Chapter 1

Introduction

1.1 Brief historical development in superconductivity

Kamerlingh Onnes [1], discovered that the dc resistivity of mercury suddenly drops to zero whenever the sample is cooled below 4.2 K, the boiling point of liquid helium. He named the new phenomenon - superconductivity. He has also discovered that a sufficiently strong magnetic field restores the resistivity in the sample. Later on it was discovered that many other metallic elements exhibit superconductivity at very low temperatures. The highest critical temperature ($T_c$) of all pure metals was discovered in Nb, $T_c = 9.2$ K.

Meissner and Ochsenfeld [2] discovered another distinct property of the superconducting state: perfect diamagnetism. They noticed that the magnetic flux is expelled from the interior of the sample that is cooled below the critical temperature in weak external magnetic fields.

John Bardeen, Leon Cooper and Robert Schrieffer [3] proposed a complete microscopic theory of superconductivity that is usually referred to as the BCS theory. The basis of the theory is the interaction of a gas of conduction electrons with elastic waves of the crystal lattice. Ordinarily the electrons repel each other by Coulomb force, but in the special case of a superconductor at sufficiently low temperatures there is a net attraction
between two electrons that form the so-called Cooper pairs. Naively one can think of an electron that polarizes its environment, i.e., attracts positively charged ionic background of the lattice, which in turn attracts another electron of the opposite momentum. Below the critical temperature the attraction permits the formation of Cooper pair that are pairs of electrons of opposite momenta and spins.

As a result of such attractive interaction, the condensed state of highly correlated pairs of conduction electrons is formed below $T_c$. All Cooper pairs move in a single coherent motion, so a local perturbation, like an impurity, cannot scatter an individual pair. Once this collective, highly coordinated state of coherent super-electrons is set in motion, its flow is without any dissipation.

**London theory**

Following the discovery of the Meissner effect, F. and H. London [4] explained the Meissner effect by modifying the Maxwell's electrodynamic equations. London derived a phenomenological equation

$$V \times J + (\mu_0 n_s e^2/m)\nabla \cdot \mathbf{H} = 0.$$  \hspace{1cm} (1.1.1)

An expression of the London's equation in one dimensional form is

$$d^2 H/dx^2 = H/\lambda_L^2,$$

where $\lambda_L$ is equal to $\sqrt{m/\mu_0 n_s e^2}$.

For a uniform, infinite superconductor in the region $x > 0$, and with the magnetic field $H_o$ applied parallel to the surface, the field inside the superconductor is given by the following solution of the above equation

$$H = H_o \exp(-x/\lambda_L)$$  \hspace{1cm} (1.1.2)

The field decreases exponentially and vanishes in the interior of the superconductor. $\lambda_L$ is the London penetration depth that measures the extension of the penetration of the
magnetic field inside the superconductor. It shows that, in order to have zero field within the bulk of the material, one must have a sheet of superconducting current which flows within $\lambda_L$ from the surface and which creates an opposite field inside the superconductor that cancels the externally applied magnetic field.

**Type-I and Type-II superconductors**

Superconducting materials that completely expel magnetic flux until they become completely normal are called type-I superconductors. The strength of the applied magnetic field required to completely destroy the state of perfect diamagnetism in the interior of the superconducting specimen is called the thermodynamic critical field $H_c$. The variation of the critical field $H_c$ with temperature for type-I superconductor is approximately parabolic:

$$H_c = H_o (1 - (T/T_c)^2),$$

(1.1.3)

