CHAPTER II

METHODOLOGY
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2.1 INTRODUCTION

After the discovery of superconductivity in 1911, the search for new superconducting materials led to a slow increase in value of transition temperature ($T_c$) over a decade. The discovery was incredible and inspiring, simply not for the increase of $T_c$, but it revealed that the oxides formed an unexpected new class of superconducting materials with great potential. These high transition temperatures of the superconducting materials have technical interest as they opened way of applications that requiring only liquid $N_2$ rather than liquid helium. The known high-$T_c$ materials captivating much crucial queries like mechanisms those responsible for high transition temperature, nature of superconducting state related to cooper-paired state as in BCS, whether same or different, how acutely the phenomenological properties of superconducting materials described by GL-theory. In view of this, there is still no consensus as to the mechanism causing high transition temperature in these materials. However, it may come out that, whatever the mechanism; the magnetic properties of these materials can be well illustrated with familiar BCS or GL concepts.

For many decades, BCS theory along with its prolongations for strong coupling regime found to be good enough for explaining all of the known superconducting elements. Until, discovery of high-$T_c$ superconductors, this theory confirmed highest $T_c$ value for any superconductors to be 23 K. After such discovery of HTSCs, particularly in cuprates, it was clear that many important questions remained to be answered. There are many recently discovered materials, where it is unlikely that, BCS theory is applicable at least in its original form. In view of this, many people have conviction that there is no need to replace completely BCS theory with a new one, rather it should be extended or standardized for describing new known superconducting materials.
2.2 **LONDON THEORY**

The consequence of flux density can be deducted by applying usual laws of electrodynamics to a conductor with zero resistance. However, though the solution of Maxwell's equation for flux density inside metals completely describes magnetic properties of a perfect conductor or it does not prominently describe the behaviour of superconductors. Meissner's effect shows that, inside a superconductor, flux density is not only constant but is always zero. So $B$ and along with $B$ must die quickly below the surface. London brothers [F. and H. London] smoothly interpreted that the magnetic behaviour of superconducting materials can be correctly observed if parameters satisfy Maxwell's electrodynamics equation like, $\nabla^2 B = \frac{1}{\alpha} B$, as earlier, $B(x) = B_s \exp\left(-x/\sqrt{\alpha}\right)$. Now modified form becomes, $B = \left(-\frac{m}{n_0 e^2}\right) \text{curl} J$, and $J_z = \left(\frac{n_0 e^2}{m}\right) E$. Which together explain electrodynamics of superconducting materials and known as "London equations" as explained earlier. This explains resistance less property of a superconductor, there being no electric field in the metal unless current is changing with explanation of diamagnetic characterisation.

The London equations are not surmised from fundamental properties and do not explain occurrence of superconductivity. Further, London equations are restrictions on ordinary equations of electromagnetism. The behaviours deduced from these laws agree with that observed experimentally. Ultimately, London equations predict a rapid exponential decay of flux density at the surface of a superconducting material. First of all, it is noteworthy to realize that London equations do not completely replace Maxwell's equations, which may of course, still be applicable to all currents and fields they produce. Finally, London equations are the supplementary cases that obeyed by superconductors. Confront of magnetic effect in superconductivity for London theory, describes superconducting...
nature of materials. This initiated a modified theory for describing properties of superconductors in magnetic fields in terms of quantum theory approach called Ginzburg-Landau (GL) theory. This is a phenomenological theory, unlike microscopic BCS-theory. It completely based on so called phenomenological order parameter. GL-theory includes more ordered state of superconductors in terms of 2nd order phase transition and gauge invariance of complex GL-order parameter, \( \psi(r) = |\psi| \exp(i\theta) \). In GL-theory, \( B \) varies over GL-penetration depth \( \lambda(T) \) and \( \psi \) over GL-coherence length. Both lengths diverge near \( T_c \) as \( \lambda \propto \xi \propto (T_c - T)^{-1/2} \). The originally calculated GL-parameter in terms of \( \lambda, \xi \), \( \kappa = \lambda/\xi \) obtained for temperature \( T \approx T_c \). The GL-theory in many cases gives qualitatively prominent results valid at all temperatures, \( 0 < T < T_c \) [1-3]. Not strictly an ‘ab-initio’ theory, but essential for problems concerning superconductors in magnetic fields. First of all, GL-theory established prominently the distinction arising between type-I and type-II superconductors and enabling the calculation of two critical fields, \( H_{c1} \) and \( H_{c2} \).

