. The reason for this is that any conductor carrying current generates its own magnetic field called the "self-field" and for these early superconductors (now called "Type 1") the self-field alone was enough to prevent high supercurrents. Increasing the external field around a superconductor further reduces the critical current at a given temperature, or, for a constant current below the critical current, increasing the temperature further reduces the critical magnetic field.

Figures 2 and 3 are schematic, but represent quite well the behaviour of Type 1 superconductors, where the superconducting transition is very sharp for both temperature and magnetic field. For Type II, or "mixed state" superconductors described below, the transitions are not quite so sharp but nevertheless the change from normal to superconducting behaviour results in many orders of magnitude change in the amount of current which can be carried without any resistive heating.

Thus it was known that the critical current ( $I_c$ ), critical temperature ( $T_c$ ) and critical magnetic field ( $H_c$ ) were all interdependent on one another, and this can be conveniently shown on a critical surface phase diagram - see Figure 4 - where the current axis is labeled  $J$ , the symbol for current density, which is simply the current divided by the cross-sectional area of the conductor.  $H$  is the symbol used by physicists for magnetic field. In the diagram, any combination of the parameters  $J$ ,  $T$  and  $H$  inside (below) the critical surface will result in superconductivity, whereas any combination outside (or above) the critical surface represents the "normal" state.

In the 1930's, superconductivity was still being regarded as an unexplained scientific curiosity - a sort of quantum-mechanical perpetual motion machine - and supercurrents were still very low in the many materials investigated. However, an important discovery was made which shed some light on the situation. It was found that superconductors below their critical temperature behave like magnets. Prototype Maglev (Magnetic Levitation) trains have been based on this principle, now known as the "Meissner Effect" after one of its discoverers (2). In the Meissner effect (see Figure 5), the flux from an external magnet is excluded by the superconductor, and this exclusion is what causes the superconductor to behave like a magnet in opposition. The Meissner effect remains a convenient and rapid way of assessing superconductivity in materials, see (3), for example. The more detailed scientific explanation is that the external magnetic field induces current loops in the superconductor which collectively generate an equal and opposite magnetic flux. However, if the external field becomes larger, the flux starts to penetrate into the interior of the superconductor and there will come a point at which it becomes "normal" ie it reverts to the normal, resistive, state and is no longer superconducting.

### *Distinction between Type I and Type II materials.*

The superconducting elements are nearly all Type I - only Niobium, Vanadium and Technetium are Type II. For the Type I materials, the ones first discovered, complete flux penetration occurs at quite low fields resulting in rather poor critical currents as stated above. Figure 6 shows the periodic table colour-coded according to whether the elements are superconducting or not at normal pressures. As can be seen, approximately half of the metals are superconducting and it is interesting to note that the elements Cu, Ag and Au are not superconducting even though they have the best normal state conductivities of all the metals. A basic rationale for this somewhat surprising fact can be found in (4).

However, for the commercially much more important Type II superconductors, which are mostly niobium alloys and copper oxide perovskites to date, the flux can penetrate easily in some regions whilst other regions are highly superconducting, and completely exclude flux. In fact, this is what enables the Type II superconductors, first classified by L.V. Shubnikov in 1936 (5), to have very high "upper critical magnetic field". The first Type II material (Pb:Bi) was actually discovered in 1930, before the Meissner effect (1933), and of course before the distinction between Type I and Type II was recognised, let alone understood. A convenient way of showing the distinctions between Type I and Type II superconductors is shown in Figure 7 a) and b). In a), the behaviour of a Type I superconductor is illustrated in terms of its response to an applied magnetic field. When the critical value  $H_c$  is reached, the currents responsible for the induced field have reached their critical value  $I_c$ , and the superconductor flips to the normal state, and the induced magnetic field collapses. However, in Figure 7b), showing what happens in the case of a Type II superconductor, there is a lower critical field  $H_{c1}$ , below which all flux is excluded, but as the field is increased between  $H_{c1}$  and  $H_{c2}$ , the superconductor is in the "mixed state" and only partially excludes the flux. When the upper critical field ( $H_{c2}$ ) is reached the flux penetrates completely and the superconductivity collapses and all of the material reverts to the normal state.

The important point is that the Type II superconductors can carry much higher critical currents in the superconducting regions, which are effectively separated from one another by normal regions. This gives rise to the concept of flux lattice vortices, or an orderly array known as the "fluxon lattice". Suffice it to say that if the flux lattice is pinned, where the pinning centres are usually due to lattice defects such as inclusions, impurities, grain boundaries or even radiation defects, then high critical currents are transported. If however, the fluxon lattice starts to move, then this dissipates energy and results in electrical resistance. Hence the crucial feature of the commercially useful Type II superconductors are the values of the critical currents and critical magnetic fields below which superconductivity is maintained, and  $J_c$  and  $H_c$  are again very much interrelated. A current always gives rise to a magnetic field, and a changing magnetic field around a conductor, or superconductor, always gives rise to a current.

The breakthrough in the understanding of superconductivity in Type I materials was formulated in 1957/58 by Bardeen, Cooper and Schreiffner (6) and they received the Nobel Prize in 1972 for this work, which is called "BCS Theory". In the early '60s Type II materials became commercially available (starting with NbZr) and around the same time Bean proposed his "critical state" model (7) for understanding the influence of an applied field on the "mixed state" – the origin of the fluxon lattice - which of course is intrinsic to Type II superconductors. Coupled with the Bean "critical state model", BCS theory is still widely used although it is not entirely adequate for the understanding of the new HTS superconductors, which are all Type II. Also in the early 1960's Josephson (8) discovered that electron pairs could tunnel through the junction between two superconductors separated by a very thin insulator. This work resulted in yet another Nobel Prize in the area of superconductivity in 1973. The applications are in electronic devices known as SQUIDS - Superconducting Quantum Interference Devices – but we do not consider these here because the general use of gold in electronic devices, for bond wires, contacts etc is well known. This rather basic treatment of BCS theory and the Bean model will be sufficient to describe the advent of practical conductors for DC (Direct Current) power applications such as superconducting magnets, although it is not entirely adequate for AC (Alternating Current) applications.

Commercially viable LTS wires, of which the most important are based on Nb:Ti and Nb<sub>3</sub>:Sn alloys embedded in a "normal" metal matrix, first became available in the 1960's. This composite structure is produced by a combination of extrusion and wire drawing processes with heat treatments. Generally, the resulting wires are "multifilamentary" – ie they consist of many long filaments of superconductor embedded in the matrix, which is typically copper. If the critical current is exceeded, the superconductor will suddenly "quench" and the copper matrix has to absorb the

electrical and heat energy because the filaments are no longer superconducting. The presence of the copper matrix is thus essential in the practical implementation of LTS conductors, and it is one of the objectives of this paper to show that HTS conductors also require a "shunt" path in the event of a quench, and this shunt path will generally be silver, gold or an alloy of gold and silver. The objective is to stabilise the conductor by preventing the formation of any local "hot spots" due to inhomogeneities, but also the system must be able to withstand the quench. For superconductors destined for power applications, whether LTS or HTS, the quench behaviour is clearly very important and we return to this point later.

### ***Current commercial applications of Low Temperature Superconductivity.***

The commercial application of low temperature superconductivity is almost entirely to be found in magnets. Superconducting coils are currently manufactured by winding LTS wires around formers, with reinforcement and insulation, and subsequently impregnating them with resin to provide an element of stability and protection. The main advantage of superconducting coils over conventional copper-wound coils is that they consume almost no power whilst being able to develop high magnetic fields for relatively small size. To date, the principal successful commercial applications have been as follows :

1. High field magnets (up to 21T) for physics research, especially solid state physics, and beam steering applications in particle physics.
2. High field magnets for NMR (Nuclear Magnetic Resonance) for molecule identification especially in the life sciences eg for genetics research. State-of-the art is 900MHz, corresponding to 21T.
3. Whole-body scanners using MRI (Magnetic Resonance Imaging) for medical diagnostics purposes. Typically 3 or 4 Tesla magnetic fields.

