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Current trends in the development and applications of superconducting materials

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Abstract. The discovery of the phenomenon of superconductivity by Kamerlingh Onnes in 1911 was the first indication of the possibility of electrical conduction without any associated Joule loss. The technological application of the property (which was essentially manifested at liquid helium temperatures) had to await the development of stable superconducting materials capable of withstanding high currents and large magnetic fields. Although many materials – elements, alloys, ternary chalcogenides, and recently oxides – have been found to be superconducting, only a few of them have received attention for significant applications. This is based on three important parameters namely T_c, the transition temperature, H_{c_2}, the upper critical field and J_c, the critical current density. T_c and H_{c_2} are considered intrinsic to the material, while J_c is influenced by the microstructure, and has to be optimised during fabrication of the material in the useful form. On these considerations, Nb–Ti, Nb_3Sn and V_3Ga have emerged as proven materials for significant applications while $PbMo_6S_8$ is still under development. Despite the fact that all these materials have to be used only at liquid helium temperatures on account of their low T_c, major developments have taken place in harnessing particularly the niobium alloys to produce superconducting magnets.

Towards the end of 1986, a break-through has been achieved in the direction of raising the T_c. Many ceramic oxides, notably $Y_1Ba_2Cu_3O_7$, have exhibited T_c in the vicinity of 100 K. These materials have also been shown to have high H_{c_2}, about 180 Tesla. Attempts are now being made to realise a high J_c. It is too early to say whether such materials can be fabricated in suitable forms capable of carrying high currents.

Among the major areas in which superconducting materials have so far been used, mention should be made of superconducting magnets for high energy particle accelerators, magnetohydrodynamic power generation, magnetic resonance imaging, and fusion research programmes. In other potential applications such as motors and magnetically levitated transportation, economic break-even has not been achieved, mostly on account of the need to use liquid helium. The discovery of the high temperature superconductors capable of operating at liquid nitrogen temperatures thus promises a revolution in electrical technology.

The paper reviews the development and applications of superconducting materials, with reference to work being done in India.

Keywords. Superconductivity; materials; applications; oxide superconductors.

1. Introduction

Superconductivity refers to an ordered state of coherent and collective behaviour among the conduction electrons in a metal. According to the most successful theory of superconductivity due to Bardeen, Cooper and Schreiffer (BCS), the electrons in the superconducting state are bound together in pairs overcoming their coulomb repulsive interaction under the mediatory influence of the metal lattice. Each pair

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consists of two electrons (Cooper pair) of equal and opposite momenta and spins, and the pairs themselves remain correlated in their motion throughout the volume of the superconductor leading to the collective behaviour.

The consequences of this long range order are enormous and are of great relevance to technology. First is the zero resistance or the infinite electrical conductivity of the superconductors. Historically, it was through this property that the phenomenon of superconductivity first came to be known. The Dutch physicist Kammerlingh Onnes, cooling the element mercury to the low temperature of 4 K in the year 1911, found its electrical resistance to completely vanish. According to this property, a current induced in a superconducting ring or a loop persists forever without decay, offering the attractive possibility of the production of intense magnetic fields without Joule losses.

Here one might add that the infinite conductivity of superconductors is not an extension of the increasing conductivity of the normal metals as they are cooled to low temperatures, but is a direct consequence of the electron pairing and the long range order caused by the strong electron–phonon interaction. For example, Cu, Ag and Au which are good electrical conductors (indicative of weak electron–phonon interaction) do not become superconductors, down to the lowest temperatures investigated (200 μK). It is now believed that there could also be other non-phonon pairing mechanisms that might lead to superconductivity.

The second consequence that has a bearing on technology is the flux quantisation. It can be shown that the magnetic flux in a closed super-conducting loop can only exist in integral units of flux quantum ($\Phi_0 = hc/2e = 2 \times 10^{-15}$ Wb).

The third consequence of the long range coherence of the electrons in a superconductor is the so-called Josephson tunnelling, theoretically predicted by Brian Josephson in 1962 and later immediately verified experimentally by others. When two superconductors are separated by a weak link such as a thin insulator, the electron correlation in the first superconductor extends into the other across the junction. Because of this a supercurrent can flow across the junction up to a maximum value without any voltage developing. When the current exceeds the critical value, a voltage appears with a switching time smaller than 10^{-11} s. Also, the junction starts emitting radiation according to the Josephson voltage–frequency relation,

$$h\nu = 2eV.$$

By impressing suitable voltages across the junction, the configuration can be used as a radiation detector in the frequency range covering radio frequency to infrared.

The properties mentioned above offer the possibility of a wide range of applications in technology (figure 1). They include large scale power transmission lines carrying over 10^6 A of electric current, stored energy greater than 10^{12} J, magnetic fields of over 20 T, micron scale devices and sensors capable of measuring 10^{-17} V or 10^{-15} T, radiation detectors and magnetic shields that potentially produce zero magnetic fields (See, for instance, Schwartz and Foner 1977).

Superconductivity is not a rare occurrence and thousands of materials exhibit superconductivity below a certain temperature T_c characteristic of each material. Although the BCS theory provides a satisfactory explanation of the phenomenon, only empirical rules have guided the synthesis of new materials. For example certain types of crystal structures like the A15 (Nb_3Sn), rock-salt (NbN) and Laves phases favour enhanced T_c. Matthias advocated the valence electron-to-atom ratio as a good

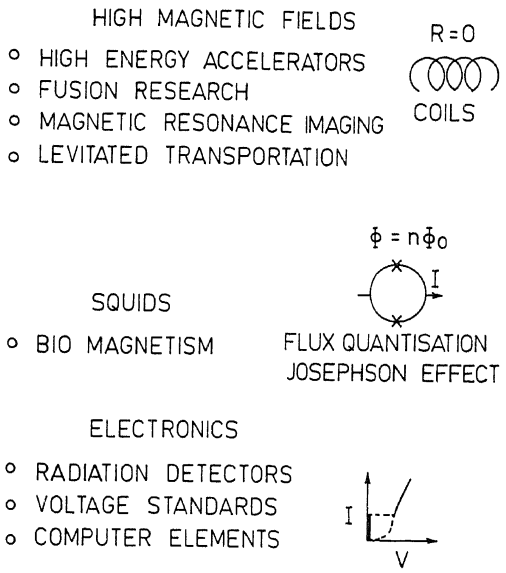

Figure 1. Applications of superconductivity.

guide to predict transition metal superconductors. Enhancement in T_c was also associated with structural instabilities and associated phonon anomalies. Prior to 1986, however, all the known superconductors were confined to low temperatures, with Nb_3Ge having the highest T_c of 23·2 K. It was even thought that 40 K might be the upper limit for T_c based on the electron–phonon mechanism. As of now, the use of superconductors in technological applications necessarily involves the rather complex liquid helium technology. Yet major developments have taken place in the utilisation of superconductors in many areas of technology (figure 1).