where $H_o$ is the extrapolated value of $H_c$ at $T = 0$. The magnetization curve of a type-I superconductor is given in Fig. 1.1(a). The Meissner effect, $B = 0$, corresponds to $M = -H$. Above the critical field $H_c$, the material becomes normal, so $M = 0$. The negative sign shows that the sample becomes a perfect diamagnet that excludes the flux completely from its interior by means of surface currents. For type-II superconductors there are two critical fields: the lower $H_{c1}$ and the upper $H_{c2}$. The flux is completely expelled only up to the field $H_{c1}$. In applied fields smaller than $H_{c1}$, a type-II superconductor behaves just like a type-I superconductor below $H_c$. Above $H_{c1}$ the flux partially penetrates into the material until the upper critical field, $H_{c2}$, is reached. Above $H_{c2}$, the material returns to the normal state. The typical magnetization curve for type-II superconductor is shown in Fig. 1.1(b). Between $H_{c1}$ and $H_{c2}$, the superconductor is said to be in the mixed state. The Meissner effect is only partial. For all partial fields $H_{c1} < H < H_{c2}$, the magnetic flux partially penetrates the superconducting specimen in the form of tiny microscopic filaments called vortices. It consists of a normal core, in which the magnetic field is large,
Fig. 1.] Variation of magnetization as a function of the magnetic field for (a) type-I superconductor and (b) type-II superconductor.
surrounded by a superconducting region in which flows a persistent supercurrent which maintains the field within the core. Each vortex carries a magnetic flux $\phi_o = h/2e = 2.067 \times 10^{-15}$ Weber, where $h$ is the Plank constant and $e$ is the charge of the electron. Penetration of flux in type -II superconductors through a lattice of flux lines had been predicted by Abrikosov [5]. The vortex tubes repel each other, and the most stable one is a triangular lattice. In that case, the distance between two vortices is given by

$$a = 1.072\sqrt{\phi_o/B}$$  \hspace{1cm} (1.1.4)

The triangular flux line lattice is directly visualized by magnetic decoration techniques [6].

**The coherence length**

The coherence length $\xi$ is the distance between two electrons of the Cooper pair within the highly correlated coherent superconducting state. Another definition of the coherence length is that it is a measure of the distance over which the gap parameter can vary, for instance, near a superconductor-normal metal boundary [7].

### 1.2 Discovery of high $T_c$ superconductors

Many technologically important metallic superconductors of relatively low $T_c$ were discovered till 1986 and they could be used only at liquid helium temperatures. Bednorz and Müller [8] discovered superconductivity in La-Ba-Cu-0 ceramics at 30 K. This triggered a wide spread search among oxide compounds.

In 1987, research groups coordinated by Wu and Chu [9] discovered that the ceramic $\text{YBa}_2\text{Cu}_3\text{O}_7$ (YBCO) is superconducting with $T_c = 92$ K. This was an important discovery, because its $T_c$ is above the boiling point of liquid nitrogen which is a much cheaper
coolant than liquid helium. This discovery simulated new research programs looking for technological applications.

Maeda et al. [10] discovered new ceramic superconducting phases in the Bi-Sr-Ca-Cu-O system. The highest $T_c$ in that system is 110 K. Sheng and Hermann [11] discovered the Tl-Ba-Ca-Cu-O system, with a maximum $T_c$ of 120 K. The problem with this system is the toxicity of thallium which necessiates careful handling and processing.

Putilin et al. [12] discovered a new layered superconductor, HgBa$_2$CuO$_{4+x}$ with $T_c$ of 94 K. This temperature is not a new record, but it raised new hopes because it was quite a high value for a compound with a single CuO layer per elementary cell. Following this trend, Schilling et al. [13] published their finding of a critical temperature of 133.5 K in the three CuO layer structure of the HgBa$_2$Ca$_2$Cu$_3$O$_{1+x}$. The search for better high $T_c$ materials continues today with more expectations. Improving the $T_c$ is not the only important matter. For most applications, large critical current densities ($J_c$) of the order of $10^4$ to $10^6$ A/cm$^2$ are required, in the presence of large magnetic fields. $J_c$ is not an intrinsic property of a superconductor, it is strongly dependent on its microstructure. Hence microstructural control is very important for practical applications. For realization of practical applications, it is also necessary that the processing routes that yield a high $J_c$ through microstructural control should also enable the shaping of the material into the necessary geometries.