The necessity for low temperature refrigeration of any devices using LTS (Low Temperature Superconductivity) wire has severely limited more widespread use of superconducting magnets – typical operating temperatures are between 2 and 20K. For example, separation of materials using superconducting magnets is one area where higher temperature operation would be beneficial and probably lead to more widespread industrial uses. Other areas are catheter steering applications in medicine, and “small parts” MRI – for examining knees, elbows etc where the use of the very large whole body magnet is unnecessary. Also, many potential applications of superconductivity for the electric power and generation industry have not been commercialized because of this requirement for low temperature operation. The same is true of the transport industry. MagLev trains are still at the development stage in Japan. A notable exception to this lack of take-up is the use of LTS magnetic separators for industrial purposes - eg for extracting Kaolin. Some of these are used in very hot climates in remote locations, which confirms that helium cooling has reached high levels of reliability. For large magnets, advances in cryogenics have meant that the helium replenishment rate has been reduced to very low levels. Some MRI magnets need topping up with helium only once a year.

A whole new industry has grown up based on the technology of drawing and winding superconducting wires since the 60's. The technology is very advanced but mature, and the enabled applications generate substantial business around the world (9). Just to take one example, the market for MRI is now in excess of 3 Billion dollars per annum, and this would not have been possible without LTS wire. Typically, 200km of wire are used for the fabrication of just one MRI magnet, and there are about 2000 such magnets built per annum. Applications other than MRI magnets include NMR magnets, research magnets, “Big Physics” magnets (eg. for the accelerator ring at CERN), SMES (Superconducting Magnetic Energy Storage) for load levelling and UPS (Uninterrupted Power Supply) and industrial separators.

For the case of very high field magnets for NMR spectroscopy, some of which cost millions of dollars, it is becoming increasingly more difficult to satisfy the market demand for ever increasing field which results in better spectroscopic resolution. There are two important reasons for this which serve to illustrate some limitations of LTS wire and lead us naturally forward to consider HTS. The first of these is that in order to generate more field it is necessary to supply more "ampere-turns" ie operate at either higher currents and/or wind more wire. Apart from the obvious limitation on current – the critical current - the problem is that winding ever more turns leads to an increased field at the center of the magnet but this in turn reduces the critical current attainable. Thus adding further outside turns to the coil, which requires substantial lengths of high quality wire, becomes progressively less effective at increasing the desired field. This “law of diminishing returns” has severe economic consequences for high field

magnets for physics research and high field NMR magnets, and is a major driving force for examining the possibility of HTS materials, where the critical currents can be much higher in field especially if they are operated at low temperatures. It is very much a case of the law of diminishing returns for the present generation of LTS wires, whereas it turns out that HTS materials have much better in-field characteristics and could be used to make "insert coils" to boost the performance of large NMR magnets with LTS outer coils. The other problem being faced for these very desirable high-field magnets is that the high fields generate enormous forces with the result that stress containment is becoming ever more difficult because the wire does not have sufficient strength to withstand such forces. Again, there is the chance of alleviating this problem with the new HTS materials.

To summarise, the attempts to introduce LTS materials into commercially viable devices other than magnets have largely failed, except for some very specialist electronic devices used for detectors. This is despite the fact that many LTS demonstrators were built in the 70's, especially for applications in the electric power and distribution industry, and, of course, for high speed computing using SQUIDS (Superconducting Quantum Interference Devices). The reason for this is that LTS devices have to be cooled to typically 4.2 to 10K, and this refrigeration penalty is too much for broader application in electrical machines eg. in motors, transformers, generators, cables etc. Even for magnet applications, some of which are reaching their technical limits using LTS conductors, the way forward is to consider HTS conductors to simplify refrigeration and, in some cases, to obtain greatly enhanced performance.

### ***High temperature superconductors.***

The comparatively recent discovery of the high temperature superconducting perovskite oxides by Bednorz and Mueller in 1986 resulted in yet another Nobel Prize (1987), and the critical temperatures for this new family of superconductors rose above liquid nitrogen temperature (77K) for the first time. For a few years many scientists tended to be too preoccupied with finding new materials with ever increasing critical temperatures rather than enhancing the other crucial parameters (critical currents and critical magnetic field) which were clearly at least as important once liquid nitrogen temperatures had been surpassed. The main focus should have been on bringing a practical HTS conductor with high critical current to market as soon as possible, but in fact this took several more years. The new ceramic superconductors were very complex oxide perovskite materials and difficult to process into forms suitable for applications. It was also found that BCS theory and the Bean model did not describe HTS materials quite so well, but this leads us to considerations beyond the scope of this paper.

Thin films of YBCO (Yttrium Barium Copper Oxide) with extremely high ( $J_c > 10^6 \text{ Acm}^{-2}$ ) current density were demonstrated on single crystal substrates (eg sapphire, and stontium titanate) using a number of different physical vapour deposition techniques at first. This work continued for electronic device applications, eg HTS SQUIDS and Fault Current Limiter (FCL) devices, but for a few years there seemed to be no way of producing a flexible wire or tape based on YBCO. In contrast, it was found that another compound, BSCCO (Bismuth Strontium Calcium Copper Oxide), could be packed in powder form into silver tubes and then subsequently processed such that tapes containing a high density of BSCCO superconducting fibres embedded in a silver matrix were produced. (There are clear analogies with the LTS multifilamentary wires where NbTi or NbSn filaments are embedded in a copper matrix.) The processing involves mechanical treatments, such as rolling and drawing, and some very sophisticated heat treatments which allow a controlled oxygen diffusion through the silver to obtain the correct stoichiometry for the BSCCO. (The silver matrix serves a number of other purposes besides mechanical support and these are considered in the section below on Quench Stability.) So-called PIT (Powder-In-Tube) conductors are now commercially available, with variations known as "2212" and "2223" referring to the precise stoichiometry. There are also "dip-coated" variants of BSCCO tapes which may be important in the future. Collectively, these are all known as "First Generation Conductors".

Unfortunately, although  $T_c$  for BSCCO (90-110K) exceeds that of YBCO (85-93K), the behaviour of the critical current in moderate magnetic field even at 77K is such that BSCCO's use will probably be primarily restricted to superconducting cables. This is because nearly all electrical machines have windings, ie coils of wire or tape, and each turn is bathed in the magnetic field generated by all the other turns. This superposition of field roughly increases the external field acting on each section of the tape by the number of turns and the critical current is thus greatly decreased from its self-field value. Operating at lower temperatures, of course, allows one to increase the currents once more, but the refrigeration penalty for the temperature drop required may outweigh the advantages of

high temperature superconductors in the first place, except perhaps for very specialised applications such as the insert coils for high-field NMR magnets.

No processing routes were found for YBCO equivalent to the PIT scenario for BSCCO. However, research into YBCO films continued in the 1990's and a very important distinction between YBCO and BSCCO was made which explained why the excellent  $J_c$  results for YBCO thin films on single crystals were not easily transferable to the case of films on flexible metallic substrates, in the initial attempts to produce a YBCO superconducting tape. It turns out that any grain boundaries in YBCO misoriented by more than a few degrees drastically lower the superconductivity (10). The percolative currents in polycrystalline film have to meander around any high angle grain boundaries or undergo scattering which results in heat and electrical resistance (11), (12). Regions such as this, which diminish the overall superconductivity, are often termed "weak links". Consequently efforts were made to produce textured films of YBCO such that the grains are nearly all just a few degrees away from the c-axis 100 orientation "out-of-the-plane" and just a few degrees away from being oriented perfectly in the a-b plane.

The net result is that in the past six years there has been a sustained effort worldwide to produce so-called "Second Generation" conductors, which consist of a thin film of YBCO (or, more generally ReBCO, where Re denotes a rare earth element) deposited on a flexible metallic substrate, with buffer layers in between – see Figure 8. The performance of short lengths of these tapes even at liquid nitrogen temperatures is very impressive, easily surpassing that of BSCCO in all but the most moderate magnetic fields. Hence the tens of millions of dollars being pumped into this field worldwide to provide a successful, commercially viable scale-up route for YBCO "coated conductor". Once this has been achieved then a whole new raft of applications will be enabled just as for the introduction of LTS wire in the 60's. However, the applications are much broader, because of the higher temperature operation.

Before considering "coated conductor" or "second generation" conductor in more detail, and the importance of gold as a protective layer, we briefly summarize the current commercial position and opportunities for HTS, differentiating between "power" and "electronics" applications.