Towards the end of 1986, a significant breakthrough was achieved in the direction of raising the T_c. Since then, many ceramic oxides, notably $Y_1Ba_2Cu_3O_7$, have exhibited T_c in the vicinity of 100 K, well beyond the temperature of liquid nitrogen (Wu *et al* 1987). Because of the ease of handling of liquid nitrogen and the relatively low costs involved, all the possibilities of superconductors in technology are being looked at with renewed enthusiasm. There are also indications of the appearance of new materials with even higher T_c, possibly even beyond room temperature. Figure 2 indicates the progress achieved in raising the T_c of superconductors.

In this paper, the current trends in the development and applications of superconducting materials are reviewed. The basic criteria for the choice of materials for applications are enumerated. The concepts dictating the form of the material needed for applications are discussed and fabrication methods employed in respect of niobium–titanium, niobium–tin and $PbMo_6S_8$ conductors are reviewed with emphasis on their microstructures and stress sensitivity. The known properties of the high T_c oxide superconductors are also reviewed and an assessment made of their potential for further development based on the information available so far. Although superconductors are capable of a diverse range of applications, the review deals with materials specific to high magnetic field applications only.

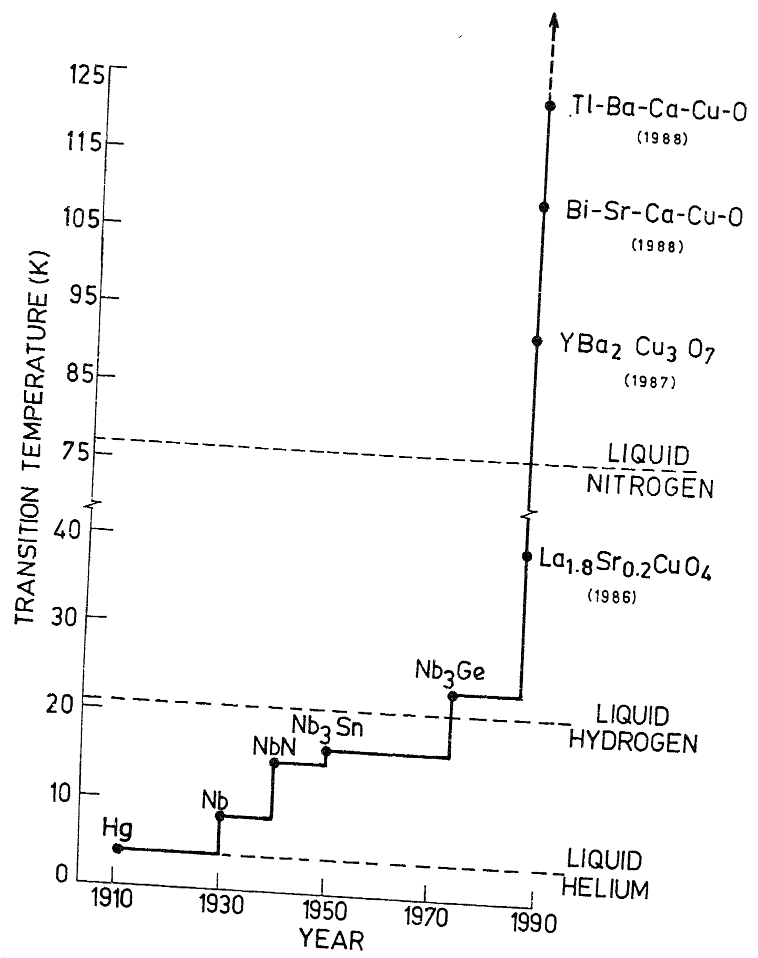

Figure 2. Progress in raising the T_c of superconductors.

2. Practical superconducting materials

Although many materials – elements, alloys, ternary chalcogenides and recently oxides – have been found to be superconducting, only a few of them have received attention for significant applications. This is based on three important parameters, viz. T_c, the transition temperature, H_{c2}, the upper critical field, and J_c, the critical current density, that characterise any superconductor. When any of these is exceeded the superconductivity is destroyed. Before discussing the specific materials suitable for technological applications, it is appropriate to consider the three parameters in some detail.

(a) *Transition temperature, T_c*

It is the temperature below which the material is superconducting. Naturally T_c should be as high as possible to save on refrigeration requirements to reach the operating temperature (see figure 2).

(b) *Upper critical field,* H_{c_2}

It is known that the T_c decreases with increase in magnetic field and, at a critical value, the material reverts to the normal state. Here one must distinguish between two types of superconductors, classified on the basis of their surface energy and magnetisation behaviour.

Type I superconductors are those that completely expel any magnetic flux from inside the superconductor by creating surface currents that produce a magnetisation exactly equal and opposite to the external field. Known as the Meissner effect, this diamagnetism persists until the material becomes normal at the critical magnetic field designated by H_c. Like the zero resistivity property, diamagnetism is another fundamental property of the superconductor. The magnetic energy gained in the process of excluding the flux decreases the free energy difference between the superconducting and normal states until it vanishes at H_c. Most elemental superconductors belong to type I. The H_c values are generally less than 0·1 T, too insignificant for practical applications.

Type II superconductors, to which class all the alloys and other multicomponent superconductors belong, behave identically to type I materials up to a field H_{c_1} which is generally low. Beyond H_{c_1}, the material breaks up into superconducting and normally conducting regions and is said to exist in the mixed state. Magnetic flux due to an external field penetrates the normal regions while the superconducting regions carry the lossless currents. The reduction in the energy of flux explusion caused by the flux penetration sustains superconductivity till a much higher field H_{c_2}, called the upper critical field.

Abrikosov who predicted the type II behaviour further postulated that the normally conducting regions are periodic arrangements of cylindrical domains. The threading of flux is in the form of quantized elements called fluxoids each carrying one flux quantum. As the field increases, the normal regions grow in number at the expense of the superconducting regions and at H_{c_2} the material becomes completely normal. It was subsequently shown by the neutron diffraction technique (Cribier *et al* 1966) that the flux lattice is triangular. It is important to recall that H_{c_2} values are far larger than H_c and hence these materials are useful for technical applications.

(c) *Critical current,* J_c

It is the maximum current that the material can support in the superconducting state and is a function of T and H. When a transport current J flows in a material in the presence of a magnetic field H, a Lorentz force $\mathbf{J} \times \mathbf{H}$ is created. This force, analogous to a magnetic pressure, causes the fluxoid to move resulting in dissipation, and the superconductivity is destroyed by the heat produced. Ideal, clean, pure type II superconductors cannot carry high currents. Defects and inhomogeneities of the size of about 50 Å (comparable with the diameter of the fluxoids) have the effect of pinning the fluxoids, thereby increasing the critical current density.

Table 1 lists the proven and potential materials for technological applications, together with their superconducting properties. It is evident from the discussions

Table 1. Properties of practical and potential superconductors

Superconductor	T_c(K)	H_{c_2}(T) at 4·2 K	J_c(A/mm^2) at 5 T
Nb–Ti	9–11	~10	3000
Nb_3Sn	18	24	16000
$PbMo_6S_8$	14	60	200 (at 20T)
NbN	13	29	23000
$Y_1Ba_2Cu_3O_7$	~100	>150	10*

*$J_c > 30{,}000$ A/mm^2 in single crystals ⊥ to C axis

above that while T_c and H_{c_2} are considered intrinsic properties of the material, J_c is influenced by the microstructures and has to be optimised during the fabrication of the material in the final form. Thus the values quoted for J_c are continually getting revised on the basis of new ideas and refinement in fabrication methods.