The two GL equations obtained by the minimization of GL free energy functional \( F\{\psi, A\} \) with respect to \( \psi \) and vector potential \( (A) \), i.e. from \( \delta F/\delta \psi = 0 \) and \( \delta F/\delta A = 0 \), where in reduced units

\[
F\{\psi, A\} = \mu_0 H_c^2 \int d^3r \left[-|\psi|^2 + \frac{1}{2}|\psi|^4 + \left(-i \nabla/\kappa - A\right)\psi|^2 + B^2 \right]
\]

(1)

In the above expression, length unit is penetration depth \( \lambda, \kappa = \lambda/\xi \) is GL parameter, \( B \) is local magnetic field, \( \psi \) is in units of BCS order parameter \( \psi_0 (\psi_0 \sim T_c - T) \) such that \( |\psi| = 1 \) in Meissner state. Here, \( |\psi| = 0 \) in the normal conducting state. \( B \) is in units \( \sqrt{2} B_c \), and \( \kappa \) is in units \( \sqrt{2} B_c \lambda \). If desired, the electric field \( E = -\partial A/\partial t \) and the dependence may be introduced by assuming, \( \partial \psi/\partial t = -\gamma \delta F/\delta \psi \), with \( \gamma \) is constant [4-7]. An extension to
anisotropic non-cubic superconductors is possible by the multiplication of the gradient term in Eqn (1) by an ‘effective mass tensor’ [8, 9].

2.3 3D ANISOTROPIC LONDON THEORY

The Phenomenological GL-theory is one of the most sophisticated and dominating concepts in physics, which was applied not only to superconductivity but also to other phase transitions, to non-linear dynamics, to dissipative systems with self organizing pattern formation, and even to cosmology [10, 11]. Besides this, HTSC’s are anisotropic materials to a good approximation exhibiting uniaxial crystal symmetry. Within the anisotropic extension of London theory, uniaxial HTSC’s are characterized by two magnetic penetration depths for currents in ab-plane, \( \lambda_{ab} \), and along c-axis, \( \lambda_c \), and by two coherence lengths \( \xi_{ab} \) and \( \xi_c \).

Anisotropy may be incorporated in the phenomenological GL-theory by introducing an effective mass tensor in kinetic energy term of GL-equation and becomes [12, 13]

\[
\left[ -i\hbar \left( \nabla - \frac{ie^*}{c} A \right) \right] \frac{1}{2m^*} \left[ -i\hbar \left( \nabla - \frac{ie^*}{c} A \right) \right] \psi + \alpha \psi + \beta |\psi|^2 \psi = 0
\]

Where, \( 1/m^* \) is the effective mass tensor.

Near the field dependent transition temperature, the order parameter is vanishingly small and non linear term can be neglected. The equation is now formally identical with Schrodinger equation of particle with charge \( e^* \) and anisotropic mass tensor \( m^* \) in a uniform magnetic field \( H_0 \). Besides this, energy levels have harmonic oscillator in the following form

\[
-\alpha = (n+1/2) \hbar \omega_c(\theta)
\]

Where, \( \omega_c(\theta) \) is angular dependence of cyclotron frequency and is encountered in effective mass theory of cyclotron resonance of
semiconductors. Defining two coherence lengths, $\xi_1, \xi_2$, and recollecting flux quantum $\phi_0 = \frac{hc}{e^2}$, upper critical field in terms of above parameters becomes

$$H_{c2}(\theta) = \frac{\phi_0}{2\pi \left( \sin^2 \theta \xi_2^2 + \cos^2 \theta \xi_1^2 \right)^{\frac{1}{2}}}$$

Selectively, for fields parallel and perpendicular to symmetry planes of materials, we have fields as

$$H_{c2}^\parallel = \frac{\phi_0}{2\pi \xi_2^2}, \quad H_{c2}^\perp = \frac{\phi_0}{2\pi \xi_1^2 \xi_2^2}$$

Hence, angular dependence of upper critical fields are characterized by two parameters of coherence length and leading to a linear behaviour of upper critical field in transition temperature $T_c$ [13].