1.3 YBa$_2$Cu$_3$O$_y$ structure [14,15]

Except for some materials (like Ba$_{1-x}$K$_x$BiO$_3$ and YNiBC), most high-$T_c$ superconductors are cuprate compounds. One of their characteristics is the presence of CuO$_2$ layers which dominate most properties. The schematic structure of YBa$_2$Cu$_3$O$_6$ is presented in
Fig. 1.2. The unit cell is developed from that of a tetragonal perovskite tripled along the c-axis and it consists of a sequence of copper-oxygen layers. It is an insulator [15]. It has to be doped to gradually become a metallic conductor and a superconductor below some critical temperature. The doping is achieved by adding additional oxygen which forms CuO 'chains'. These oxygen ions attract electrons from the CuO$_2$ planes which therefore become metallic. Therefore $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$, where x corresponds to partial oxygen content, for $0 < x < 0.4$, is an insulator, and for $\sim 0.4 < x < 1$, is a superconductor. Numerous diffraction studies indicate that most oxygen vacancies occur within planes made of CuO chains (ab-plane) rather than within the pyramids. In $\text{YBa}_2\text{Cu}_3\text{O}_6$, the chains along the b-axis are oxygen depleted and Cu(l) coordination is only 2 (only two neighboring oxygen ions). This compound is an insulator. By increasing the oxygen concentration one gradually dopes the ab-plane with charge carriers (holes) and it eventually reaches the $\text{YBa}_2\text{Cu}_3\text{O}_7$ composition in which there are no oxygen vacancies. Very detailed studies indicate that the maximum in $T_c$ is reached for $x \sim 0.93$ ($T_c = 94$ K) and that for $x = 1$ the critical temperature is lower, $T_c = 92$ K. The orthorhombic cell dimensions $\text{YBa}_2\text{Cu}_3\text{O}_7$ are: $a = 3.88 \text{ Å}$, $b = 3.84 \text{ Å}$, $c = 11.63 \text{ Å}$, with a cell volume $\sim 173 \text{ Å}^3$ [14]. Other rare earth compounds having the general formula, $\text{REBa}_2\text{Cu}_3\text{O}_7$, where RE represents one of the rare earth elements, that can replace yttrium in the original 123 structure of Fig. 1.2, are also found to exhibit superconductivity. However, an exception is $\text{PrBa}_2\text{Cu}_3\text{O}_7$ which does not exhibit superconducting properties to low temperatures.
Fig. 1.2 Schematic diagrams of (a) YBa$_2$Cu$_3$O$_6$ an insulator and (b) YBa$_2$Cu$_3$O$_7$, superconducting oxide.
1.4 Preparation of bulk superconductors

1.4.1 Sintering

Sintering is commonly used in ceramic processing. In general sintered samples are prepared from starting powders by shaping them and then subjecting them to solid state reaction at high temperatures. Although sintering is very common and has many advantages in ceramic processing, it has failed to produce oxide superconductors with high \( J_c \) values, primarily due to the presence of weak-links at the grain boundaries. The weak link nature of grain boundaries is ascribed to impurity segregation, chemical or structural variation, the presence of nonsuperconducting phases, and cracking. It has also been pointed out that high angle grain boundaries are intrinsically weak-links, due to a combination of small coherence length and a large anisotropy [16,17]. Because the \( J_c \) supported by the material is at least an order of magnitude more in the a-b plane than in the c-direction, many researchers have tried to align the grains in the preferred orientation, that is, along the ab plane. Sintering in magnetic fields or under uniaxial pressure was effective in aligning grains. However, the coupling between the grains was not drastically improved. Since sintering is a solid state reaction, the diffusion rate of atoms is not high enough to construct an ideal structure in large dimensions and it is likely that defects are created at grain boundaries. This problem of weak link nature of grains has been overcome by the process called melt textured growth [18].

Sintering also causes substantial amount of shrinkage. In large green bodies of complex shapes, the retention of shape without distortions and cracks, and of the main-tainance of dimensional tolerances after sintering is a difficult task.
Ceramic components have also been produced by processes which involve the infiltration of molten metals into shaped preforms. Examples are the production of Reaction Bonded Silicon Carbide (RBSI) components and the Lanxide process for the production of ceramic matrix composites [19]. The advantage of such processes are the absence of shrinkage during processing enabling large shaped components to be made with a minimum of machining after the heat treatment.