3. Stability of superconducting materials

When a superconducting material is in service such as in a magnet, the flux pinning can be destabilised due to mechanical, thermal or electromagnetic disturbances. This is known as a flux jump and results in some energy release. Unless the associated heat generated is localised and removed efficiently by the surrounding coolant, more flux jumps will be triggered off and the material may become normal, with sudden release of stored energy. It is worthwhile to note that the stored energy in a small laboratory superconducting magnet is several kilojoules and it ranges up to several megajoules in large magnets.

There are many approaches to preventing the problems associated with flux jumps at the stage of material fabrication itself. The most effective way is the fabrication of the superconductor in the form of multiple filaments of diameter 1–20 μm, in good electrical and thermal contact with a host matrix such as copper. By reducing the dimensions of the superconductor, the energy released in a flux jump is kept below a certain non-propagating threshold. In addition the filaments are also twisted in the final stages of manufacture to decouple them electromagnetically.

The effect of mechanical stress on the superconducting properties is another important consideration in the application of the superconductors. The stress can arise during the fabrication of the magnet due to winding tension and bending strain, due to differential thermal contraction because of dissimilar materials in the composite superconductor, and because of the Lorentz force experienced by the superconductor in operation. Apart from purely mechanical effects caused by the stress on the superconductors, degradation in the superconducting parameters T_c, H_{c_2} and J_c are also caused.

Thus the characteristics of a good superconducting material can be summed up as follows:

(i) high T_c, H_{c_2} and J_c,

(ii) easy formability – so that it can be fabricated in multifilamentary form in a highly conducting normal matrix and

(iii) low sensitivity to stress.

These aspects will be discussed for the materials listed in table 1. (For a general reference on superconducting materials see Narlikar and Ekbote 1983.)

4. Niobium–titanium

Niobium–titanium is the most widely used superconductor today on account of its superior mechanical properties. It is a disordered solid solution alloy and forms in the entire range of Ti composition. Although Nb-rich alloys have higher T_c, Ti-rich alloys in the range of 46–58 wt% Ti (64–73 at% Ti) are employed in commercial fabrication. The choice is dictated by the fact that Ti-rich alloys have higher H_{c_2} which is a consequence of the increase in the normal state resistivity of the alloy as the Ti concentration is increased. The critical field H_{c_2} is given by

$$H_{c_2}(0) = 3{\cdot}11 \times 10^3 \rho_n \gamma T_c \,\text{Tesla},$$

where γ is the electronic specific heat coefficient.

In Nb–Ti alloys, the H_{c_2} values are restricted to 12 T at 4·2 K and 14·5 T at 2 K. By addition of substantial amounts of tantalum an increase in H_{c_2} by one Tesla has been obtained (Hawksworth and Larbalestier 1980).

Although the Nb–Ti alloy has been under development for over 15 years, only now are many of the basic properties of the material being understood on the basis of the phase diagram and the low temperature structural transformations.

Figure 3 shows the phase diagram of Nb–Ti (Collings 1983). At high temperatures the alloy exists in the *bcc* β phase. On quenching to room temperature, the β phase is retained but is metastable. The equilibrium phase is $\alpha + \beta$, but the formation of α is diffusion-controlled and being sluggish it requires prolonged heating at 400°C. In the Ti composition range of interest, many of the properties of the alloy can be

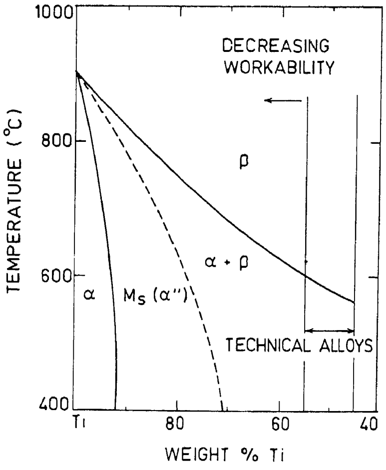

Figure 3. Phase diagram of niobium–titanium in the composition range of interest.

Figure 4. Dislocation sub-bands in severely cold-worked niobium-titanium alloys.

ascribed to the instability of the β phase. The instability is relieved by low temperature structural transformations. The transformed structure is either an orthorhombic phase or a partial ω phase. They can form athermally in diffusionless reactions and are reversible.

The $\beta \rightarrow \omega$ transformation is effected by a sequential displacement of (111) planes (Sikka *et al* 1981) termed as dynamical ω fluctuations. It has been shown (Hariharan *et al* 1986a) that the large resistivity characteristic of the unstable β phase is associated with these fluctuations. In general, as Ti concentration increases, the resistivity increases until interrupted by the orthorhombic martensitic transformation in which case the resistivity drops considerably.

Nb–Ti alloys are ductile and can be extensively cold-worked. Depending on the alloy composition, area reduction up to $1:10^5$ is possible with or without intermediate heat treatments. The cold-working produces fine dislocation sub-bands of density as high as $5 \times 10^{11}\,\mathrm{cm}^{-2}$. Figure 4 is a transmission electron micrograph (V S Raghunathan 1982, unpublished data) of a dislocation sub-band in a Nb–65 at% Ti alloy. The sub-band diameter becomes progressively lower with increasing cold area reduction. J_c shows an inverse correlation with sub-band diameter underlying the importance of cold-working for flux-pinning (West and Larbalestier 1980).

A second aspect of importance for the development of high J_c is the presence of fine scale α precipitates as flux-pinning entities. The precipitates can be formed by heat treatment for several hours at 375°C at or near the final size.

For reasons of stability as discussed in §3, Nb–Ti is produced in a fine multifilamentary form in a copper or cupro-nickel matrix depending on the application. A filament size of 15–20 μm is usual, but for applications in very large accelerators it is necessary to obtain filament sizes in the 2–5 μm range. One of the chief difficulties in this process is the embrittlement caused by Cu–Ti precipitates that form during the heat treatment to develop α. This is overcome by applying a diffusion barrier between copper and Nb–Ti. The best laboratory scale conductors developed in this way reached a J_c of 3500 A/mm² at 5 T and 4·2 K (Larbalestier *et al* 1986b). In large

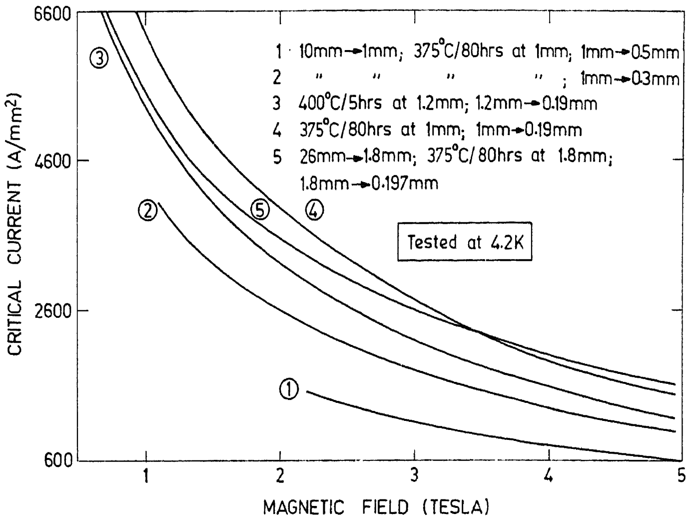

Figure 5. Short-sample tests as a part of the indigenous programme that has led to the development of Nb–Ti multifilamentary wires. Sensitivity of T_c to process conditions can be seen.

scale production, however, J_c values have remained at the level of 2700 A/mm^2, mainly due to the inhomogeneity of the Nb–Ti ingot.