As deliberated earlier, upper critical field in layered type-II superconductors can be depicted by GL-equations with phenomenological anisotropic mass tensor. Quite close to lower critical field, the solution of non linear GL-equation is difficult to obtain in anisotropic case. Application of London model is less accurate in lower critical regime providing a reasonable description for large value of GL-parameter. In the reference frame aligned with principal axes, this mass tensor is diagonal, and diagonal elements $m_i \ (i = 1, 2, 3 = a, b, c)$ are normalized such that $(m_am_am_c) = 1$. It is significant to mention the behaviour of physical characteristics of high temperature superconductors, perfect agreement both with BCS microscopic theory of superconductivity, Ginzburg-Landau (GL) theory, and anisotropic formulation of GL-theory.
2.4 THEORY OF VORTEX OVERLAPPING

After discovery of superconductivity in 1911 in Leiden, it took more or less 50 years until this fascinating phenomenon was understood microscopically; when in 1957, BCS theory was established. But long before this, there were powerful phenomenological theories able to interpret most thermodynamic and electromagnetic considerations on superconductors [1, 2], also are very useful today [14-18]. Quite universal Ginzburg-Landau theory, containing London theory at a particular limit also predicts the two types of superconductors depending on the surface energy. The penetration of vortices in to type-II superconductors was projected first by Alexi Abrikosov, when he discovered the two dimensional periodic solution of GL-equation [19] in terms of periodic arrangement of the flux lines and flux line lattice (FLL). Further, the vortex core is a tube in which superconductivity is weakened and defining the position of vortex by lines at which superconducting order parameter vanishes. For isolated vortices, the radius of tube of magnetic flux equals to the magnetic penetration depth $\lambda$, and core radius is somehow larger than superconducting coherence length $\xi$.

Since the exploration of high temperature superconductors (HTSCs), various authors have used the anisotropic formulation of London theory to study energy and magnetization in intermediate field range that arbitrarily oriented. The theory of vortex overlapping can be applied for fields $B_s < 0.25 B_{c2}$ and that outside critical region. As vortex overlapping makes the theory in applicable at higher field, to study the high field behaviour, overlapping of vortex is incorporated in usual London theory. The HTSCs remaining in mixed state and have smaller coherence length than interspacing between vortex cores for small applied field range. The overlapping of vortices is weak and conforms in applicable of London theory [20]. If applied field $B_s \gg (\phi_0/\lambda^2)$, the inter vortex distance is smaller than $\lambda$ and the overlap is strong. At higher applied fields with strong overlap of vortices, $|\psi|^2$ varies in space. The spatial average of normalized order
parameter $\langle |f|^2 \rangle$ is $1-b$ with $b = B_a / B_{c2}$ where, $B_a$, $B_{c2}$ are magnetic flux density and upper critical field respectively [21, 22]. Further, the normalized order parameter is the ratio of order parameter in a field to that in zero fields. In view of this, in higher fields overlapping of vortices can completely be incorporated in usual London theory. Further, with the increase of applied magnetic field, magnetic flux density increases and interspacing between the vortices, $L = (B_v / B)^2$ decreases creating strong vortex overlapping. Finally, the magnetic interaction range ($\lambda$) increases in terms of effective penetration depth ($\lambda_{df}$) as

$$\lambda_{df}^2 = \frac{\lambda^2}{f^2} = \frac{\lambda^2}{1-b} \quad (6)$$

If the flux density becomes low, $\lambda_{df}$ reduces to weak field penetration depth and diverges at upper critical field $B_{c2}$. For a given local magnetic field and high-$\kappa$ approximation, free energy per unit length or line tension by London equation can be written as

$$\Delta F = \frac{1}{8\pi} \left[ \int [h^2(r) + \lambda_{df}^2 |\text{curl} \ h(r)|^2] \, ds \right] \quad (7)$$

Including Eqn. (7) and usual London equation, magnetic field becomes [2, 23]

$$H = B + \frac{\phi_0}{8\pi \lambda_{df}^2} \ln \left( \frac{B_a}{B_{c2}} \right) \quad (8)$$

$$\Rightarrow (B-H) = -\frac{\phi_0}{8\pi \lambda_{df}^2} \ln \left( \frac{B_a}{B_{c2}} \right)$$

The above expression is as much same as the result of variational model [23] with inappreciable core energy. In case of 3D superconductors, there is no thermal fluctuation of vortices, rather the energy change comes out due to vortex interaction and feebly depends upon the lattice structure.
in dense vortex phase. Further, in case of Josephson coupled layered superconductors, the thermal fluctuations also contribute to free energy. The thermal fluctuation of the vortex lines gives an entropy contribution to free energy and finally to magnetization \( M = \frac{\partial F}{\partial B_a} \). For 3D layered HTSCs, the magnetization becomes

\[
M = M_L = \frac{B - H}{4\pi} = -\frac{\phi_0 f^2}{32\pi^2 \lambda^2} \ln \left( \frac{B_{c2}}{B_a} \right)
\]  

(9)