1.4.2 Various melt growth processes

Melt Textured Growth process [18]

In order to obtain highly oriented samples, Jin et al., [18] used a 'melt process' (Melt Textured Growth, MTG Process). The process can be understood with reference to Fig. 1.3 where a pseudo-binary Y-Ba-Cu-O phase diagram is shown. A sintered YBa$_2$Cu$_3$O$_7$ sample is heated to 1100 °C to 1200 °C for decomposition and melting. The sequence of events during melting and subsequent solidification by slow cooling is

\[
YBa_2Cu_3O_7^{\text{solid}} \rightarrow Y_2BaCuO_y^{\text{(solid)}} + \text{liquid (off-stoichiometric)} \rightarrow YBa_2Cu_3O_x^{\text{solid}}.
\]

The melt textured samples prepared by this technique are essentially 100% dense, consisting of long platelet-shaped grains. The platelet axis appears to coincide with either the a or b direction in the orthorhombic phase. Such crystallographic alignment should be beneficial for the flow of supercurrent.

Modified MTG process [20]

For grain growth of the 123 phase, both the Y$_2$BaCuO$_5$ (211) and the liquid must be
supplied. Therefore, when the distribution of the 211 is not uniform, the reaction will not proceed continuously where the 211 density is low. When the samples are cooled in the 211 + L region, the 211 grows to a large size and is distributed inhomogeneously, which will result in weak connectivity of the superconducting phase. In order to avoid coarsening of the 211 phase, several groups have modified the MTG process. For example, coarsening of 211 can be reduced by decreasing the heating temperature to the point just above the peritectic temperature. The connectivity of the superconducting phase could be greatly improved by such a modification and it is also found that the size of the 211 inclusions trapped in the 123 phase can be reduced down to the order of 1-5 microns.

Quenched and Melt Growth (QMG) process and Melt Powder Melt Growth (MPMG) Processes [21,22]

In this process sintered 123 sample or a mixture of calcined powders, are heated to the \( Y_2O_3 + L \) region (see Fig. 1.3) and quenched using copper plates. Here the sample consists of \( Y_2O_3 \) particles and the solidified liquid phase (a mixture of barium cuprates and amorphous phases).

The quenched material is then reheated to the 211 plus liquid region, where \( Y_2O_3 \) reacts with the liquid and produces the 211 phase. Since the 211 nucleates from Y2O3, it is possible to control the distribution of the 211 phase if the distribution of \( Y_2O_3 \) is controlled. In the QMG process, the \( Y_2O_3 \) particles are segregated to some extent due to sedimentation, which causes a non-uniform distribution of the 211 phase. In the MPMG process, the melt quenched material is crushed into a fine powder and mixed well. By this process, coarse \( Y_2O_3 \) can be refined and its distribution can be made uniform. The pellets are rapidly heated to the 211 + L region. Here, the sample should not be kept for a long time since the 211 will grow into coarse grains. However, when the holding time is too short, the density of the sample will be poor and a number of pores will remain
Fig. 1.3 A pseudobinary phase diagram for the Y-Ba-Cu-O system [46].
in the final microstructure. After an appropriate holding time in this region (20 min to 1 h), the sample is rapidly cooled down to a point just above the peritectic temperature and then very slowly cooled down to 850 to 900 °C. Through this process a uniform distribution of fine 211 in the textured 123 matrix is obtained.

Powder Melting Process

Instead of using the melt quenched powders in the first phase of MPMG process, it is possible to use a mixture of \( \text{Y}_2\text{O}_3/\text{BaCuO}_2/\text{CuO} \) or a mixture of \( \text{Y}_2\text{BaCuO}_5/\text{BaCuO}_2/\text{CuO} \) as starting materials [23,24]. They are heated to the 211 + L region and slowly cooled through the peritectic temperature as in the MPMG process. The microstructure of the PMP processed samples is essentially identical to that of MTG processed samples.

**Platinum** doped melt growth (PDMG) process

Ogawa *et al* [25] have found that a small amount Pt addition is effective in reducing the size of the 211 inclusions in the 123 matrix. The size reduction of 211 is explained based on the assumption that Pt acts as a nucleation site for the 211. However, recent works have shown that even when 211 phase particles are fine, they can grow to a large size in relatively short time when heated to the 211 + L region, but the grain growth can be reduced by Pt addition. Therefore Pt works so as to retard the Ostwald ripening of the 211 inclusions.

It has also been found that the addition of \( \text{BaSnO}_3 \) [26,27] and \( \text{CeO}_2 \) [28-31] are also effective in reducing the size of the 211 inclusions, thereby increasing \( J_c \) values.