There has been a sustained and intense indigenous programme on the development of niobium–titanium wires for over a decade. A good technical base and adequate expertise have been established for processing of high purity niobium and titanium and the production of the alloy ingots. At the start of the programme, single core wires in a copper matrix were developed and the superconducting properties evaluated by setting up a short sample testing facility (Bose *et al* 1979). Subsequently multifilamentary composites have been produced. Figure 5 shows the J_c–H plots (Sundaram 1985) generated using the above test facility on a number of multifilamentary composites with varying process conditions.

The flow sheet being followed (Balaramamoorthy *et al* 1987) consists of electron-beam melting of Nb–Ti, swageing the ingots, followed by several vacuum annealing stages, copper cladding the Nb–Ti rods with hexagonal outer/circular inner tubes, stacking them into billets up to 300 mm dia, and evacuating and sealing the billets for extrusion and cold drawing. Annealing at 600°C at intermediate size helps strain-anneal the copper matrix. A precipitation heat-treatment is also given at 375°C at or near the final size. Presently alloy billets weighing up to 4 kgs are being processed. Nb–Ti/Cu composite wires of 0·56 mm dia having 45, 54 and 84 filaments have been produced in twisted and enamelled condition. A J_c value of 2300 A/mm^2 at 5T and 4·2 K has been obtained (Balaramamoorthy *et al* 1987).

Being a disordered solid solution, the Nb–Ti alloy is not very sensitive to stress and radiation damage and hence is very popular for technical applications. Nevertheless, the operating magnets are often subject to degradation and show training behaviour. The underlying mechanism although not clear is connected with the β phase instability and the stress induced low temperature structural transformations (Hariharan *et al* 1986b; Obst *et al* 1980).

5. Niobium-tin

When fields in excess of 10 T are required, the A15 superconductors are presently the only alternatives. Among the many intermetallic compounds with the A15 structure that are superconducting, Nb_3Sn, V_3Ga, Nb_3Al and Nb–Ge are those receiving attention for development with a view to application. Nb_3Sn and V_3Ga have been successfully produced in the form of multifilamentary wires. V_3Ga is superior to Nb_3Sn for fields higher than 12 T, with an overall J_c of 1000 A/mm^2 (20 T, 4·2 K). Development of Nb_3Sn is more widespread and in this section we shall be concerned only with this material. Much of the discussion is however applicable to V_3Ga as well.

The crystal structure of Nb_3Sn is shown in figure 6. The Nb atoms are arranged in the form of mutually orthogonal chains and the chain structure is considered responsible for superconductivity. Any disruption in the long range order of the structure produced by whatever means – non-stoichiometry, thermal disorder or radiation damage – results in the rapid decrease of T_c.

Since the A15 compounds are brittle, special fabrication procedures are necessary. Formerly the CVD method was used to produce Nb_3Sn on hastealloy substrates. These have now become obsolete and techniques for producing multifilamentary wires have been developed. Among them the bronze-route of formation is the most widely employed. Conceptually this is similar to the fabrication method adopted for Nb–Ti. Nb rods are inserted in the bronze matrix (containing about 13 wt% Sn) and the wire is drawn to final size in the multifilamentary (filament thickness $\sim 3\,\mu m$) form as before. Subsequent heat treatment (700–750°C) of the wire causes Sn to diffuse and react with the Nb filaments to form Nb_3Sn. Usually the Nb_3Sn phase forming heat treatment is given after the coil is wound on the former in the construction of the magnets.

High J_c in Nb_3Sn is obtained by optimising several process parameters (see, for example, Sharma 1987). These are bronze to filament volume ratio, heat treatment

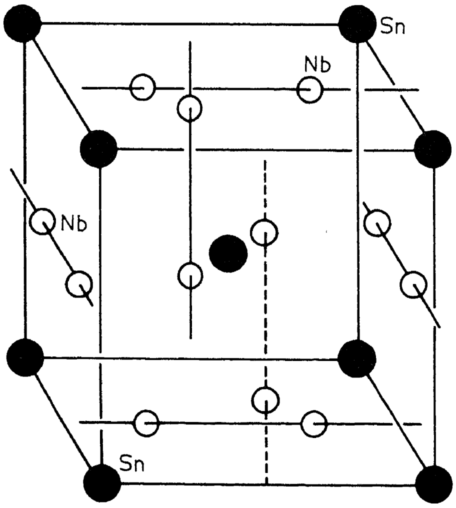

Figure 6. Crystal structure of Nb_3Sn. Nb orthogonal chains are responsible for superconductivity.

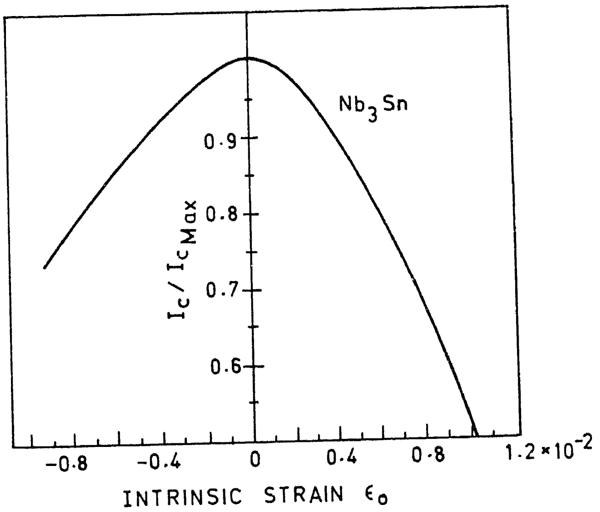

Figure 7. Degradation of critical current in Nb$_3$Sn as a function of mechanical strain.

conditions, filament size, impurity additions etc. Heat treatment is the dominant factor which controls the thickness of the A15 layer, the grain size and the Sn compositional profile across the A15 layer. Since the grain boundaries are the dominant pinning entities in A15 superconductors, low temperature heat treatment is preferred to keep the grain size small. On the other hand, higher temperature reaction is conducive to better stoichiometry of the A15 layer and can influence the overall H_{c2} and hence the J_c. A two-stage heat treatment (700°C for 4 days + 730°C for 2 days) is thus preferred. The main drawback of the bronze-processed conductors is that they have a high sensitivity to mechanical strain (see discussion in §3). Figure 7 (Ekin 1981) depicts the degradation in J_c as a result of both compressive and tensile strains.

