1.1 DISCOVERY OF SUPERCONDUCTIVITY:

Superconductivity is a phenomenon of sudden disappearance of electrical resistance below a certain temperature. This temperature below which a material becomes superconductor is called transition temperature and denoted by $T_C$.

![Fig. 1.1: Electrical resistivity versus temperature curve for Hg.](image)

It was first discovered by Kamerleingh Onnes (1911) in mercury at a transition temperature $T_C = 4.2$ k. Now many elements like Li, Na, K etc. in periodic table are found to be superconductors. Li, Na and K remains normal conductor down to 0.08 k and 0.09 k and 0.08 k respectively. Similarly Cu, Ag and Au are found to be normal conductor even at temperature down to 0.05 k, 0.35 k, and 0.05 k respectively. Thus they do not superconduct even at such low temperatures. Theoretically it has been predicted that if Na, and K superconduct at all, the transition temperature will be much less than $10^{-5}$ k.
Superconductivity is absent in most of the ferromagnetic metals and rare earth elements except lanthanum (which has an entirely empty 4f electronic shells). It is well known that magnetic impurities have a deleterious effect on superconductivity in their host solid.

1.2 PROPERTIES OF A SUPERCONDUCTOR:
The superconducting state is characterized by Meissner effect, flux quantization, exponential specific heat and isotope effect etc.

1.2.1 Meissner effect:
Meissner effect is a phenomenon of complete expulsion of magnetic field by a superconductor, so a superconductor is a perfect diamagnetic with magnetic susceptibility $\chi = -1$. The flux at the transition temperature is ejected due to the induction of current in the specimen, which produces a flux equal and opposite to the original flux due to the magnetic field. Since in superconducting state resistivity is zero, the current due to induction in the specimen persists as along as the field is on. Due to this persistent current, specimen acquires a negative moment, producing a field in a direction opposite to the direction of applied field. Due to the negative magnetic moments, the specimen behaves as a diamagnetic one. When the external field is removed persistent current goes off.

1.2.2 Flux Quantization:
Also it is observed that in mostly recent discover superconductor like oxypnictides and boro carbides, flux through a superconductor is integral multiple of $\hbar/2e$.

1.2.3 Exponential Specific heat:
It also shows exponential electronic specific heat. In normal metals the electronic specific heat varies as the absolute temperature. It is of the form:
\[ C_n(T) = \gamma T + \beta T^3 \]

So that \( C_n(T)/T \) verses \( T^2 \) graph is a straight line. The first term in above equation is the specific heat of electrons in the metals and the second term is the contribution of lattice vibrations at low temperatures. The specific heat of the superconductor shows a jump at \( T_C \). Since superconductivity affect electrons mainly, it is natural to assume that the lattice vibration part remains unaffected. On subtracting this, we find that the electronic specific heat (\( C_{es} \)) is not linear with temperature. It, instead, fits an exponential form:

\[ C_{es}(T) = A \exp(-\Delta KT) \]

Where \( \Delta = b KT_C \); \( b \) is a constant.

An exponential dependence implies that it requires a finite gap \( \Delta \), to excite an individual electron in a superconductor (in normal metal, the energy required is zero). Thus this exponential form is an indication of the existence of a finite gap in energy spectrum of electrons separating the ground-excited state. The number of electrons thermally excited across this gap varies exponentially with the reciprocal of the temperature. The energy gap is believed to be a characteristic feature of the superconducting state, which determines the thermal properties, as well as high frequency electromagnetic response of all superconductors.

1.2.4 Isotope effect:

A superconducting state may be also characterized by another effect called isotope effect. According to isotopic effect transition temperature of superconductor metal varies with isotopic mass \( (T_C \propto M^{-1/2}) \). In mercury \( T_C \) varies 4.185 k to 4.146 k as the isotopic mass varies from 199.5 to 203.4 a.m.u.

1.3 BCS THEORY:

In order to understand all these properties a theory was needed and the break through came with Bardeen. Cooper and Schieffer’s complete atomic theory of
superconductivity in 1957. This theory is known as BCS Theory and is based on the bound electron pairs.