**OCMG** process

Light rare earth \( \text{REBa}_2\text{Cu}_3\text{O}_{7-\delta} \) (RE = Nd, Sm, and Gd) superconductors when processed in ambient atmosphere form solid solutions of type \( \text{RE}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_{7-\delta} \), which have low \( T_c \) [32-35]. To suppress the low \( T_c \) phase formation, Yoo *et al.* [36] melt processed
in reduced oxygen partial pressures. In inert atmosphere, due to the absence of oxygen, \( \text{RE}_{1+x} \text{Ba}_{2-x} \text{Cu}_3 \text{O}_{7-\delta} \) phase formation is not promoted. Using this process, \( T_c \) of 95 K has been obtained in the \( \text{NdBa}_2 \text{Cu}_3 \text{O}_{7-\delta} \) (Nd-123) system.

**Seeding [37,38]**

For most applications, bulk materials in usable shapes of large dimensions are needed. It has been demonstrated that single crystals of \( \text{SmBa}_2 \text{Cu}_3 \text{O}_x \) and \( \text{NdBa}_2 \text{Cu}_3 \text{O}_x \), which have a higher melting point than Y-123, can work as seeds for crystal growth and thus make it possible to control the crystal orientation. Long crystals with controlled orientation can be fabricated by this technique.

**Directional solidification [39,40]**

The former sections deal with solidification without sample transport. The motion of a sample relative to a temperature gradient can be employed to obtain long samples which are highly textured along the growth direction. The basic mechanism of grain growth is essentially the same as solidification without sample transport. The techniques used involve either moving a heating source or moving a sample through a hot zone. The latter technique is preferred from a commercial point of view, because it permits long samples to be processed in a continuous fashion. Lian et al. [23] employed zone melting where \( \text{Y}_2 \text{BaCuO}_5/\text{BaCuO}_2/\text{CuO} \) powders are pressed in the form of bars and continuously melted and solidified by moving the samples through a tubular furnace which has a narrow high temperature zone for melting and a steep temperature gradient for unidirectional solidification. The temperature gradient \( G \) at 1000 °C was about 180 °C/cm, the microstructures obtained by this technique were identical to those by solidification without sample transport.
1.5 Magnetic response of HTSC

1.5.1 Critical state models

All the high $T_c$ superconductors are type-II superconductors. To explain the hysteresis in the magnetization of type-II irreversible superconductors, critical state models [41-44] have been proposed. The models assume that penetrated supercurrents flow with a density equal to the critical current density, and that the flux vortex array is stable and there is no flux creep, and that the lower critical field is zero. Bean [41] derived the full hysteresis loop by assuming that the $J_c$ is constant. But in high $T_c$ superconductors, $J_c$ is found to decrease with the applied field. Many workers assumed different functional behaviors of $J_c$. Examples are:

**Kim**' model [42] : $J_c(H) = K/(H_o + H)$, where $A'$ and $H_o$ are constants;

**Exponential Model** [43,44] : $J_c(H) = \exp(-H/H_o)$;

**Power-law model** [45] : $J_c(H) = A' H^{-n}$, where $n$ is a constant.

In the present study Bean, Kim, exponential and power law models are used to analyze the experimental data and to obtain physical parameters.

**Bean's critical state model**

The basic premise of this theory is that there exists a limiting macroscopic superconducting current density, $J_c(H)$, that a hard superconductor can carry, and further that any electromotive force, however small, will induce this full current to flow locally. This model assumes that the critical current density, $J_c$, is a constant, which means that it is independent of the local internal field, that the flux vortex array is stable and there is no flux creep, and that the lower critical field is zero. If this magnitude of current flows everywhere in the specimen, it is in the critical state. If we assume that this current density is independent of field, the process of magnetization of a slab of thickness $D$ ($=2a$) in a field parallel to its surface is shown in Fig. 1.4. The field within the specimen
Fig. 1.4 A plot of local fields and current density, as well as magnetization curves, for fields 0, H*/2, H* and 2 H* applied parallel to the surface of a slab of thickness D. The critical current density is assumed independent of field.
decreases linearly with distance as a consequence of Ampere’s law, \( \nabla \times B = 4\pi J / 10 \). In the initial stages of magnetization, the current flows in superficial layers whose thickness \( \Delta \) is just enough to reduce the internal local field to zero, i.e., \( \Delta = 10H/4\pi J_c \). At fields of \( H > \pi J_c D/5 = H^* \), currents flow through the entire volume of the specimen.