The sensitivity to mechanical strain is minimised in alternate fabrication routes which aim to produce discontinuous filaments, with superconducting performance comparable to that of the bronze route material. The *in situ* process is based on the fact that Nb and Cu are completely miscible in the liquid state and virtually immiscible in the solid. Solidification of a Nb–Cu melt results in a fine dispersion of Nb in copper. After drawing into wire, a discontinuous A15 phase is formed by external diffusion. Another route is a powder process that is more generally applicable to all A15 conductors. In the discontinuous filament methods, superconductivity is sustained by the proximity effect.

The strain sensitivity of Nb$_3$Sn arises out of the structural (cubic to tetragonal) transformation induced due to mechanical strain. Nb$_3$Sn is also susceptible to radiation damage. These aspects are receiving a lot of attention in basic studies. Despite the problems posed by the stress effects, A15 conductors have been employed to produce fields up to 17·5 T.

6. Ternary molybdenum chalcogenides – PbMo$_6$S$_8$

PbMo$_6$S$_8$ belongs to the family of ternary molybdenum chalcogenides also known as Chevrel phase compounds. The structure (figure 8) has an overall rhombohedral

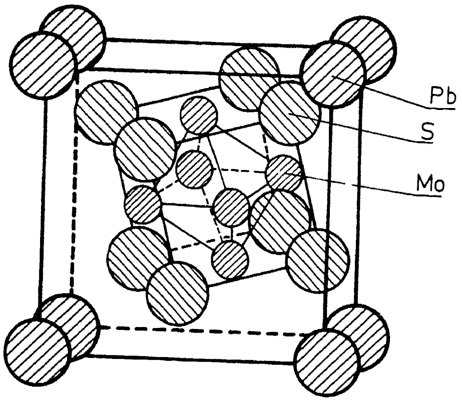

Figure 8. Crystal structure of $PbMo_6S_8$. Clusters of Mo are responsible for superconductivity.

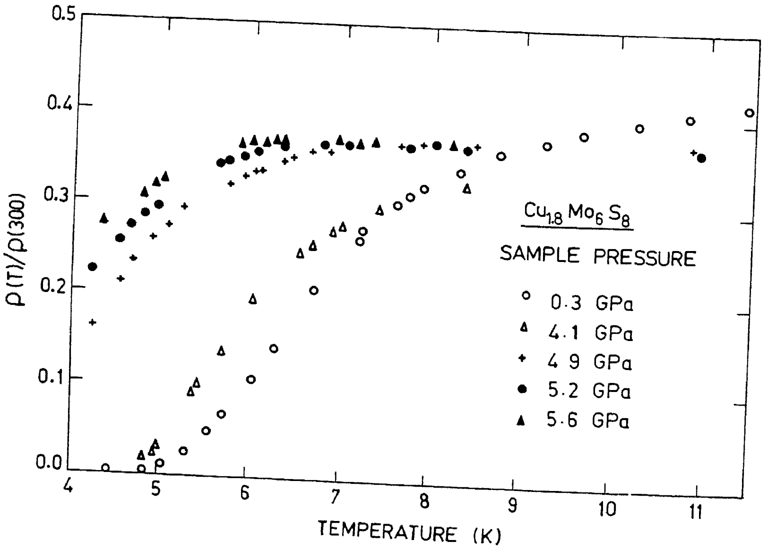

Figure 9. Degradation of T_c in $CuMo_6S_8$. This is typical of other chevrel-phase compounds like $PbMo_6S_8$.

symmetry and is made up of sulphur cubes, each containing an Mo octahedral cluster. The metal atom, e.g. Pb is located in the channels running along the rhombohedral axes. The superconductivity is thought to arise from 4*d* electrons of molybdenum with the central atom playing only a charge transfer role. The structure is highly anisotropic and superconductivity is readily degraded by extrusion or quasi-hydrostatic stress (Janawadkar *et al* 1987) that have to be necessarily employed in any manufacturing route. Figure 9 depicts the degradation in T_c due to stress.

In spite of the difficulties, until recently there was still an interest in the development of wires on account of the high H_{c_2} as seen in table 1. Being brittle, the material has been drawn into wire form by cold extrusion in a copper matrix. During extrusion, degradation of J_c occurs which can be recovered by annealing at about 900°C. In this process copper enters the channel with deleterious effects on T_c and H_{c_2}. Inserting barrier materials like Nb, Mo, Ag and Ta help overcome this problem. Still, the overall J_c has remained low at about 200 A/mm^2 (20 T, 4·2 K). The degradation of T_c is associated with possible structural instability to triclinic form and is a subject of much investigation (Jorgensen *et al* 1987).

7. Applications of superconducting magnets

Section 1 contained a brief reference to the possible areas of applications of superconductors in technology. A summary of the applications has also been given in figure 1. It is evident from the consideration of the various materials and their properties in the preceding sections that only three materials viz. Nb–Ti, Nb_3Sn and V_3Ga possess adequate characteristics as of now, for high current applications. All the three materials have to be operated at liquid helium temperatures.

One of the largest applications of Nb–Ti has been in accelerators for high energy physics (Larbalestier *et al* 1986a). The Fermi Lab energy doubler – the 800 GeV proton storage accelerator – has a ring of 744 dipole and 240 quadrupole type superconducting magnets making a total length of 6·4 km. Each dipole magnet produces a field of 4·5 T and is 6 m long with a 65 mm aperture. The refrigeration load for the magnet system is about 4000 l/h of liquid helium.

The successful operation of many superconducting accelerators has led particle physicists to propose a superconducting supercollider (SSC), the construction of which is due to start in the US after 1988. SSC will have two magnet rings each 60 miles (96 km) in circumference to accelerate protons in opposite directions to 20 TeV. Like the energy doubler, the SSC will have a number of Nb–Ti magnets in the ring, each producing a field of 6·6 T in a 50 mm bore. A significant challenge to the 60 mile long cryogenic system is the removal of the heat generated by synchrotron radiation due to the circulating proton beams. This load is estimated at 10 MW at the temperature of liquid helium.

Fusion research requires fields in excess of 12 T over large volumes in complicated geometries for plasma confinement. The required field configuration is achieved by employing Nb_3Sn. The MFTF-B tandem mirror facility at Livermore uses a pair of Nb–Ti coils producing 8 T and weighing 340 t together with a 36 cm bore Nb_3Sn windings.

Magnetic resonance imaging (MRI) for medical diagnostics represents the first large scale commercial application of superconductivity. MRI systems need relatively low fields in the range of 0·5–2 T but over large volumes, typically of 1 m length and 500 mm diameter. The field homogeneity requirement is stringent, better than 0·1 ppm over 100 mm diameter, in order to observe nuclear magnetic resonance from human tissues. An MRI system based on a superconducting magnet is in service at the Institute of Nuclear Medicine and Allied Sciences, New Delhi.

Applications in many other areas have been demonstrated and developments to varying extents have taken place. Clearly economic considerations have not forced the predominance of these developments. Some of them are the superconducting energy storage, magnetohydrodynamic power generation, electric power transmission, superconducting motors and generators etc. Potential application of superconductors in these areas are from time to time reassessed on the basis of new technologies and new materials in the hope of making them economically viable.