### ***Commercial applications for HTS.***

During the last fifteen years since the discovery of HTS (13), frequent re-examination of both existing and potential markets for superconducting devices for power applications has taken place and a number of demonstrator devices – motors, transformers, SMES units etc - have been built using BSCCO tape around the world. If operating temperatures are reduced well below 77K, then their performance is reasonable but the self-field limitation at the higher operating temperatures precludes serious commercial interest in most applications. On the other hand, BSCCO current leads for LTS magnets have been a commercial reality for some years now, and BSCCO cables for power transmission in very confined spaces (eg. existing ducts where the conventional copper cables cannot carry an increasing power demand) are already being installed. In the downtown Copenhagen network since 2001, a BSCCO cable has been servicing the power requirements of 50,000 homes. There are now several manufacturing facilities worldwide capable of producing many tens of km of BSCCO "wire" per annum, and there are still improvements in  $J_c$  values. However, the necessity for the silver or silver alloy matrix places a limit on the possible price reduction in the future and there will be limited market penetration in terms of replacement of conventional copper cables. A US DOE (Department of Energy) forecast for HTS wire demand is shown in Figure 9, assuming at least a factor of two improvement in  $J_c$  values from today's materials (14). The demand has been calculated from an analysis of the requirements of HTS in the North American power distribution networks – see Table 1.

Meanwhile in the case of electronic applications YBCO thin films on single crystal substrates have been very successfully demonstrated and commercialization is already taking place eg for narrow bandwidth filters for the base stations of mobile phone networks, and also in SQUIDS for detecting and amplifying minute signals in instrumentation eg in sensors for instrumentation used by earth scientists during geophysical exploration, in medicine for recording brain activity, and in industrial applications for Non-Destructive Testing – NDT. As for the use of LTS in electronic applications, HTS applications in the electronics area require some use of gold for bond wires and contacts etc, but this will not be a major usage and will simply fall under the existing "electronic applications" classification with one possible exception – YBCO thin film fault current limiters, which can really be better classified as power devices. The Connecticut 2001 survey compares and forecasts LTS and HTS usage in the electronics and power sectors, and the most rapidly growing one is the power sector – see Figure 10 and Table 2.

YBCO thin film based FCL devices are already commercially available and serve the purpose of a self-regenerating electrical fuse or circuit breaker, by virtue of the fact that transient currents exceeding the critical current will cause the superconducting film to become normal for short periods, and provided the heat generated can be removed safely and quickly via a protective metallic layer, the YBCO film recovers and returns to the superconducting state. Such devices can be used to protect local power distribution networks and can prolong the design life of power equipment by protecting against surges which could otherwise stress the equipment during fault conditions or peak demand cycles. There is already a market and it is part of the rapidly growing "red" areas (HTS power uses) of Figure 10. The protective metallic film, which is primarily a form of quench protection, is invariably gold for the reasons which will be discussed in the next two sections.

Undoubtedly, the next major commercial advance in the uptake of HTS will be the use of coated conductor in power applications. This may well proceed via niche applications – such as the HTS insert coils required to boost the high-field NMR magnets. For a comparison of the performance of BSCCO and YBCO conductors for a range of fields and temperatures, see (15). Such coils would ideally run in persistent mode, and the YBCO coated conductor is the better candidate from this viewpoint. However it must be emphasised that in most power applications AC losses will be very important. This is an area too complex to consider in this introductory paper.

### ***Coated Conductors – the second generation***

For coated conductors, the thin films of YBCO (or other ReBCO compound) must be smooth and very well textured i.e. as near to the case of a long single crystal as possible. The “c” axis of all the grains must be aligned in essentially the same direction, close to the normal of the plane of the film deposition, and the number of high-angle grain boundaries in the ab-plane must also be minimized, since these also act as “weak links” or obstructions to the percolative supercurrents. The current tries to go around such obstructions, which affects the  $J_c$  values. In order to achieve this well-oriented texture, and smooth surface, there are essentially three approaches, which we consider in turn.

The first is called the “RABiTS” (Rolling Assisted Biaxially Textured Substrate) approach whereby the flexible substrate is itself textured, and subsequently serves as the template for imparting texture to buffer layers and the YBCO layer all of which are deposited epitaxially. Originally conceived by workers at Oak Ridge National Laboratories in the US (16), the RABiTS process consists of fabricating the textured substrate by a series of rolling/reduction operations and heat treatments on nickel and nickel alloys, which have the correct cubic lattice and atomic spacing for successful YBCO growth. The substrate tape is typically between 30 and 100 microns thick, and currently a very successful substrate is Ni:W (17). Buffer layers are required to prevent diffusion of unwanted chemical species, especially ferromagnetic impurities, between substrate and YBCO layer and vice versa. The widely reported buffer layers are CeO (Cerium Oxide) and YSZ (Yttrium Stabilised Zirconia), but many other buffer layers and combinations thereof are under consideration. The layer thicknesses are much less than the substrate thickness, and this gives rise to a  $J_c$  (engineering current density) value much less than the  $J_c$  of the YBCO film itself. (The concept of  $J_c$  is just as valid for LTS conductors and BSCCO, although the proportion of superconductor to supporting matrix is much higher for LTS wires and BSCCO.) The result is a tape typically 50-100 microns thick having excellent texture, with the grains all having their c-axes pointing in the 100 direction, and having very little in-plane misorientation in addition. Physical vapour deposition processes such as thermal co-evaporation (18) have been successfully used to produce RABiTS-based coated conductors but there are many other film deposition techniques under investigation.

The second approach starts with a smooth polycrystalline substrate where the grains are randomly oriented, usually Hastelloy, followed by a buffer layer deposition method whereby texture is induced during the deposition process. This first textured buffer layer can be deposited by IBAD (Ion Beam Assisted Deposition) or IAD (Ion Assisted Deposition). In IBAD (19), (20), during deposition of a YSZ film, a precisely angled ion beam is used to bombard the surface and force the buffer layer, usually YSZ or MgO, to grow in the preferred orientation. Shadowing, channeling and resputtering effects have been suggested as explanations for this textured growth. In the case of IAD, the ions are directed from a plasma in an unbalanced magnetron (21). The IBAD technique is much more developed and gives excellent results but many regard it as rather slow. However, only a thin seed layer is required on which other thicker buffer layers can be grown. IAD is showing promise and may be capable of much higher rates, but the degree of texture attainable is not yet sufficient.

The third approach, ISD, is also very promising – see for example. Again the substrate is untextured, but the buffer layer is deposited by Pulsed Laser deposition (PLD), or by Thermal Evaporation (TE). Texture is achieved at specific deposition angles for much the same reasons as for IBAD. For PLD, the precise angle can be achieved by ensuring that the substrate is positioned correctly with respect to the laser plume (22), whereas for TE shadow masks can be used to select or collimate the vapour (23).

The objective is always the same – to produce a textured buffer layer on top of which further buffer layers and the highly superconducting YBCO films can be grown. Otherwise the superconducting properties will resemble those of bulk material with  $J_c$  values in the range  $10^2$  to  $10^4$   $\text{Acm}^{-2}$  rather than the much higher performance thin films deposited on single crystals for superconducting electronics applications, where  $J_c$  can reach values between  $10^6$  and  $10^7$   $\text{Acm}^{-2}$ . Values in the range  $3 \times 10^5$  and  $3 \times 10^6$   $\text{Acm}^{-2}$  are currently regarded as satisfactory targets for coated conductors, depending on application.

Starting with a textured substrate, as in the RABiTS approach, may well prove to be the most economical solution and lengths of several hundred metres of high quality substrate are already being produced using large scale production machinery. On the other hand, the best results to date, in terms of quality of the YBCO layers, have been produced using IBAD substrates. A major advantage of the IBAD and ISD approaches is that the substrate is stronger, and can therefore be thinner, than the RABiTS materials. Thinner substrates obviously lead directly to higher  $J_c$  values, for given  $J_c$  and YBCO layer thickness values.