The volume average of the local field, by definition is

\[
B = \frac{\int H \, dv}{\int dv}
\]

\[
M = \frac{B}{\mu_0} - H
\]

In other words, \( B \) is merely the volume average of the local field while \( M \) is the average field created by the currents. For infinite slab, the initial magnetization curve, \( M(H) \) becomes,

\[
M = -H + \frac{H^2}{2J_c a} \quad 0 < H < H^*
\]

\[
M = -\frac{J_c a}{2} \quad H > H^*
\]

These results are sketched in Fig. 1.4(c). The reverse curve for the high \( -H_m \) case is given by

\[
M(H) = -\frac{J_c a}{2} + H_m - H - \frac{(H H)^2}{4J_c a} \quad H_m - 2H^* < H < H_m
\]

\[
M(H) = \frac{J_c a}{2} \quad -H_m < H < H_m - 2H^*
\]

where \( H \) is the applied magnetic field, \( H_m \) is the maximum applied field, and \( a \) is half the thickness of a slab.

The critical current density of superconductors can be determined from magnetic measurements based on Bean's model, where \( J_c \) is constant. When \( H_m \) is larger than \( 2H^* \), \( J_c \) is related to the magnetization, \( M \), for slab of thickness \( 2a \) as follows,

\[
M(H)^+ - M(H)^- = J_c a.
\]
Therefore, $J_c$ can be calculated by measuring the width of a hysteresis loop at a given field, after the hysteresis loop is obtained.

For the orthorhombic sample,

$$M(H)^+ - M(H)^- = J_c a (1 - a/36)$$

where $a$ and $b$ are dimensions of the cross section of a sample, $b > a$.

1.5.2 Flux pinning [46]

Critical currents of type-II superconductors can be low due to the motion of vortices due to Lorentz force. It has to be prevented to have high critical current density. This can be achieved by the vortex pinning (or flux pinning), by creating normal sites out of which the vortex cannot leave without large energy increase [47]. The vortex will be pinned to such inclusions as it does not have to spend energy to destroy superconductivity in that inclusion. An inclusion is most efficient when its diameter is equal to the coherence length $\xi$, i.e., when the diameter of the tube which is in normal state within the vortex is equal to $\xi$.

A magnetic field enters a type-II superconductor to compensate for the energy needed to repel a magnetic field when the external field exceeds $H_{el}$. The system can lower its total free energy by allowing the magnetic field to enter the superconductor, although the region where the fluxoid has penetrated locally loses the condensation energy. The loss of energy due to the penetration of fluxoid is thus called the penalty energy and is $H_c^2/2\mu_0$ per unit volume.

When the fluxoid interacts with the nonsuperconducting region, the penalty energy can be saved per interacted volume, since such a region is normal conducting. The saved energy is $U_p = (H_c^2/2)\pi \xi^2 d$, where $d$ is the size of a nonsuperconducting particle. The
penalty energy must be paid to move the fluxoid from the normal superconducting region, whereby the fluxoids are pinned at normal regions.

The pinning force $f_p$ is given by $f_p = \frac{dU_p}{dx}$ and in a simple case

$$f_p = \frac{U_p}{\xi} = (\frac{H_c^2}{2}) \pi \xi d$$

This $f_p$ is called an elementary pinning force. In the case of very small pinning centers, the interaction volume becomes $(4/3)\pi \xi^3$ and thus

$$f_p = (2H_c^2/3)\pi \xi^2$$

Since oxide superconductors are highly anisotropic, the pinning forces are also anisotropic and it depends on the direction of the field and the Lorentz force.