8. High T_c oxide superconductors – the changing scene

Superconductivity had always been designated a low temperature phenomenon. Based on the phonon mechanism of pairing (BCS), an upper limit to T_c of about 40 K has been estimated. Although the implications of finding superconductive pairing at elevated temperatures were clearly understood and theories had been proposed from time to time on newer mechanisms of pairing (non-BCS) that could lead to high T_c, experimental effort had proceeded on conventional lines investigating high symmetry structures in intermetallic compounds. Nevertheless some unusual superconductors like $SrTiO_3$, $LiTiO_3$, and $BaPb_{1-x}Bi_xO_3$ had been known earlier but with low T_c.

Bednorz and Müller (1988) had been investigating materials containing Fe^{4+}, Ni^{2+} and Cu^{2+} in an octahedral oxygen environment. This was with the idea of inducing large electron–phonon interactions and consequently high T_c, based on a polaronic mechanism (Chakravarty 1981) as well as mixed valence states. In April 1986, they first reported superconductivity in an oxide material, La–Ba–Cu–O (Bednorz and Müller 1986) at a temperature of 35 K. By the end of 1986 many other laboratories all over the world had joined the activity of investigating the oxides. The usual chemists' intuition soon led to even higher T_c values of around 93 K (Wu *et al* 1987). The unprecedented activity has led to an explosion in the number of publications. Initial reports were hasty and did not use well-characterised samples. Nevertheless some clear trends have emerged. Superconductivity has been firmly established, on the basis of zero resistivity property, diamagnetism, flux quantisation and occurrence of Josephson effects, reproducibly on samples whose structures are well-characterised. Mainly two classes of oxide superconductors have been identified. These are $La_{1\cdot8}Sr_{0\cdot2}CuO_4$ with a K_2NiF_4 structure and $Y_1Ba_2Cu_3O_7$ based on the defect perovskite structure, with T_c values of about 40 K and 93 K respectively. In what follows an assessment will be made of the possibilities of use of oxide superconductors for technological applications based on existing information. It must be said at this stage, that the field is rapidly changing as a result of the intense activity. The treatment will be more specific to $Y_1Ba_2Cu_3O_7$ on account of its higher T_c.

8.1 *Synthesis*

Oxide superconductors are ceramics and are synthesised by solid state reaction methods. Initially, the compositions of different elements were chosen so that a certain amount of mixed valency occurred for copper on the basis of charge transfer. Later, the structure and the T_c value were the guides for producing optimum stoichiometry.

Appropriate amounts of Y_2O_3, $BaCO_3$ and CuO are heated together at 950°C for 24 h in air with repeated grindings and pelletisation. The final oxygen treatment is given at 900°C for a few hours. The slow cooling of the pellet in an oxygen atmosphere down to at least 200°C is considered essential. Thermogravimetric studies (Strobel *et al* 1987) of samples quenched from high temperatures indicate a mass increase corresponding to 0·5 oxygen atoms per formula unit in the range 250–350°C and a mass loss above 550°C. Below 200°C the samples exhibit no significant variation of mass and retain the maximum oxygen content. These results are supported by other workers (O M Sreedharan 1987, private communication; R M Iyer 1987, private communication). The mass increase is associated with structural change from tetragonal to orthorhombic and vice versa.

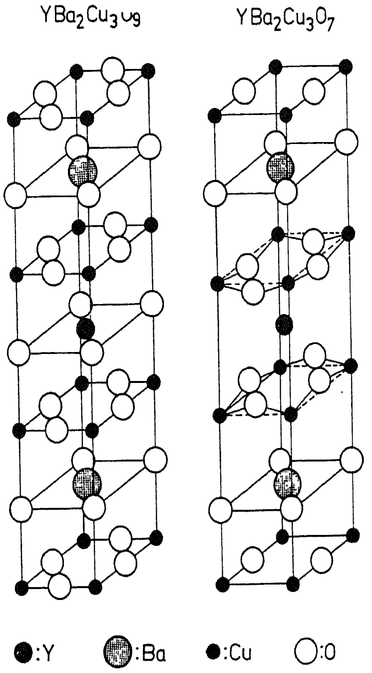

Figure 10. Crystal structure of the defect $Y_1Ba_2Cu_3O_7$. Structure of the defect-free $Y_1Ba_2Cu_3O_9$ is also shown for comparison.

8.2 *Structure*

The crystal structure of $Y_1Ba_2Cu_3O_7$, as assigned using X-ray diffraction (Siegrist *et al* 1987), is shown in figure 9. Classified as a defect perovskite, this structure is orthorhombic ($a = 3{\cdot}82$ Å; $b = 3{\cdot}88$ Å; $c = 11{\cdot}66$ Å) and can be derived from the $Y_1Ba_2Cu_3O_9$ (ABO_3) structure (also shown in figure 10). It is seen that the missing oxygens in the Y plane and the basal plane containing copper have changed the structure of the superconductor into a layered one with two-dimensional Cu-O sheets extending infinitely.

There are five inequivalent positions occupied by oxygen ions. There are two types of coordination of the Cu atoms with oxygen. In the first one the missing oxygen from the top and bottom layers of the unit cell lead to a square planar arrangement (CuO_4) perpendicular to the copper–oxygen sheets. The second one is the square pyramidal arrangement involving the Cu atoms (CuO_5) on either side of the yttrium ion. The latter (CuO_5) sheets are slightly puckered towards the Y plane.

It is suggested that the mass changes observed in TGA represent the removal of the oxygen ions from the b-axis leading to tetragonality. The compound $Y_1Ba_2Cu_3O_6$ is known and is tetragonal and non-superconducting (Bordet *et al* 1987). Other reports suggest that the tetragonal phase of $Y_1Ba_2Cu_3O_7$ has an appreciably lower T_c (Dhar *et al* 1987).

8.3 *Transition temperature*

There is general agreement on the T_c of $Y_1Ba_2Cu_3O_7$ putting it around 93 K

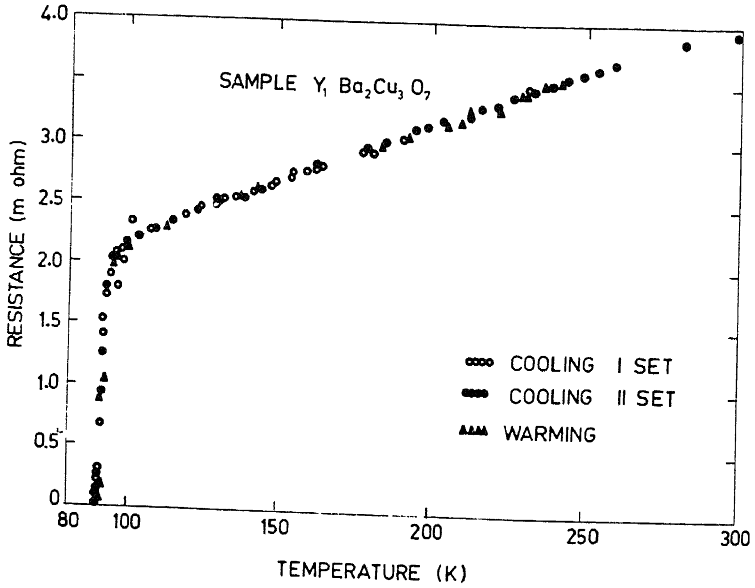

Figure 11. Resistivity vs. temperature of $Y_1Ba_2Cu_3O_7$ showing a T_c of 93 K. Reproducibility has been shown in cooling and warming cycles in view of the varying claims for T_c of this material (Data due to S Kalavathi, U De and T S Radhakrishnan).