Meanwhile, the major technical issues for scale-up of the tape, complete with buffer layers, YBCO film and metallic protective layers, are concerned with continuous processing of long lengths using the various film deposition techniques such as sputtering, thermal evaporation, CVD (Chemical Vapour Deposition), sol-gel etc etc. Good progress is now being made and 100m tapes will probably be available in the time scale of 1-3 years, with one km tapes following perhaps 3-5 years behind (24). However, there is an alternative approach (25), called the "3-C's approach" which has recently emerged which seeks to eliminate the requirement for long lengths of coated conductor by depositing and patterning multilayer films to make standardised modules using cylindrical substrates. The cylindrical modules form the basis of electrical machines – the new approach is not so much targeted at making cables, but there are possibilities in this area.

Whatever the precise details of manufacture of the coated conductor, including the 3-C's approach, it is absolutely imperative to have a metallic protective layer on top of the YBCO to act as a stabilizing layer in the event of local fluctuations when operating near the critical current. Either gold or silver is currently used, for very good technical reasons. This additional layer is not a big technical problem to deposit using any number of known techniques, but it is an important part of the overall structure and is highly likely to be the most expensive part when commercial exploitation starts in earnest. It is therefore possible to predict a large consumption of the gold or silver (or both) in the metallic protection layer in the future. Before attempting to calculate this consumption, we must consider "quench stability" in more detail.

### ***Quenching and quench stability – a comparison between LTS and HTS***

Commercially available LTS wires (NbSn and NbTi), and commercially available HTS tapes (BSCCO) are both composites. For LTS wires, the superconducting fraction is in the form of long continuous filaments embedded in a metal matrix, usually copper. If the critical current is exceeded, the filaments flip to the normal state and now a large transient current has to be mostly carried by the copper matrix, with consequent Joule heating effects. This is known as a "quench". In the worst case, the temperature of the wire can increase such that it melts, and even in the best case there will be boil-off of expensive liquid helium. High field superconducting magnets can store megajoules of energy, and so the problem of "quench stability" is taken very seriously. Any local inhomogeneity or disturbance giving rise to a local increase in electric field or a temperature gradient can potentially give rise to a quench, and therefore the thermal and electrical design of the overall conductor is very important. Copper has excellent electrical and thermal conductivity and serves to stabilise the embedded superconducting filaments. However, the situation for LTS is further complicated by the fact that at low temperatures the behaviour of metals, even the non-superconductors, has a number of anomalies and transitions, albeit generally not so sharp as the superconducting transition. Thermal conductivity can be a strong function of temperature at these low temperatures. Also, the specific heat capacity of copper is three orders of magnitude lower at very low temperatures than at 77K, a typical operating temperature for HTS. Whilst these "anomalous factors" greatly reduce the refrigeration power

necessary to keep the LTS system cold at these very low temperatures – a major reason for the success of large superconducting magnets, such as those used in MRI - it does mean that LTS systems have more severe stability problems than their HTS counterparts are likely to have in the future.

Nevertheless, HTS tapes must also be stabilised against unwanted quenches. For the BSCCO tapes, this is achieved by embedding the "colonies" of micaceous BSCCO platelets in a silver or silver alloy matrix. Usually, the long colonies are referred to as fibres although they are generally flat and may well be discontinuous – making operation in "persistent current" mode very unlikely. If the HTS material starts to go "normal", because of excessive or transient currents, then clearly all this current must be transferred to the matrix because the superconducting oxide is now in its normal state and therefore very poorly conducting compared with the silver matrix. Silver is an excellent conductor, both electrically and thermally and acts as a "shunt path" for any excess current. It is also compatible with the high temperature oxidation processes required in the manufacture of BSCCO tapes because oxygen can diffuse rather easily through silver and thus BSCCO stoichiometry can be achieved. At HTS operating temperatures, there is no anomalous behaviour of the metal matrix involved near the superconducting transition temperature of the superconducting oxide, and therefore HTS conductors, even at the present stage of development, are inherently more stable when operating near their critical current limit and especially under AC or transient conditions – a major criterion for power applications.

In summary, the metallic matrix plays a very important role for LTS and First Generation HTS, not just as a structural component during processing and in the final form. Its main task in service is to suppress any tendency of the wire or tape to "quench" when operated near its critical current. Such a quench will begin at some inhomogeneity or disturbance in the system, and if not suppressed will quickly propagate through the system, perhaps with disastrous consequences. In the event of a complete quench, when the superconductor becomes normal, very high currents can be forced to flow in the metal matrix and the temperature rise due to Joule heating can be catastrophic. The ability of the matrix material to suppress electric field and thermal gradients depends on its electrical conductivity, contact resistance, thermal conductivity and, in terms of acting as a heat sink and minimising temperature excursions at a potential source of quenching, its specific heat capacity. Copper, silver and gold are the prime candidates for this purpose, although copper is not compatible with the HTS materials, partly because of its oxidation characteristics. It is also interesting to note that copper, silver and gold are not ferromagnetic – a very important factor when considering AC losses, which are beyond the scope of this paper.

This sets the stage for consideration of the protection layer for coated conductors, which of course have a substantially different structure from that of LTS wires or BSCCO tapes. There is no "matrix material". Instead there is a "protection" or "shunt" layer in contact with the YBCO layer and this is most frequently gold eg. (26), (27) but silver has also been used (28) and we now compare the two.

#### *Comparisons between gold and silver for the protective layer.*

The purposes of the protective metallic layer, also known as the "shunt layer" which, in conventional coated conductor tape design is the final layer immediately on top of the YBCO superconducting layer are generally stated thus :

1. to prevent the formation of localised hot spots in cases where the critical current in the YBCO layer is exceeded momentarily or locally
2. to equilibriate the electric field between the superconducting layer and tape substrate when the transport current is near its critical value

The aim is to prevent a superconducting "quench" which occurs if the critical current is exceeded resulting in an instantaneous transfer of the current from superconducting layer into protective layer. Exceeding the critical current even locally will inevitably result in a temperature increase as the superconductor reverts to "normal", with substantial electrical resistance and joule heating. A thermal runaway situation (higher temperature, more electrical resistance, more joule heating, higher temperature etc etc ) ultimately leading to destruction of either YBCO or metal layer is to be avoided, whereas a reversible transition, without destruction, can be tolerated and indeed is the mechanism governing the behaviour of so-called FCL (Fault Current Limiter) devices which have self-limiting behaviour and can be regarded as a "self-regenerating electrical fuse". The switching behaviour of FCL devices with a gold protective layer has been examined in some detail (29), but it is very important to remember that in such

devices the YBCO film is in excellent contact with the single crystal sapphire substrate with its excellent thermal conductivity at the operating temperature of 77K. Consequently, the gold film is primarily used for electrical purposes and its thermal role is minimal. For this reason it can be thinner than for coated conductors.

The key question is “What are the intrinsic properties of the shunt layer relevant to 1. and 2. above?”

Obviously, high thermal conductivity is required to suppress the formation of hot spots by conducting localised heat away rapidly, preventing extreme temperature excursions which could lead to melting in the worst case. Also high electrical conductivity is required to maximise the effect of the shunt and to prevent localised high potentials which could lead to electrical breakdown in the worst cases, when the critical current is exceeded, and result in permanent damage to the materials. For metals, where the thermal conductivity and the electrical conductivity are both essentially governed by the same entity – the conduction electron’s transport characteristics – and there is the well-known “Weidemann-Franz Law” which states that the ratio of thermal conductivity to electrical conductivity is a constant over a very wide temperature range. Consequently silver and gold, both having high electrical conductivity, also have high thermal conductivity. (Copper is similarly endowed, but it is not suitable here because it is not oxidation resistant enough for the film deposition stages.) Gold has lower conductivity, both thermal and electrical, than silver by about a factor of 0.75, but in our opinion this is more than adequately compensated by a factor of two higher specific heat capacity at liquid nitrogen temperatures, allowing the gold layer to absorb twice as much energy as a silver layer of similar thickness for the same temperature rise. This is in turn a consequence of the increased density of gold – almost a factor of two. This is clearly because both gold and silver have almost the same ionic radius and the same FCC structure, but gold has nearly twice the atomic weight. Additionally, the lattice matching of gold is closer to that of the underlying YBCO film and nickel substrate, and the linear expansion coefficient is closer to that of the YBCO film and nickel substrate too. See Table 3 for the important comparisons.