**Bulk pinning force**

The bulk pinning force, $F_p$, per unit volume, is the sum over all the contributions from various pinning centers, and if the number of interactions per unit volume is $TV$, $F_p$ becomes equal to $Nf_p$. Critical current density is then simply obtained from the relation

$$F_p = Nf_p = J_c B.$$  

**Flux pinning sites in melt textured YBCO**

Melt processed YBaCuO contains many defects which may act as pinning centers. Those defects are twin planes [48-52], stacking faults [53-54], cracks, oxygen defects [55] and dislocations [56,57]. Presence of nonsuperconducting particles such as that of $Y_2BaCuO_6$ (Y-211) phase cause secondary defects in $Y$-$123$ matrix. Such defects occur only when the radius of curvature of the $123/211$ interface is smaller than approximately 0.25 $\mu$m [58,59]. In light $RE$-$123$, solid solution regions of the type $RE_{1+\varepsilon}Ba_{2-x}Cu_3O_{7-\delta}$
whose $T_c$ is lower than that of the stoichiometric 123 phase have been proposed to act as pinning centers [60-64].

**Depairing critical current**

There is an intrinsic critical current that a superconductor can support which is called depairing critical current. It is the current which destroys pairs and thus superconductivity. The maximum current is

$$J_c = \frac{4/3\sqrt{6}}{H_c/\lambda_L}$$

At 77 K, YBCO has a $H_c$ of 0.3 T and a $\lambda_L$ of 0.1 $\mu$m, which gives the ideal $J_c$ value to be $2.4 \times 10^8$ A/cm$^2$. This is three orders of magnitude larger than the required values, indicating that YBCO superconductors have intrinsically a potential for high $J_c$.

1.5.3 **ac susceptibility**

One of the most useful methods to study the magnetic properties of superconductors is to measure magnetization induced by ac magnetic fields. ac magnetization is usually evaluated as ac susceptibility. Measurements of the ac susceptibility, which is expressed as complex susceptibility, $\chi - x' \sim i\chi''$, have been used to determine the critical temperatures in conventional metallic superconductors [65] and recently, to determine the onset temperature for high $T_c$ oxide superconductors [66]. It has provided important information on flux dynamics [67-72]. The real part of the susceptibility, $\chi'$, represents diamagnetic shielding and the imaginary part, $\chi''$, represents bulk hysteresis loss. The ac field dependence of the loss peak in the susceptibility is analyzed to gain information on the movement of magnetic flux and the pinning strength.
1.5.4 Magnetic flux penetration

When magnetic fields are applied to a type-II superconducting sample, flux begins to penetrate into the sample preferentially from the regions with weaker pinning forces. Several kinds of the techniques for measurements of flux distribution have been reported. Higashida et al. [73] have found by the Bitter [6] decoration technique, that flux lines are trapped at 211 inclusions in melt-processed YBCO. Another method for the observation of dynamic flux behavior in superconductors was recently developed using magneto-optic Faraday effect in ferromagnetic iron garnet thin films [74-77]. The results clearly show that the critical state is established even in oxide superconductors and the 211 inclusions act as flux pinning centers. Many researchers measured the trapped field using a Hall probe in bulk melt textured samples [78,79] in order to characterize them for practical applications. There is another method for measuring the flux distribution in superconductors suggested by Campbell [80]. This is an inductive method, the penetration of the flux is detected by a lock-in amplifier operated in the wide-band mode. This was extensively used to study low $T_c$ superconductors. In this thesis, we present the methodology of measuring the flux profiles using this technique and apply it to various samples.

1.6 Motivation and aim of the work

A polycrystalline high $T_c$ superconductor is formed by small grains, typically a few microns in size, electrically coupled by weak links. This interconnected network [66] is supported by a nonsuperconducting matrix containing different impurities, voids and sometimes lower $T_c$ superconducting phases. The most important limitation in the performance of these materials comes from the weak intergrain connections, which limit the current carrying capability and make the sample very sensitive to magnetic fields. The
weaklink nature of the grain boundaries can be avoided by grain alignment by melt textured growth. Through this process large values of bulk \( J_c \) could be obtained in YBCO, containing optimal amount of 211 inclusions and silver, even in the presence of external dc fields. Recently Yoo et al. [36] melt processed \( \text{NdBa}_2\text{Cu}_3\text{O}_{7-\delta} \) (Nd-123) system in reduced oxygen atmosphere. This resulted in the samples with high \( J_c \) even in the high fields. A peak effect is seen in the \( M - H \) loops [36,60]. This has been attributed to the presence of \( \text{Nd}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_{7-\delta} \) phase inclusions which turn normal in the presence of high external fields [60-64].