(figure 11). Many workers have reported zero resistance and sharp transitions at considerably higher temperatures in essentially single phase materials (Ganguly *et al* 1987; Gopalakrishnan *et al* 1987). There is evidence for superconductive pairing at still higher temperatures – up to 240 K – in some multiple samples (Chen *et al* 1987; Cai *et al* 1987). On the basis of the reverse Josephson effect, evidence for pairing at 26°C (Gupta *et al* 1987) has also been reported. Partial substitution by fluorine has resulted in high T_c of 151 K in bulk samples of $Y_1Ba_2Cu_3F_2O_y$ (Ovshinsky *et al* 1987). Attempts to synthesise this phase by other laboratories have not been successful so far.

Partial or full substitution at the site of yttrium by other rare earth elements have been reported (Subba Rao *et al* 1987). Except in the cases of Ce, Pr, Tb and La, other samples are superconducting (Tarascon *et al* 1987). The remarkable feature is that the T_c is influenced very little, if at all, by these substitutions.

Despite all these claims, only $Y_1Ba_2Cu_3O_7$ and variants of $Ln_1Ba_2Cu_3O_7$ (Ln = Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb) with T_c around 93K have been reliably established to be bulk superconductors on the basis of single phase samples, crystal structure, zero resistivity and the Meissner effect.

8.4 *Upper critical field*

For type II superconductors, H_{c_2} values are large and are usually estimated on the basis of $[dH_{c_2}/dT]_{T_c}$ values derived from $H_{c_2} - T$ measurements and using the theory of dirty superconductors. The results in the case of oxide superconductors vary widely, indicating poor sample quality. Unlike the conventional superconductors, the widths of the transitions in the case of high T_c materials are large extending to several Kelvins in magnetic fields. This poses an additional complication and H_{c_2} values based on onset T_c and midpoint T_c become widely different.

In the case of La–Sr–Cu–O, on the basis of midpoint T_c, a $[dH_{c_2}/dT]_{T_c}$ value of $-2{\cdot}2$ T/K has been measured (Orlando *et al* 1987), leading to a $H_{c_2}(0)$ of 58 T. On the basis of the onset T_c, a value of 125 T has been derived. The sample has been directly seen to be superconducting till a pulsed field of 45 T at 4·2 K. In the case of $Y_1Ba_2Cu_3O_7$, $[dH_{c_2}/dT]_{T_c}$ values are $-3{\cdot}5$ T/K (midpoint) and $-4{\cdot}5$ T/K (onset). The corresponding $H_{c_2}(0)$ estimates are 200 T and 250 T respectively (Takita *et al* 1987).

8.5 *Critical current*

J_c values of polycrystalline samples have been low – about 10 A/mm^2 at 77 K. Epitaxial films grown on oriented $SrTiO_3$ substrates with the (100) direction perpendicular to the plane of deposition have shown a remarkably high T_c of 1500 A/mm^2 at 77 K and 20,000 A/mm^2 at 4 K (Chaudhari *et al* 1987). The films were grown by evaporating Y, Ba and Cu from three separate electron beam sources at an oxygen pressure of 10^{-2} Pa with the substrate heated to 400°C. Subsequent annealing was necessary at 900°C in oxygen atmosphere. J_c was estimated by direct d.c. and pulsed current measurements as well as from magnetisation measurements. Another study on a tiny (200 μm) single crystal of $Y_1Ba_2Cu_3O_7$ (Dinger *et al* 1987) has yielded similar high values for J_c in favourable directions. Along the *c* axis, J_c has been low indicating a high anisotropy. These are only preliminary studies and it is generally agreed that J_c values reported can be exceeded.

8.6 *Fabrication*

Several attempts have succeeded in making thin flexible wires ($<0{\cdot}1$ mm dia) of $Y_1Ba_2Cu_3O_7$ in metallic cladding, by hot extrusion. Superconductivity is always degraded and lost after extrusion and it has been necessary to heat-treat the wire in an oxygen atmosphere at about 900°C to rejuvenate the superconducting phase. Copper has not been an ideal matrix for such purposes. Silver has been successfully used as a host matrix. J_c values in polycrystalline wires (Malik *et al* 1987) have been low, around 2 A/mm^2.

An interesting method was successfully followed in the case of La–Sr–Cu–O. A ternary amorphous ribbon of La–Sr–Cu was obtained first by the melt-spinning method. Subsequently the crystalline phase was grown by heat-treatment in an oxygen atmosphere. It is yet to be seen whether this method could be applied to Y–Ba–Cu–O. The present studies indicate that texture is important and should be preserved in any manufacturing route.

8.7 *Stress sensitivity*

Being highly anisotropic, both Y–Ba–Cu–O and La–Sr–Cu–O show a high degree of sensitivity to stress. Figure 12 shows that superconductivity is degraded by quasi-hydrostatic compressive stress which has a shear component (Sastry *et al* 1987). In the case of La–Sr–Cu–O superconductivity was lost. Y–Ba–Cu–O showed two transitions to metallic phase at about 100 K and 40K under pressure although the

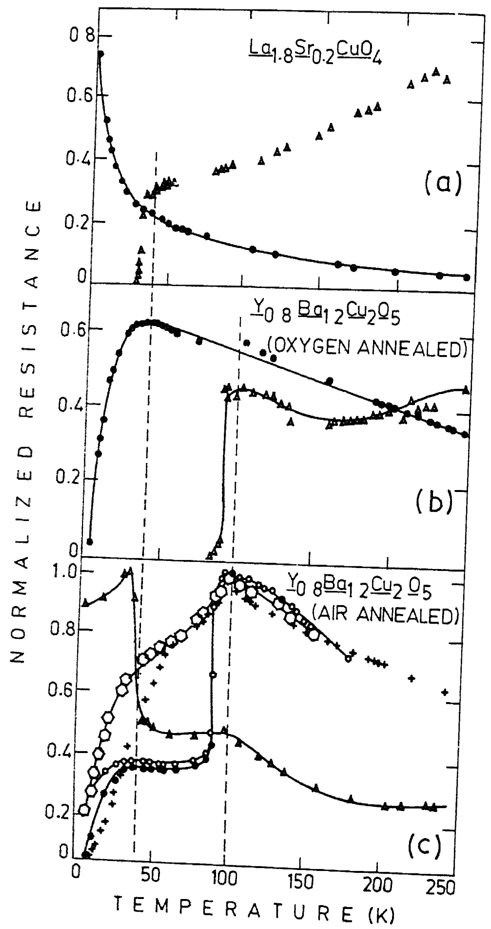

Figure 12. *R* vs *T* behaviour of La–Sr–Cu–O and Y–Ba–Cu–O for different synthesis conditions and quasi-hydrostatic pressures up to 6 GPa. (▲) ambient pressure; (○) and (●) 0·5 GPa; (⬡) 3 GPa; and (+) 6 GPa.

superconductivity which was observed at ambient pressure at 93 K was lost. These results are also in agreement with a Japanese study (Okai *et al* 1987). Hydrostatic pressure measurements have shown a varied behaviour. In the case of La–Sr–Cu–O, T_c increased to 55 K at a pressure of 2 GPa. Y–Ba–Cu–O also has shown a slight increase with pressure.