According to this theory two electrons bind together by the help of Phonons & make a pair. These pairs are called cooper pair & condense in ground state with zero resistivity.

According to BCS theory transition temperature is given by-

\[ T_c = 1.14\hbar \omega_0 \exp[-1/N(0)V] \]

Where, \( \omega_0 \) = Phonon frequency.

\( N(0) \) = No. of density state.

\( V \) = cooper pair interaction.

So, the BCS ground state involve pairs of electrons, thus flux quantization in terms of pair charge 2e is a consequence of the theory.

The basis of the formulation of BCS theory are the two experimental conclusions namely the isotope effect and the variation of specific heat of superconductors. From isotope effect \( T_C M^{1/2} \) = constant, one can infer that the transition resulting in superconducting state must involve the dynamics of ion motions, lattice vibrations or phonons. Further we note that \( T_C \) attains a value zero when \( M \) approaches infinity. This all suggests that nonzero transition temperature is a consequence of the finite mass of the ions, which can contribute phonons by their vibrations. Frohlich and Bardeen, in 1950, pointed out that an electron moving through a crystal lattice has a self-energy accompanied by ‘virtual’ phonons. This means that an electron moving through the lattice, distorts the lattice and lattice in turn acts on the electron by virtue of electrostatic forces between them. The oscillatory distortion of the lattice is quantized in terms of phonons and so one can interpret the interaction between the lattice and electron as the constant emission and re-absorption (creation and annihilation) of phonons by the latter. So the basic interaction responsible for superconductivity appears to be of a pair of electron by means of an exchange of virtual phonons.

BCS theory also showed that the energy difference between the free state of the electron (i.e., energy of individual electron- a case of normal state) and the paired state
(the energy of paired electron- a case of superconducting state) appears as the energy gap at the Fermi surface. The normal electron states are above the energy gap in the semiconductors and insulators. Since pairing is completed at 0\(k\), the difference in energy of free and paired electron states (i.e., normal and superconducting electron states) is maximum or in other words energy gap is maximum at absolute zero. At \(T = T_C\), pairing is dissolved and energy gap reduces to zero. Across the energy gap there are many excited states for superconducting cooper pairs. BCS theory thus predicts many electron ground states as well as exited states for the superconductor in the range 0 to \(T_C\), and in these states cooper pairs are supposed to be in condensed state with a definite phase coherence. At critical temperature, this coherence disappears and the pairs are broken resulting in the transition of superconducting state to normal state.

The paired electrons (cooper pairs) are not scattered because of their peculiar property of smoothly riding over the lattice imperfections without ever exchanging energy with them. Consequently, they can maintain their coupled motion up to a certain distance called coherence length. The latter is to be of the order of \(10^{-4}\) cm.

### 1.4 EFFECT OF APPLIED MAGNETIC FIELD:

A superconducting state may be destroyed by application of sufficiently strong magnetic field through superconductor. The threshold or critical values of the applied magnetic field for the destruction of the superconductivity is denoted by \(H_c(T)\) and is a function of the temperature \(T\). At the transition temperature the critical field is zero [i.e. \(H_c(T_C)=0\)].

It was also noticed that superconductivity is absent in many metals having localized magnetic moments. The mechanism of their destructive effect on the superconducting state may be understood with in the frame work of the BCS theory if one takes into account the exchange interaction of conduction electrons with the localized atomic magnetic moments.
As according to BCS theory in a cooper pair electrons are united with zero momentum and opposite spin. An applied magnetic field $\mathbf{H}$ or magnetic moment $\mathbf{\mu}$ of an ion in the superconductor can interact with the superconducting electrons in two ways-

(i) Via the Zeeman interaction of $\mathbf{H}$ or $\mathbf{\mu}$ with the conduction electron spins ($\mathbf{S} \cdot \mathbf{H}$).

(ii) The electromagnetic interaction of vector potential associated with $\mathbf{H}$ or $\mathbf{\mu}$ with the momenta $\mathbf{P}$ of the electrons ($\mathbf{P} \cdot \mathbf{A}$).