In terms of effective penetration depth Eqn. (9) becomes as

\[
M_L = \frac{B - H}{4\pi} = -\frac{\phi_0}{32\pi^2 \lambda_{\text{eff}}^2} \ln \left( \frac{B_{c2}}{B_a} \right)
\]

(10)

All the magnetization curves \( M(B_a, T) \) should cross in one point if \( M \) is plotted versus temperature \( T \) with applied field as a parameter. The detailed observation will be given in the ultimate chapter. For the applied field along any arbitrary direction, upper critical field \( (B_{c2}) \) be replaced by \( B_{c2}(\theta) \), as that depends on the orientation of the vortices. The upper critical field is related to \( B_{c2}^\infty \) as [23]

\[
B_{c2}(\theta) = \gamma \frac{B_{c2}^\infty}{\varepsilon(\theta)}
\]

(11)

For \( \varepsilon(\theta) = (\sin^2 \theta + \gamma^2 \cos^2 \theta)^{1/2} \) and \( \theta \) is the angle between the applied magnetic field and crystallographic c-axis.

In case of YBCO \([\text{YBa}_2\text{Cu}_3\text{O}_7]\), the Josephson inter layer coupling region has been realized at all the temperature below 75 K and above this temperature there is no thermal or quantum fluctuation of vortex cores. Thus the possible melting of vortex lattice in HTSCs due to quantum fluctuations was considered remarkably [24-27]. The magnetization due to thermal fluctuation is given by
\[ M_n = \frac{K_B T}{\phi_0 s} \ln \frac{16\pi K_B T \kappa^2}{\alpha \phi_0 s B_a \sqrt{e}} \]  

Where, \( s \) = inter layer spacing, \( \kappa \) = a dimension less parameter of order unity, and \( K_B \) = Boltzmann constant.

Thus, finally, for Josephson-Coupled layered superconductors in applied field parallel to c-axis, the total magnetization becomes

\[ M = M_L + M_{th} = -\frac{1}{\phi_0} \left( 1 - \frac{B_a}{B_{c2}} \right) \ln \left( \frac{B_{c2}^{1/2}}{B_a} \right) + \frac{k_B T}{\phi_0 s} \ln \frac{16\pi k_B T^2}{\alpha \phi_0 s B_a \sqrt{e}} \]  

Where, \( \lambda_{ab} \) is the in plane penetration depth and \( B_{c2}^{1/2} \) as upper critical field along c-axis. Particularly, Eqn. (13) demonstrates experimental data in the vicinity of transition temperature.

**2.5 SPECIFIC HEAT OF CONVENTIONAL SUPERCONDUCTORS**

The study of specific heat anomaly at critical temperature of a superconducting material is a relevant test for conventional as well as bulk superconductors. In great enthusiasm generated by the discovery of new high-\( T_c \) superconducting materials, the essence of phase transformation at transition temperature has been the subject of deep study by specific-heat measurements, also carries some controversy on theoretical grounds [28-31]. In conventional superconductors, electrons and phonons are the two systems which contribute to total specific heat. These two contributions are basically depicted by normal state density of electronic state along with low temperature limit of Debye temperature (\( \theta_D \)). At low temperature, the phonon contribution can be represented in terms of gas constant (\( R \)), and number of atoms per molecule (\( n \)) as

\[ C_i = n (12/5) \pi^4 R (T/\theta_D)^3 \]

\[ = \beta T^3 \]  

(14)
In metals there are other contributions to free energy, entropy, electronic specific heat, and thermal expansion from electrons, magnetic spins etc. The electronic contribution is governed by volume dependence of electronic density of states at Fermi surface, \( \frac{dN(E_F)}{dE} \), just as the specific heat component is a measure of density of states \( N(E_F) \). In terms of Sommerfeld coefficient (\( \Gamma \)) and Boltzmann constant (\( k_B \)), the electronic contribution depends on the temperature linearly along with the Gruneisen parameter as

\[
C_m = \frac{2}{3} \pi^2 k_B^2 v N(E_F) = v \Gamma \quad (15)
\]

Similarly, the superconducting electronic part of specific heat decreases exponentially as

\[
C_s = A \exp\left(-\frac{2\Delta_0}{K_B T}\right) \quad (16)
\]

The cross over from superconducting state to normal state depends upon applied magnetic field and rounding the transition temperature, there is a leap in specific heat. Depending upon the applied field, specific heat coincides with zero field specific heat at very low temperature and increases gradually as well as rapidly to a peak above the zero field value. As applied field equals to lower critical field, specific heat peak signifies the access of external magnetic flux into the sample. Periodically, in terms of phase transition, the transition from superconducting state to mixed state is of first order. Whereas, the transition from the mixed state to the normal state shows no any intimation of latent heat giving rise to second order phase transition.