The sensitivity to quasi-hydrostatic pressure is important, and points to sensitivity of superconducting properties to mechanical strain reminiscent of chevrel phase compounds. This aspect could be of considerable technological importance.

9. Conclusion

Following the discovery of superconductivity in 1911 other experimental and theoretical advances took place for another 50 years culminating in the Josephson effects in 1962. Although the technological possibilities were immediately obvious from the beginning, it was Abrikosov's discovery of type II superconductivity in 1957 that gave the real impetus to the development of suitable and stable materials leading to the applications. The development of materials has been one of the main concerns of research in superconductivity for the last 30 years. Nb–Ti, Nb_3Sn and V_3Ga have been developed following ingenious fabrication methods and have found application in diverse fields of technology.

The discovery of high T_c oxide superconductors in 1986 has rejuvenated enthusiasm in superconductivity research leading to unprecedented activity in different directions. The new materials show rich promise for applications. There is the prospect of a revolution in electrical technology.

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References

Balaramamoorthy K, Malik M K and Vijayaraghavan R 1987 *Proceedings of the 116th TMS Annual Meeting held at Denver, Colorado J. Less Common Metals*

Bednorz J G and Müller K A 1986 *Z. Phys.* **B64** 189

Bednorz J G and Müller K A 1988 Nobel Lecture; *Angew. Chem.* **100** 757

Bordet P, Chaillout C, Capponi J J, Chenavas J and Marezio M 1987 *Nature* (*London*) **327** 687

Bose D K, Gupta C K, Radhakrishnan T S, Hariharan Y and Venkataraman G 1979 *Bull. Mater. Sci.* **1** 43

Cai X, Joynt R and Larbalestier D C 1987 *Phys. Rev. Lett.* **58** 2798

Chakravarty B K 1981 *J. Phys.* **42** 1351

Chen J T, Wenger L E and McEwan C J 1987 *Phys. Rev. Lett.* **58** 1972

Chaudhuri P, Kock R H, Laibowitz R B, Maguire T R and Gambino R J 1987 *Phys. Rev. Lett.* **58** 2684

Collings E W 1983 *Sourcebook on titanium alloy superconductivity* (New York: Plenum) p. 215

Cribier D, Jacrot B, Farnoux B and Madhava Rao L 1966 *J. Appl. Phys.* **37** 952

Dinger T R, Worthington T K, Gallaghan W J and Sandstrom R L 1987 *Phys. Rev. Lett.* **58** 2687

Dhar S K, Paulose P L, Grover A K, Sampathkumaran E V and Nagarajan V 1987 *J. Phys.* **F17** L105

Ekin J W 1981 in *Superconductor materials science: Metallurgy, fabrication and applications* (eds) S Foner and B Schwartz (New York: Plenum) p. 455

Ganguly P, Raychaudhuri A K, Sreedhar K and Rao C N R 1987 *Pramāṇa–J. Phys.* **27** L229

Gopalakrishnan I K, Yakhmi J V and Iyer R M 1987 *Nature* (*London*) **327** 604

Gupta A K, Jayaraman B, Agarwal S K, Gupta A and Narlikar A V 1987 *Pramāṇa – J. Phys.* **29** L117

Hawksworth D G and Larbalestier D C 1980 in *Advances in cryogenic engineering materials* (eds) A F Clark and R P Reed (New York: Plenum) **26** 479

Hariharan Y, Janawadkar M P and Radhakrishnan T S 1986a *Solid State Commun.* **59** 127

Hariharan Y, Janawadkar M P, Radhakrishnan T S, Terrance A L E, Dixit G A and Raghunathan V S 1986b *Pramana – J. Phys.* **26** 513

Janawadkar M P, Hariharan Y, Sankara Sastry V and Radhakrishnan T S 1987 *Proceedings of the 18th International Conference on Low Temperature Physics, LT18, Kyoto, Japan*; *Jpn. J. Appl. Phys.* **26-3** 1287

Jorgensen J D, Hinks D G and Felcher G P 1987 *Phys. Rev.* **B35** 5365

Larbalestier D C, Fisk G, Montgomery B and Hawksworth D 1986a *Phys. Today* **39** 24

Larbalestier D C, Lee P J, Chengren Li and Warner W H 1986b in *Proc. Workshop on Superconducting Magnets and Cryogenics held at Brookhaven National Laboratory*, p. 45

Malik M K, Nair V D, Raghavan R V, Chaddah P, Mishra P K, Ravikumar G and Dasannacharya B A 1987 *Pramana – J. Phys.* **29** L321

Narlikar A V and Ekbote S N 1983 *Superconductivity and superconducting materials* (New Delhi: South Asian)

Obst B, Pattanayak D and Hochstuhl P 1980 *J. Low Temp. Phys.* **41** 595

Okai B, Takahashi K and Ohta M 1987 *Jpn. J. Appl. Phys.* **26** L820

Orlando T P, Delin K A, Foner S, McNiff E, Tarascon J M, Greene L H, McKinnon W R and Hull G W 1987 *Phys. Rev.* **B35** 5347

Ovshinsky S R, Young R T, Allred D D, Demaggio G and Vander Leeden G A 1987 *Phys. Rev. Lett.* **58** 2579

Sharma R G 1987 (preprint)

Sastry V S, Kalavathi S, Guha B K, Baskaran R, De U, Janaki J, Radhakrishnan T S, Thomas K A and Subba Rao G V 1987 *Phase Transitions* **10** 97

Schwartz B B and Foner S (eds) 1977 *Superconductor applications – Squids and machines* (New York: Plenum)

Siegrist T, Sunshine S, Murphy D W, Cava R J and Zahurk S M 1987 *Phys. Rev.* **B35** 7137

Sikka S K, Vohra Y K and Chidambaram R 1981 *Prog. Mater. Sci.* **27** 245

Strobel P, Capponi J J, Chaillout C, Marezio M and Tholence J L 1987 *Nature (London)* **327** 306

Subba Rao G V, Varadaraju V V, Srinivasan R and Radhakrishnan T S 1987 *Phase Transitions* **10** 181

Sundaram C V 1985 Application-related metallurgy of zirconium, niobium and beryllium; First Brahm Prakash Memorial Lecture, Indian Institute of Metals, Bangalore

Takita K, Ipposhi T and Masuda K 1987 *Jpn. J. Appl. Phys.* **26** L668

Tarascon J M, Mckinnon W R, Green L H, Hull G W and Vogel E M 1987 (preprint)

West A W and Larbalestier D C 1980 in *Advances in cryogenic engineering* (eds) A F Clark and R P Reed (New York: Plenum) **26** 471

Wu M K, Ashburn J R, Torng C J, Hor P H, Meng R L, Gao L, Huang Z J, Wang Y Q and Chu C W 1987 *Phys. Rev. Lett.* **58** 908