The Y-211 inclusions modify practically all microstructural features of the melt processed Y-123 material: eg. platelet width, inter-platelet crack width, 211 size and morphology etc. The \( J_c \) of melt processed Y-123 is only a few hundreds of Amperes/cm\(^2\) in the absence of Y-211 inclusions, but it increases by orders of magnitude when an optimal amount of Y-211 inclusions are incorporated into the Y-123 matrix. The low field \( J_c \) of stoichiometric Nd-123 is relatively small and there is a possibility of enhancing that by the addition of Nd-422 inclusions.

In order to study the effect of Nd-422 inclusions on the microstructural features and magnetic response, we have melt processed Nd-123 with various amounts of Nd-422 inclusions. The microstructural aspects are studied by polarized light optical and scanning electron microscopy. There exists some initial study on the effect of Nd-422 on the critical current density of melt processed Nd-123. The aim of the present work was to study quantitatively the variations of different microstructural parameters such as the platelet width, the width of the inter-platelet gaps, and the size and morphology of the Nd-422 inclusions as a function of Nd-422 concentration. Similarities and differences in the behavior between the two systems were expected to throw light on the mechanism
of microstructural evolution on melt processing in these samples. Experiments were also done by cooling the samples at different cooling rates through the peritectic temperature. The main purpose of these experiments was to isolate the microstructural features which are modified by solidification instabilities. It is also useful to know if the samples can be melt processed at faster rates which can be of practical use. Nd-123 has also been melt processed in this work, using a process called the Infiltration and Growth (IG) process. This process involves the infiltration of liquid phase into Nd-422 preforms at high temperatures and subsequent formation of textured Nd-123 by slow cooling through the peritectic temperature. This process, which is akin to the methods used for the fabrication of RBSC and lanxide composites, avoids shrinkage and distortions in the textured material. Macroscopic hollow regions which occur in the interior of conventionally melt processed samples are also avoided by the IG process. The IG process offers a means of making high $J_c$ bulk products of large complex shapes with good dimensional tolerance and surface finish. The work described herein involves a study of an extension of the IG process to the Nd-123 system.

To avoid the possibility of forming low $T_c$ solid solution phases of the formula $\text{Nd}_{1+z}\text{Ba}_{2-z}\text{Cu}_3\text{O}_{7-\delta}$, the samples were processed in flowing high purity Argon gas. In order to detect any low $T_c$ phase left back, ac susceptibility was measured in bulk samples. Temperature variation of susceptibility at various ac field strengths was used to examine the nature of domain boundaries in the melt textured sample in comparison with the polycrystalline samples. The experimental data has been analyzed in terms of the critical state models.

Bulk melt textured samples, when processed without any imposed temperature gradient can contain more than one domain. Measuring the magnetization and $J_c$ using a VSM or a SQUID magnetometer characterizes only small sized samples which are very
often single domain. The behavior of large sample would be governed to a large extent
by the nature of the domain boundaries. Measurements on larger \textit{samples} having several
domains can be of practical value. Such measurements are demonstrated to be possible
in this work, using a home-made facility, where flux \textit{profiles} are measured. Measuring
the flux distribution in the melt textured sample gives information about the weaklink
regions. Flux distribution in sintered and various \textit{melt} textured samples was measured
using the home-made facility. The observations on the melt textured samples are cor-
related to the microstructural features of the samples. Critical current density could be
obtained on a large sized samples. The features observed in the flux profiles of sintered
samples could be simulated well using the critical state models. The effect of Nd-422
inclusion on melt textured samples has been studied using this technique. Magnetization
measurements were also carried out on the samples using a SQUID magnetometer as a
function of temperature and magnetic field. The melt processed \textit{Nd-123} samples with
various amounts of Nd-422, and also the \textit{IG} processed samples were studied. The behav-
ior of \textit{J_c} has been discussed as a function of the microstructural variations introduced
through Nd-422 and compared with the data available on other \textit{RE-123} system.
References