### 2.6 EXPLANATION OF SPECIFIC HEAT AND ENTROPY OF HTSCs

The usual effect of applied magnetic fields on specific heat anomaly near transition temperature of HTSCs is considerably different from the
effect on conventional superconductors. Like conventional superconductors, the temperature dependence of upper critical field along with anisotropy can be determined from the peak position of specific heat in applied magnetic fields. These specific heat measurements in HTSCs have been done in applied fields of order of 1 Tesla. The uniaxial approximation is a reasonable primary step for description of anisotropic properties of high temperature superconducting materials. The equilibrium vortex lattice structure for an arbitrary field orientation with respect to uniaxial crystal is a subject of investigation that was made properly in this particular chapter. Depending on the vortex core size with respect to coherence length and penetration depth, the London approach is applicable in a wide domain of $B_s << B_{c2}$. The field induced changes in both linear and cubic terms of low temperature heat capacity have been predicted theoretically \cite{20, 32} after by analyzing free energy of superconducting electrons in an applied magnetic field.

With the induced field, free energy density of an isotropic material changes as

$$F = \frac{1}{8\pi} \int \left[ h^2 + \lambda^2 (\nabla \times h)^2 \right] d^3x$$

(17)

Where $\lambda^2 (\nabla \times h)^2$ is kinetic energy density, $h(x,y)$ is local magnetic field, spatial average of which is $B$.

Major effects of strong uniaxial anisotropy can be taken into account by replacing kinetic energy density term in London free energy density of an isotropic material with an invariant combination in terms of effective mass tensor $(\lambda^2 m_k \text{Curl} h \cdot \text{Curl} h)$ \cite{33, 34}. Here, $\lambda^2$ is quite proportional to average mass $M_{av} = (M_1 M_2 M_3)^{\frac{1}{3}}$ with $M_s$ being principal values of mass tensor $M_{ik} = m_{ik} M_{av}$. Further, $m_{ik}$ is called as \textquotedblleft effective mass tensor\textquotedblright. Finally, $(\lambda^2 m_{ik})$ most likely includes all possible sources of anisotropy of HTSCs.
With this, free energy per unit length in the direction of vortices can be interpreted as

\[ F = \int \left( h^2 + \lambda^2 m_i \text{Curl}_i \cdot \text{Curl}_i h \right) dx dy / 8\pi \]  

(18)

Here \((dx dy)\) is an elemental area in the plane normal to direction \(\hat{z}\), of vortex axes. In an isotropic material along \(\hat{z}\), the field \(h\) has non-zero component, \(h_x\) and \(h_y\) unless the vortex axes coincides with one of the principal crystal directions. Further, \(\lambda^2 m_i (\nabla \times h)_i (\nabla \times h)_i\), the kinetic energy density is fully responsible for field induced change of the linear term in the \(C(T)\).

Assuming uniaxial symmetry, \(m_1 = m_2\), equation (18) can be expanded to second order in \(L/\lambda\) to capitulate

\[ 8\pi F = B^2 + B^2 \left( \frac{m_\infty}{m_1} \left( \frac{L^2}{\lambda^2} \right) \sum \delta_r \left( m_{\infty} g_x^2 + m_\sigma g_y^2 \right)^{-1} \right) \]  

(19)

With, \(m_{\infty} = m_1 \sin^2 \theta + m_2 \cos^2 \theta\), \(g_i / B G_i\) is a dimension less reciprocal lattice vector, \(G_i\) is reciprocal lattice vector of the fluxoid array. For the periodic array of fluxoids, each carries one flux quantum \(\phi_0\). Further, taking \(L^2 = \text{const.} \times \frac{\phi_0}{B}\), if we evaluate the derivative of free energy density with respect to applied field and define \(\delta_r = \left( m_{\infty} g_x^2 + m_\sigma g_y^2 \right)\), then the magnetic field becomes

\[ H = B \left[ 1 + \frac{1}{2} \frac{m_\infty}{m_1} \frac{L^2}{\lambda^2} \sum \delta_r^{-1} \right] \]  

(20)

From London free energy density, Gibb's free energy difference can be obtained as

\[ \Delta G = F - \frac{BH}{4\pi} \]  