Both of these interactions raise the energy of one member of a cooper pair and lower the energy of the other & hence tearing the cooper pair apart which causes collapse of superconductivity. Such pair breaking interactions are very destructive for superconductivity and generally lead to strong depressions of $T_C$.

In a type II superconductor which does not contains ions which carry magnetic moment, the Zeeman interaction of the applied magnetic field $\mathbf{H}$ with the spins of the superconducting electrons and the electromagnetic interaction of $\mathbf{H}$ with the momenta of superconducting electrons both break superconducting electron – pairs.

The Zeeman interaction leads to the paramagnetic limiting field $\mathbf{H}_p = \left[ N(E_f) / (\chi_n - \chi_s) \right]^{1/2} \Delta$. Where $N(E_f)$ is the density of states at the fermi level $E_f$ and $\chi_n$ & $\chi_s$ are the normal superconducting states susceptibilities respectively. While electromagnetic interaction yields the orbital critical field $\mathbf{H}_c = \phi_0 / 2 \pi \xi^2$. Where $\phi_0$ = flux quantum and $\xi$ is the superconducting coherence length.

According to BCS theory-

$\chi_n(0) = 0 \& \mathbf{H}_p = \mathbf{H}_{po} = 1.84 \ T_C(T)$.

However spin – orbit scattering can increase $\chi_n$ and in turn $\mathbf{H}_p$, but inspite of this severe effect many materials are discovered which show the co-existence of superconductivity with magnetism.
1.5 SUPERCONDUCTIVITY CO-EXISTS WITH MAGNETISM:

In the experiment reported in Science, the scientists (M. Kenzelmann et al.) cooled a single crystal of CeCoIn$_5$ (a metal compound consisting of cerium, cobalt and indium) to a temperature close to absolute zero. To their great surprise, they discovered that magnetism and superconductivity coexist and disappear at the same time when they heat the sample or increase the magnetic field.

This discovery is extraordinary, since magnetic order exists exclusively when this sample is in the superconducting state. In this unique case, magnetism and superconductivity do not compete with each other. Instead, superconductivity generates magnetic order.

Now the question arises how does a superconductor overcome these magnetic pair breaking interactions?

The materials which show the coexistence of superconductivity and magnetism are rare earth compounds (RMo$_6$S$_8$, RMo$_6$Se$_8$ & RRh$_4$B$_4$ etc.), boro carbides (YNiB$_3$C$_{0.2}$, LnNi$_2$B$_2$C & YPd$_5$B$_3$C$_{0.3}$ etc.), heavy fermion systems (CeCu$_2$Si$_2$, UBe$_{1.3}$, UPt$_3$, URu$_2$Si$_2$ & UNi$_2$Al$_3$ etc) and recently discovered oxypnictides.

These materials exhibit a number of remarkable phenomena which includes:

(i) The coexistence of superconductivity and antiferromagnetic order.

(ii) The destruction of superconductivity by the onset of ferromagnetic order at a second critical temperature $T_{c_2} = T_m < T_{c_1}$, where $T_m$ is the Curie temperature and $T_{c_1}$ is the superconducting critical temperature. In addition, the superconducting – ferromagnetic interactions produce a new sinusoidally modulated magnetic state that co-exists with superconductivity in a narrow range of temperatures above $T_{c_2}$.

(iii) The induction of superconductivity through the application of high magnetic fields.

Rare earth and actinides have $f$ – electrons & partially filled $f$ shells which there by carry magnetic moments. The localized $f$ – states are hybridized with conduction
electron states and there are strong correlations with the $f$-shell. Depending on the strength of hybridization, manifestation of various phenomenon takes place. In Weak hybridization region $\text{RM}_{6}\text{X}_8$ ($\text{X} = \text{S, Se}$), $\text{RRh}_4\text{B}_4$ & $\text{Ni Boro Carbides}$ come. Here, $f$-electrons have well defined localized magnetic moment & interact with the spins and momenta of conduction electrons. When hybridization is moderate like in heavy fermion systems, a large density of states $N(E_f)$ at the fermi level $E_f$ & corresponding large effective mass of electron $\approx 10^2 - 10^3\ m_e$ is observed. This class shows coexistence of ferromagnetism & superconductivity. 