The above phenomenological model needs to be described mathematically and made quantitative. There is at least one model in the literature (30) which attempts to calculate the interchange of current between the HTS film and shunt layer using analytical and finite element methods, but this is concerned more with equivalent circuit models and contact resistance considerations for gold layers and no comparisons are made with silver.

### ***Ballpark calculations of tonnage of gold required.***

The first calculations of future gold usage for the protective layer application has proceeded in three ways, giving essentially the same results. The starting point is to choose a value for the thickness of the layer deemed to be adequate to give sufficient protection. Typical values in the literature range from 0.3 to 3 microns, with the higher performance YBCO tapes needing thicker protective layers, obviously. A convenient value to take is one micron, and a convenient tape geometry is one cm wide with a one micron thick YBCO layer with a current density of one million amps per square cm in self-field at 77K. This has been the typical target structure for several years and has now been realised by a number of groups around the world, although there is no universally agreed layer thickness.

Such a tape will carry 100A at 77K, and as much as 1000A at 4.2K, requiring much more protection (a thicker gold layer), but we restrict the argument here to the higher temperature usage. A one metre length of this tape will have a gold layer volume (length × width × thickness) of (100cm × 1cm × 0.0001cm) ie. 0.01 cc. Since the density of gold is 19.3 gm/cc, the mass of gold used is about 0.2 g for every metre of tape manufactured.

We now proceed to estimate usage of gold from three different forecasts of coated conductor usage :

1. A standard superconducting MRI magnet uses 200km of LTS wire, and there are approximately 2000 such magnets made every year, representing half of the world’s use of superconducting wire. Assuming a direct replacement scenario, which is unlikely from a technical standpoint, but nevertheless serves as a useful starting point, the weight of gold required for the one micron thick protective layer is :

$$0.2 \times 200,000 = 40,000\text{g} = 0.04 \text{ metric tonnes per magnet.}$$

For 2,000 magnets (50% of the world’s use of LTS wire), this equates to 80 tonnes per year.

2. The production capacity of the largest US BSCCO plant (American Superconductor) will be 20,000km by 2010, but most observers hold that this will translate directly into YBCO coated conductor capacity if certain key scale-up problems can be solved and the tapes carry 200A, requiring double the protection. If one assumes that the world demand will be a factor of ten greater than the US demand, then the weight of gold required will again be 80 tonnes per year, this time assuming a two micron gold layer thickness because the current requirement in the tapes will be at least 200A..
3. The US DOE (Department of Energy) also forecasts a 20,000km per year usage for the US power distribution network alone by 2020, and again this translates into a factor of ten greater worldwide, and again results in a figure of about 80 tonnes per year for a two micron gold thickness. However, it is likely that other uses, for example, in transport (Maglev trains, lightweight transformers and ship's motors etc), will be significant too, and another order of magnitude use is conceivable if HTS is adopted in a range of markets.

Clearly, a crucial point is the thickness of gold required for protection. This may vary from application to application depending on the risk scenarios. One micron thickness was assumed here for the first calculation – replacement of existing MRI LTS wire. For the other calculations, which relate to future uses of coated conductor, a two micron layer protective thickness has been assumed because as the current carrying capacity requirement is increasing, the protective layer thickness will advance in proportion. A combination of experimental tests and modelling work is required to determine the effect of varying the thickness on the degree of protection afforded, and at the end of the day it will be a judgement made on techno-commercial grounds.

### *3-C's concepts – the alternative approach to coated conductors*

Very recently, there have been radically new concepts proposed for coated conductors at international conferences (31), (32). These are known as the "3-C's" concepts. A radically new approach to the fabrication of electrical machines based on coated conductor has been developed. Instead of long lengths of coated conductor tape being wound into coils in a conventional manner, a combination of thin film deposition and patterning techniques is used with an essentially coaxial cylindrical geometry to produce multilayer coils. These patterned coated conductor cylinders can subsequently be configured in different ways to form a variety of superconducting electrical machines all based on highly manufacturable "standard" cylindrical modules with high engineering current density. There is still the texture requirement for the films deposited on cylindrical formers, and many of the materials considerations are the same, although the new ideas greatly alleviate the problems associated with the thermo-mechanical properties of long length coated conductors, including handling and storage considerations. The immediate systems benefits include high engineering current density (no repetitive wasted substrate) and low ac losses.

The cost benefits of such standardized manufacturing may be very significant in future applications of coated conductor, but a principal driving force is that the scale-up to long lengths of coated conductor is proving very difficult worldwide whereas the measured properties of short samples are excellent for many applications. The 3-C's approach is expected to accelerate the development and use of coated conductors in electrical machines considerably, reducing time-to-market. See Figure 11 for a schematic test structure which will demonstrate i) fault current limiters (inductive and resistive) ii) transformers (step-up and step-down) iii) energy storage magnets and iv) a linear motor module. This captures the essence of the invention – a unified approach to different electrical machines.

The importance of the protective metallic layer remains the same as for the long lengths approach, but some of the details are different. Because of the emphasis on YBCO multilayers, which would be subjected to the various heat treatments during fabrication, it is increasingly likely that specialized silver-gold alloys would be developed, the precise composition of which would govern the retention and uptake of oxygen for the different layers of the coil. For example, inner layers may be subjected to more heat treatments than the outer layers deposited later, and this may require a different regime of oxygenation with different degrees of containment or access to preserve or reach the correct stoichiometry. Nanoengineering and microengineering concepts will be involved in the development of specific structures which facilitate a true YBCO multilayer approach.

## *Conclusions and Recommendations*

In this paper we have traced the history of LTS and HTS, from a technical and commercial standpoint, and have highlighted a particular area where gold is likely to have an important role to play in the future – as the protective layer of choice in the new generation of HTS conductor presently under development for power applications. The gold tonnage requirement for either the long tape coated conductor methods, or the emerging alternative approach of coating rotating cylindrical formers, is predicted to be very substantial and dwarves any demand for gold in any superconductor devices destined for applications in the electronics area.

The main alternative to gold for the protective layer is silver, and more work needs to be done on comparing these two candidates. In the author's view, it is likely that a range of silver-gold alloys will be required for the multilayer technology being proposed, especially for the 3-C's approach. However, even for the mainstream long length coated conductors, the fundamental attributes of gold and silver need to be compared by both modelling and experimental methods in order to build up an understanding of the thicknesses required as a function of the level of protection demanded by a plethora of applications, some of which – current leads and fault current limiters – are already commercial realities.

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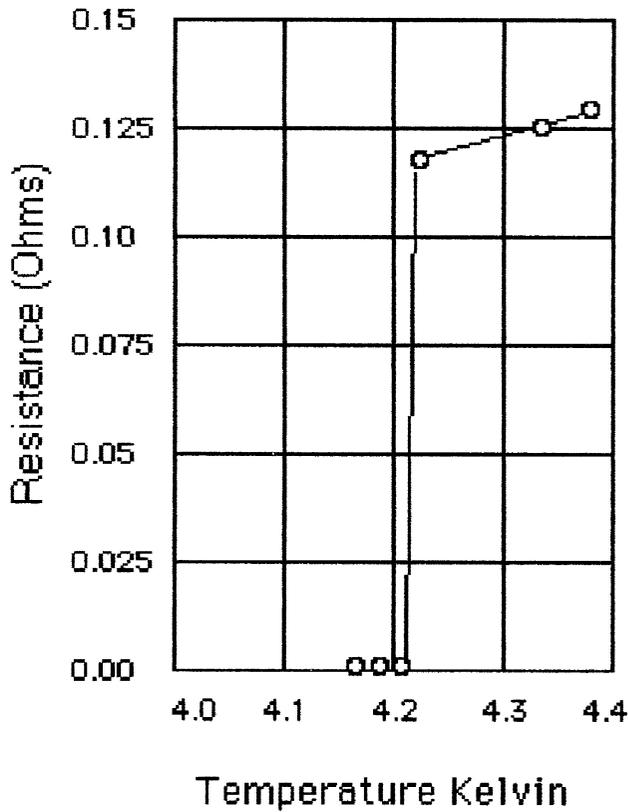


FIGURE 1 : Omnes result for Hg.