(21)
Similarly, the difference of entropy can be calculated as

$$\Delta S = -\left[ \frac{\partial A}{\partial T} \right]_T$$  

(22)

This expression ignores the contribution to entropy made by electrons in normal cores. Further, the specific heat enhancement caused by applied magnetic field can be found from derivative of entropy change as

$$\Delta C = T \left[ \frac{\partial \Delta S}{\partial T} \right]_T$$  

(23)

Using Eqn (20) in Eqs. (21-23) we can obtain change in specific heat as

$$\Delta C = \frac{T}{4\pi} \left[ \left( \frac{\partial B}{\partial T} \right)^2 + B \left( \frac{\partial^2 B}{\partial T^2} \right) \right]$$  

(24)

Taking $\frac{\partial H}{\partial B} = 0$, the partial derivative of applied field with respect to $T$ can be obtained properly. In the crystal frame $(X, Y, Z)$, $B_z = B \sin \theta$, $B_x = B \cos \theta$ and $m_x B^2 = m_1 B_x^2 + m_3 B_z^2$, we can obtain the relation between $B$ and $H$ as

$$H_z = B_z + \frac{\eta \phi_0}{2 \lambda^2} \frac{m_3 B_z}{B^{\infty \pi}} \ln \left( \frac{B_{c2}}{B} \right)$$  

(25)

and

$$H_x = B_x + \frac{\eta \phi_0}{2 \lambda^2} \frac{m_1 B_x}{B^{\infty \pi}} \ln \left( \frac{B_{c2}}{B} \right)$$  

(26)

The quantity $\left( \frac{\eta \phi_0}{\lambda^2} \right)$ is of order of upper critical field $(B_{c2})$. It is therefore small with respect to both $H$ and $B$ in field domain of interest. $H_x, H_z$ are the components of $H$ parallel and perpendicular to $c$-axis respectively.

Finally, the change in specific heat $(\Delta C)$ by applied magnetic field can be obtained as
\[ \Delta C = C(0,T) - C(B_n,T) = T \left( \frac{\partial^3 \Delta G}{\partial T^4} \right) \]  

(27)

Following the procedure obtained by Ota [35], we can get the expression as

\[ \Delta C = \left[ \frac{B}{T_c} \frac{2 \alpha}{\lambda_m^2(0)} \left( \frac{t}{1-t} \right) \right] + \Theta \left[ \left( \frac{L}{\lambda_m} \right)^4 \right] \]  

(28)

The second term in Eqn. (28) is negligible and not reliable. Following GL-temperature dependences,

\[ \lambda_m(T) = \left[ \frac{\lambda_m(0)}{\sqrt{2}} \right] (1-t)^{-1/2} \quad \text{and} \quad B_{c2}(T) = B_{c20}(1-t) \]  

(29)

This is valid near transition temperature with reduced temperature \( t = T/T_c \). Further, in terms of reduced temperature \( t \), applied field \( B_n \) and mean penetration depth \( \lambda_m \), the expression for change in specific heat can be obtained as

\[ \Delta C = \left[ \left( \frac{B}{T_c} \right) \frac{t}{1-t} \right] \left[ \alpha \theta(y) \right] \lambda_m^2(0) \]  

(30)

Similarly, for high-\( T_c \) superconducting materials over any spherical shell, the temperature dependant change in entropy can be obtained by polycrystalline average of the sample as [35, 36]

\[ \Delta S = -2 \frac{\alpha B_x}{T_c} \left[ \frac{\theta(y)}{2} \ln \left( \frac{ey B_x^{c2}}{B_a} \right) - g(y) \right] \]  

(31)

Where, \( g(y) = \frac{1}{3} \int_0^1 \sqrt{1+(y^2-1)x^2} \ln \sqrt{1+(y^2-1)x^2} dx \), \( x = \cos \theta \)

Basing on evaluated equations above, variation of change in specific heat along with change in entropy with respect to temperature and applied field for different HTSCs has been observed. The detailed explanation has been given in suitable section of the succeeding chapter.
2.7 MAGNETIZATION OF CONVENTIONAL SUPERCONDUCTORS

It has been recognized that the magnetic properties of hard superconductors differ qualitatively from those of soft superconductors. In particular, the hard superconductors generally exhibit hysteresis and demonstrate superconducting properties in the fields that are quite greater than critical fields of soft superconductors. In addition, it is becoming increasingly unambiguous that these two types of materials differ in their micro structures. Magnetization measurement of different superconducting materials acts as an important contraption for studying magnetic behaviour of different superconducting materials. The measurement of reversible magnetization of type-II superconductors is one of the important methods for determining superconducting parameters like penetration depth ($\lambda$), coherence length ($\xi$) and Ginzburg-Landau order parameter ($\kappa$) [37, 38].

Further, the identification of mixed state can be characterised by magnetization curve. Depending on applied field and magnetization, one can distinguish mixed state of superconducting materials. It can be well understood about the variation of magnetization in Meissner's state with applied magnetic field.

2.8 EXPLANATION OF MAGNETIZATION OF 3D SUPERCONDUCTORS

The information of London penetration depth provides much important information about the nature of superconducting state. The reversible magnetization of superconducting materials with GL-parameter $\kappa (= \frac{\lambda}{\xi} \gg 1)$ is a linear function of $\ln B$ [1]. This characteristic behaviour of $M(B)$ stems from logarithmic interaction of straight vortices for inter vortex distances smaller than penetration depth and is well obeyed in both conventional as well as HTSCs [39-45]. In high-$T_c$ superconductors, there exist a broad domain, and for which reversible magnetization is linear in logarithm of applied field. This dependence of $M(\ln B)$ obtained with strong...
uniaxial anisotropy. There are several different regimes of temperatures and magnetic field with different models applicable remarkably in describing thermodynamic properties of different HTSCs.

In particular, GL-theory was the fundamental work for isotropic classic superconductors applicable in London limit and superconducting order parameter is not too large near transition temperature. Further, in London model, both magnetic flux density and super current density of an isolated vortex diverge on axis of vortex as vortex core is ignored, where the order parameter suppresses to zero. Again, Hao, Clem [23, 46-47] developed variational model, including an energy term arising from the suppression of order parameter in vortex core. With such, experimental data of magnetization allows GL-parameter and critical field to be determined as fitting parameters for variational approach solution of extreme type-II superconductors. Here, GL-parameter satisfies condition $\kappa >> 1$ in the reversible magnetization regime.

Up to present, high-$T_c$ superconductors are found to be layered perovskite type oxide superconductors. Near transition temperature, the magnetic properties are different for different systems including anisotropy in almost all layered superconductors. In the presence of strong vortex fluctuation, it is observed experimentally that, surrounding of $T_c$, magnetization also shows some peculiar behaviour. For lower temperature range, magnetization is proportional to the factor $(T-T^*)$, where $T^*$ is almost field independent and very close to $T_c$. In case of 3D superconductors, there is no thermal fluctuation of vortex cores and energy change in mixed state arises due to interaction between vortices.

Incorporating vortex overlapping in Landon theory, the magnetization of 3D superconductors become as [48]

$$M_L = \frac{B - H}{4\pi} = \frac{\Phi_0 (1-b)}{32\pi^2 A^2} \ln \left( \frac{B_{c2}}{B_a} \right)$$

(32)
However, for Josephson coupled layered superconductors, with different applied field orientations, thermal fluctuation of vortex cores are enhanced in quasi two dimensional (2D) structures above $T_c$. With BLK approach [49], the thermal fluctuating magnetization becomes as

$$M_{th} = \frac{K_B T}{\Phi_0 s} \ln \frac{32\pi^2 T \xi^2 \lambda_j^2}{\alpha \Phi_0^2 s \ln (\lambda_j / \xi_{ab})} \text{ for } B << B_c$$

and

$$M_{th} = \frac{K_B T}{\Phi_0 s} \ln \frac{16\pi e T \kappa^2}{\alpha \Phi_0^2 s B} \text{ for } B >> B_c$$

(33)

(34)

where, $\lambda_j (= \gamma s)$ is the Josephson length and $\gamma = \lambda_c / \lambda_{ab}$ is the anisotropic ratio.

Further, taking unitary Josephson length with modification near transition temperature, the thermal magnetization becomes as

$$M_{th} = \frac{K_B T}{\Phi_0 s} \ln \frac{16\pi K_B T \kappa^2}{\alpha \Phi_0^2 s B \sqrt{e}}$$

(35)

Taking these two, for Josephson coupled layered superconductors with magnetic field parallel to $c$-axis, the total magnetization becomes

$$M = M_L + M_{th}$$

$$\Rightarrow M = \left[ \frac{\Phi_0 (1-b)}{32\pi^2 \lambda^2} \ln \left( \frac{B_{c2}}{B_a} \right) \right] + \left[ \frac{K_B T}{\Phi_0 s} \ln \frac{16\pi K_B T \kappa^2}{\alpha \Phi_0^2 s B \sqrt{e}} \right]$$

(36)