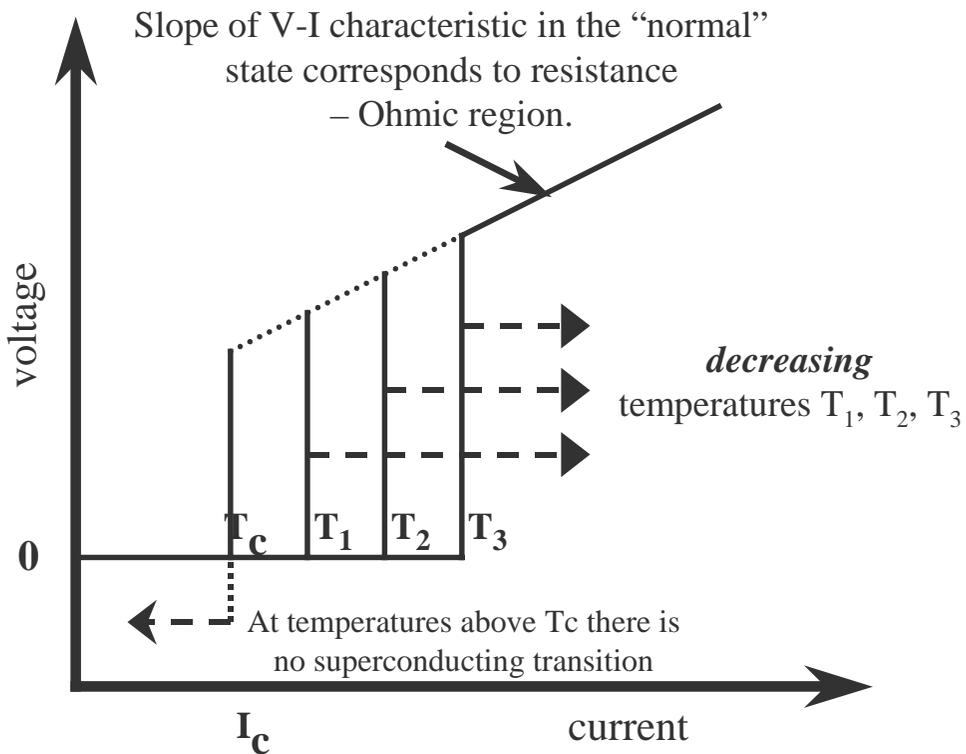


FIGURE 2 : Showing how critical current increases as temperature is decreased below  $T_c$ .

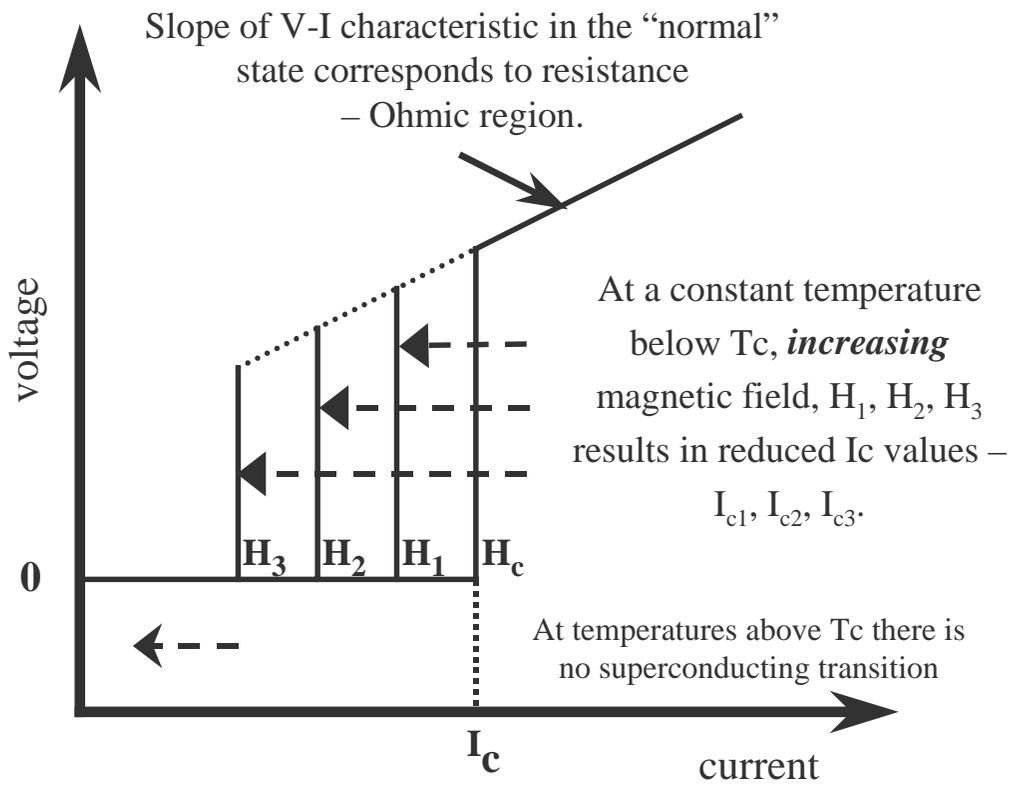


FIGURE 3 : Showing how critical current decreases as magnetic field is increased above  $H_c$ .