With this, field dependence of magnetization slope modifies as

$$\frac{dM}{d \ln B} = \frac{\Phi_0}{32\pi^2 \lambda^2} \left[ 1 - 2 \left( \frac{B_a}{B_{c2}} \right) \ln \left( \frac{B_a}{\eta B_{c2}} \right) \right]$$

$$\Rightarrow \frac{dM}{d \ln B} = \left[ \frac{\Phi_0}{32\pi^2 \lambda^2} \right] - \left[ \frac{\Phi_0}{16\pi^2 \lambda^2} \left( \frac{B_a}{B_{c2}} \right) \ln \left( \frac{B_a}{\eta B_{c2}} \right) \right]$$

(37)

Mixed state magnetization is small and replacing $B_a$ with $B$ and $f (=1-b)$ in terms of field, equation for magnetization becomes as
Finally, taking differentiation and neglecting \( \left( \frac{B}{B_{c2}} \right) \) as \( B \ll B_{c2} \), it becomes

\[
\frac{dM}{d \ln B} = \frac{\phi_0}{32\pi^2 \lambda^2} \left[ 1 - \left( \frac{B}{B_{c2}} \right) \ln \left( \frac{B}{B_{c2}} \right) \right]
\]

(39)

2.9 IMPACT OF OXYGEN DEFICIENCY ON HTSCs

For layered cuprate high-\( T_c \) superconductors, critical current density, upper critical field, superconducting magnetization, specific heat, entropy, coherence length, penetration depth, condensation energy and related properties as a function of temperature as well as applied field can be tested with the effect of oxygen stoichiometry. Clear effects of oxygen composition on superconducting properties of \( \text{YBa}_2\text{Cu}_3\text{O}_{7-\delta} \) (hereafter Y-123) still not well understood due to difficulty in controlling and varying content of oxygen in single crystal of such systems. With in small interval of oxygen deficiency (0 < \( \delta \) < 0.2) it is explicitly intriguing to examine different properties those are strongly affected while transition temperature nearly remains constant in the same range. This small range of composition of \( \delta \) has great practical relevance, as for dense and bulk materials, always oxygen vacancies present [50]. Further, in the situation of overlapping of vortex cores of layered HTSCs, oxygen vacancy has great impact on variation of change in specific heat as well as change in entropy.

With the effect of overlapping of vortices, field oriented penetration depth related with anisotropic factor by considering phenomenological Ginzburg-Landau (GL) theory of type-II superconductors [48, 51]. By introducing effective penetration depth (\( \lambda_{\text{eff}} \)) it has also analytically pointed out that, anisotropic ratio can also be related with oxygen deficiency of
layered oxide type-II superconductors. In particular, for Y-123, field dependent change in specific heat can be expressed as

\[ \langle \Delta C \rangle_i = \frac{B_z}{T_{c_i}} \left( \frac{t_i}{1-t_i} \right) \frac{\alpha \theta(y)}{\lambda_i^2(0)} \]  

(40)

Here \( T_{c_i} = T_{c_0} + \Delta_i \), where \( i \) represents a particular concentration value. \( T_{c_0}, T_{c_1}, T_{c_2} \) represent critical temperatures value at different concentration. \( \Delta_i \) is the change in \( T_c \) value with respect to concentration, \( \delta \). Again taking binomial expansion and neglecting the quadratic in reduced temperature \( t \left( = \frac{T}{T_{c_0}} \right) \), change in specific heat becomes

\[ \langle \Delta C \rangle_i = \frac{B_z}{T_{c_0}} \left( \frac{t_i}{1-t_i} \right) \frac{\alpha \theta(y)}{\lambda_i^2(\eta_i)} \]  

(41)

Here, also \( \eta_i = \left( \frac{\Delta_i}{T_{c_0}} \right) \). Finally effective penetration depth in terms of mean penetration depth becomes as

\[ \lambda_{\text{eff}}(\delta_i) = \frac{\lambda_{\text{eff}}(0)}{(1-\delta_i)} = \frac{\lambda_m(0)}{(1-\delta_i)(1-\delta_i)^{1/2}} \]  

(42)

Further, oxygen dependent anisotropic ratio can be expressed as

\[ \gamma_i = \frac{\gamma(0)}{(1-\delta_i)} \]  

(43)

This explains oxygen deficiency dependence of penetration depth as well as anisotropic ratio in foot print of theory of vortex core overlapping properly. The detailed physical analysis of such variation has been made briefly in the next chapter.
REFERENCES
CHAPTER-II
REFERENCES


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