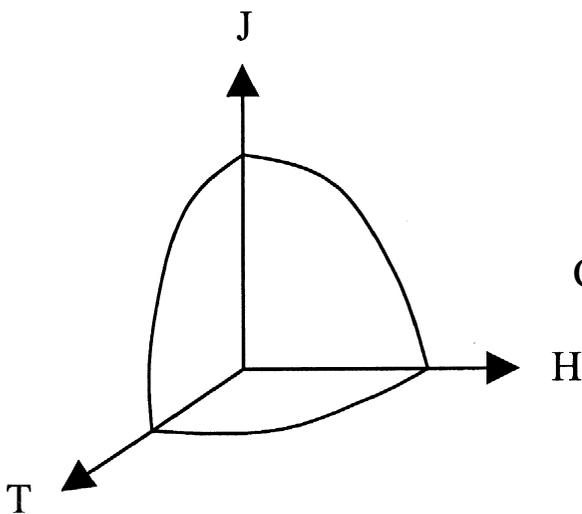


FIGURE 4 :  
Critical Surface Phase Diagram



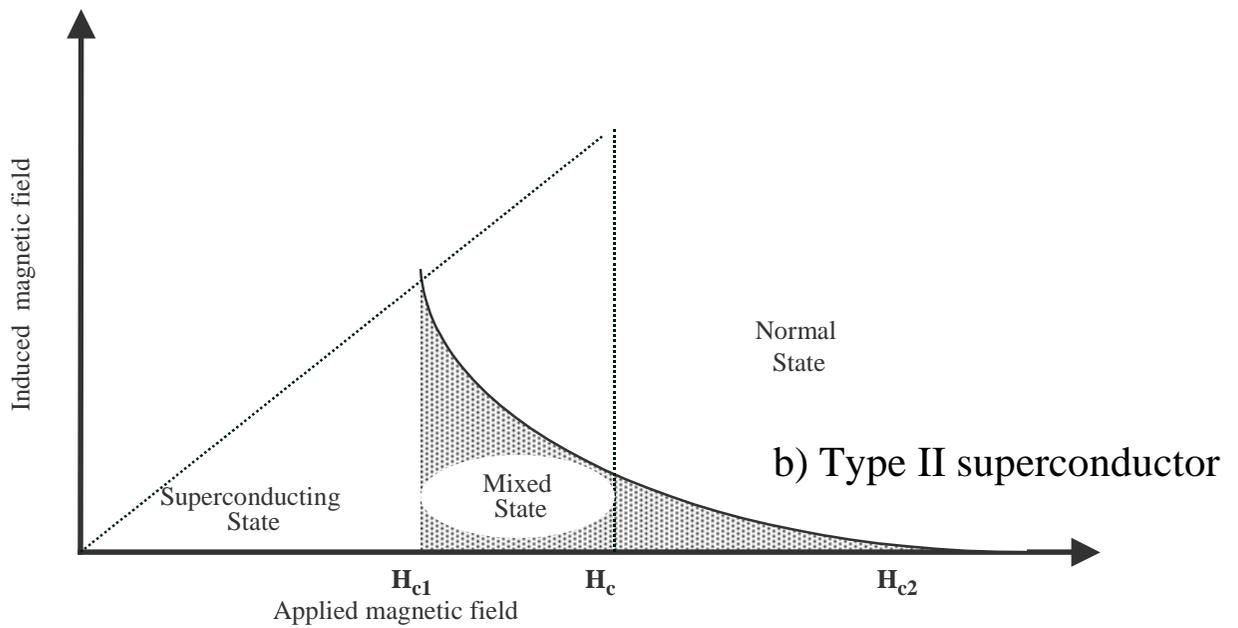
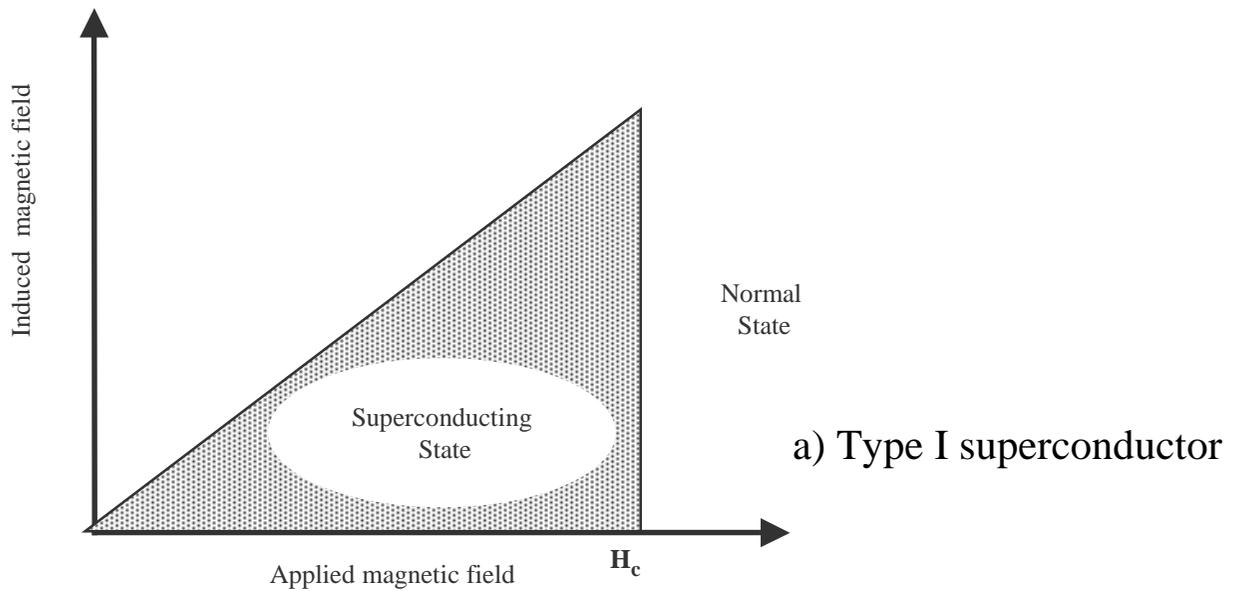


FIGURE 7 : Flux exclusionThe Meissner Effect – comparison of Type I and Type II materials..

- A new generation of HTS superconductor consisting of a flexible metallic substrate, a buffer layer(s) a YBCO coating for high  $J_c$  and excellent performance “in field”, AND a metallic protective overlayer.
- The buffer and YBCO layers are always textured.
- The substrate may be textured (RABiTS), or texture may be induced in the first buffer layer (eg by IBAD or ISD).

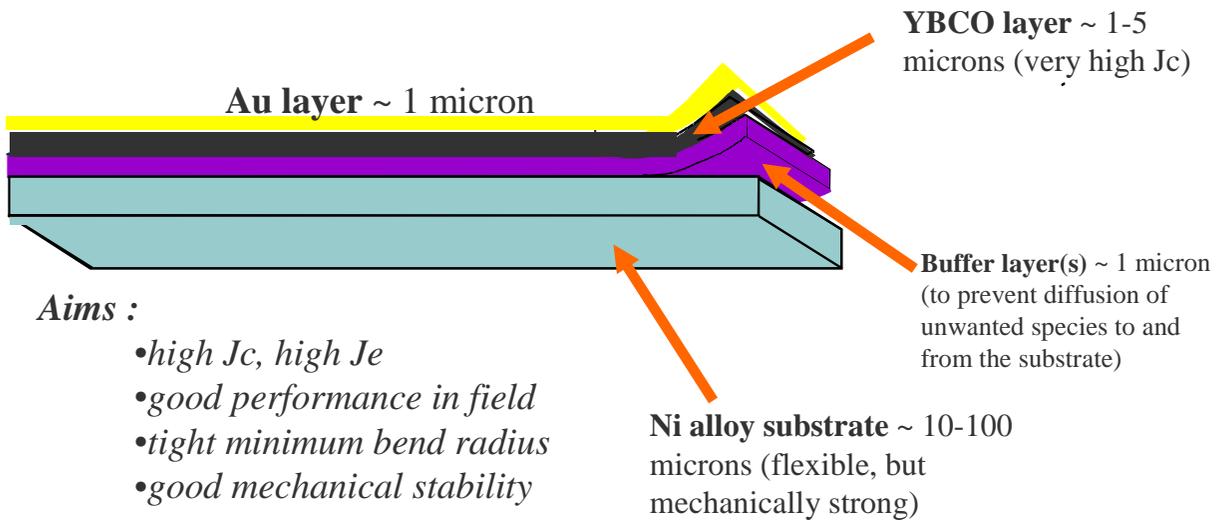


FIGURE 8. Structure and Principle of Coated Conductor

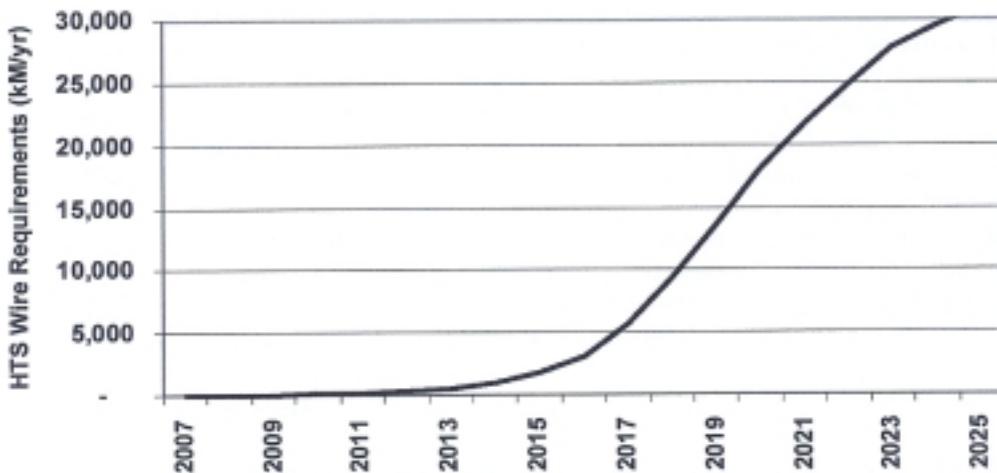


FIGURE 9 : US DOE forecasts for HTS wire demand

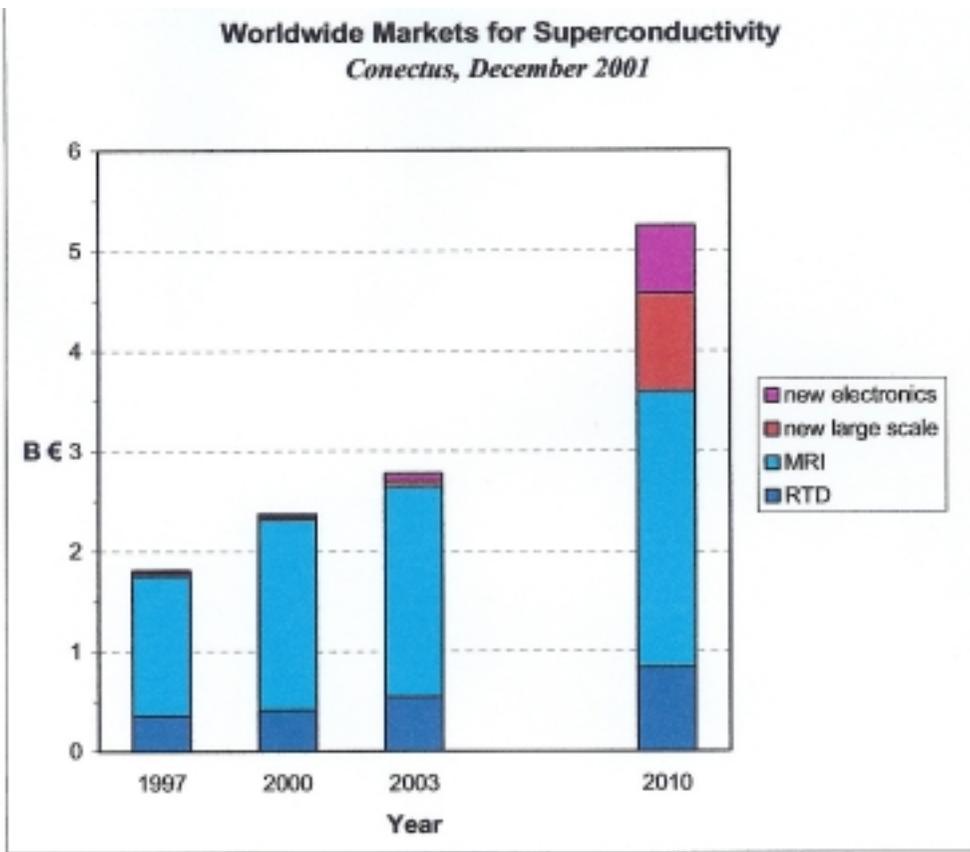


FIGURE 10 : Extracts from Conectus Survey Dec. 2001

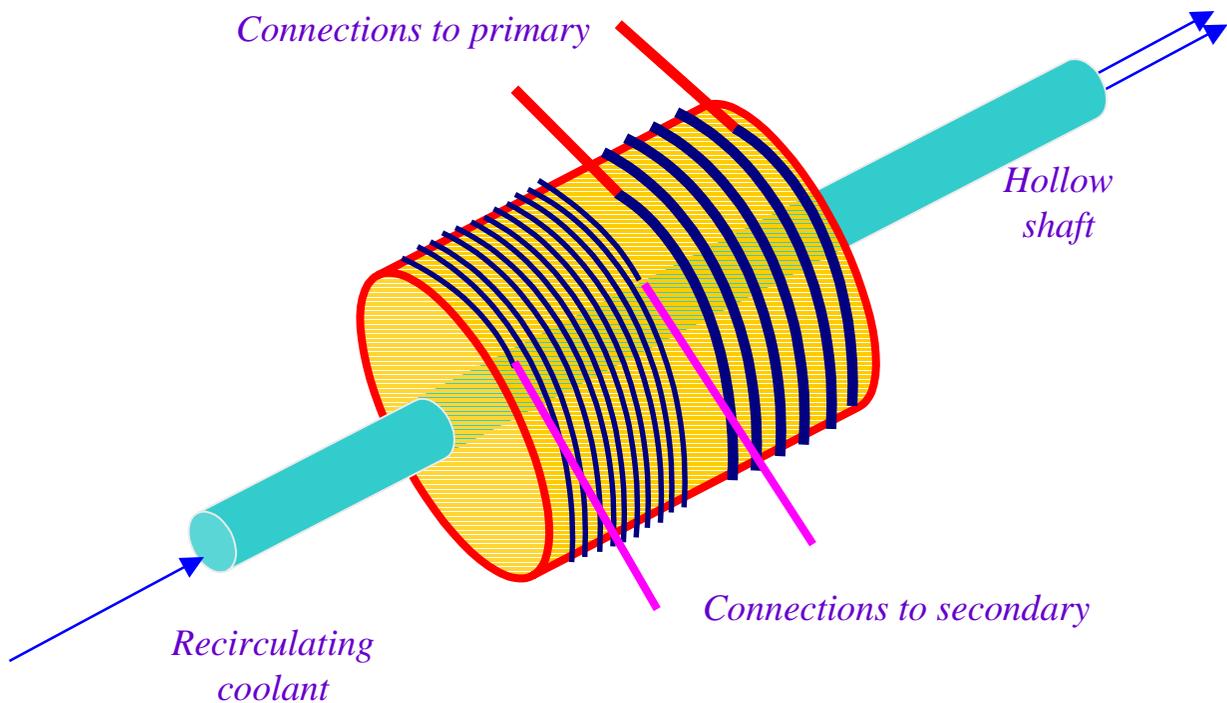


FIGURE 11 : 3-C's proposed single layer test structure

**Projected Market for HTS Devices (Thousands of Dollars)**

<b>Year</b>	<b>Motors</b>	<b>Transformers</b>	<b>Generators</b>	<b>Cables</b>	<b>Total</b>
2011	228	0	6,926	4,117	11,270
2013	956	0	24,710	14,405	40,071
2015	4,025	243	83,634	48,335	136,236
2017	15,399	1,451	227,535	135,001	379,386
2019	50,968	9,353	445,693	318,844	824,857
2021	108,429	56,081	592,904	488,783	1,246,196
2023	148,770	222,277	656,499	570,326	1,597,872
2025	164,072	390,964	675,656	586,284	1,816,975

Table 1 : DOE Forecasts for HTS Devices for US National Distribution System.

<b>Worldwide Markets for Superconductivity &amp; Market Shares for Low-Tc / High-Tc Superconductors (in M €)</b>				
<b>Business Field</b>	<b>Year 1997</b>	<b>Year 2000</b>	<b>Year 2003</b>	<b>Year 2010</b>
Research & Technological Development (RTD)	355	415	550	840
Magnetic Resonance Imaging (MRI)	1400	1900	2100	2750
<b>TOTAL of RTD &amp; MRI</b>	<b>1755</b>	<b>2315</b>	<b>2650</b>	<b>3590</b>
New Large Scale Applications	35	25	55	980
New Electronics Applications	20	30	75	680
<b>TOTAL of Emerging New Businesses</b>	<b>55</b>	<b>55</b>	<b>130</b>	<b>1660</b>
<b>TOTAL WORLDWIDE MARKET</b>	<b>1810</b>	<b>2370</b>	<b>2780</b>	<b>5250</b>
Market Shares for Low-Tc Superconductors	1805	2355	2730	3650
Market Shares for High-Tc Superconductors	5	15	50	1600

TABLE 2 : Extracts from Conectus Survey Dec. 2001

property	comment	units	copper	silver	gold	nickel
symbol			Cu	Ag	Au	Ni
atomic no			29	47	79	28
atomic wt		atomic mass	63.54	107.88	196.97	58.69
lattice parameter		Angstroms	3.61	4.09	4.08	3.52
density		g/ml @ 20 deg C	8.9	10.5	19.3	8.9
electrode potential		volts	0.34	0.80	1.68	0.23
melting point		deg C	1085	962	1064.0	1455
specific heat	or heat capacity	cal/deg/mole	0.0035	0.0146	0.0350	
<i>(low temp)</i>			<i>(-250 deg C)</i>	<i>(-238 deg C)</i>	<i>(-185 deg C)</i>	
specific heat	or heat capacity	cal/deg/mole	0.0909	0.0556	0.0303	0.106
<i>(high temp)</i>			<i>(0 deg C)</i>	<i>(0 deg C)</i>	<i>(18-99 deg C)</i>	<i>(0 deg C)</i>
therm expan coeff	at 20 deg C	ppm per deg C	16.5	18.9	14.2	13.4
therm conductivity	at -100 deg C	watts/cm deg C	4.05	4.22	3.3	0.97
therm conductivity*	at 0 deg C	watts/cm deg C	3.85	4.18	3.1	0.91
electrical resistivity	at -195 deg C	ohm cm*10E-6	0.2	0.3	0.5*	0.55
electrical resistivity	at 0 deg C	ohm cm*10E-6	1.56	1.51	2.04	6.14

**Table 3 : Comparisons between Cu, Ag, Au and Ni.**  
(Cu is included as a reference in terms of electrical and thermal properties,  
and Ni is included because it is the base substrate for coated conductors.  
Nearly all data is from Kaye and Laby.)