The different possibilities that can arise are-

(i) One way which has been experimentally established is to set up a modulated spin structure with a period (lattice constant) $a \leq \xi$. This is satisfied in the known antiferromagnetic superconductors in which $\xi \geq 10^2\ \text{Å}$. 

(ii) In ferromagnetic superconductors, this condition can be satisfied by setting up a new sinusoidally modulated state that screens the exchange interaction at large wavelengths. Another method involves the presence of a negative exchange field that compensates the applied magnetic field, allowing superconductivity to persist in magnetic field much higher than the critical field.

In high $T_C$ cuprates superconductor, superconducting phase occurs near matter insulating transition with the destruction long range antiferromagnetic order of copper spins but short range antiferromagnetic order survives in superconducting state. So the presence of superconducting phase in these materials raises a question that “Is magnetism helping to achieve superconductivity in these materials?” To understand this question first we should understand properties of these materials and also the role of magnetism in these materials. Now, in the forward part of introduction, some important features in these materials have been described in details to understand the actual mechanism behind for co-existence between magnetism and superconductivity:
1.5.1 HEAVY FERMION SUPERCONDUCTORS:

Heavy-Fermion (HF) systems are stoichiometric lanthanide or actinide compounds whose qualitative low-temperature behavior in the normal state closely parallels the one well-known from simple metals. The characteristic temperature $T^*$ which can be considered as a fictitious Fermi temperature or, alternatively, as an effective band width for the quasiparticles is of the order $10 – 100$ k. Residual interactions among the heavy quasiparticles lead to instabilities of the normal Fermi liquid state. A hallmark of these systems is the competition or coexistence of various different cooperative phenomena which results in highly complex phase diagrams. Of particular interest are the SC phases which typically form at a critical temperature $T_c \leq 2$ k. The exceptionally high transition temperature of $\sim 18.5$ k was recently reported for the actinide compound PuCoGa$_5$. Heavy Fermion superconductors are described in two parts:

1.5.1.1 Ce-based HF Superconductors:

The discovery of superconductivity in CeCu$_2$Si$_2$ forced condensed-matter physicists to revise the generally accepted picture of the electrons occupying the inner shells of the atoms. Traditionally, the corresponding states were viewed as localized atomic-like orbitals which are populated according to Hund’s rule in order to minimize the mutual Coulomb repulsion. This leads to the formation of local magnetic moments which tend to align and which are weakly coupled to the delocalized conduction electrons. The latter were viewed as "free" fermions which occupy coherent Bloch states formed by the valence orbitals of the atoms. An attractive residual interaction among the conduction electrons causes the normal metallic state to become unstable with respect to superconductivity. The cooper pairs which characterize a superconducting phase are broken by magnetic centers. The damaging effect of 4f- and 5f ions was well established by systematic studies of dilute alloys.
The key to the understanding of the origin and the nature of the unanticipated superconductivity in CeCu$_2$Si$_2$ lies in a better appreciation of the physics of the highly unusual normal state out of which it forms. The characteristic features summarized above show that the magnetic degrees of freedom of the partially filled f-shells form a strongly correlated paramagnetic Fermi liquid with an effective Fermi energy of the order of 1-10 meV. The existence of a Fermi liquid state with heavy quasiparticles involving the f-degrees of freedom has been confirmed experimentally.

The superconducting phases of HF materials are characterized by BCS-type pair-correlations among the heavy quasiparticles of the normal state. This picture is inferred from the fact that the discontinuities observed in various thermodynamic properties at the superconducting transition scale with the large effective masses of the normal state. The unusual energy and length scales in HF superconductors, however, lead to novel phenomena. First, the effective Fermi temperature typically exceeds the superconducting transition temperature only by one order of magnitude. This fact implies that standard weak-coupling theory which keeps only the leading contributions in an expansion with respect to the ratio $T_C/T^*$ can provide only qualitative results. Pronounced strong-coupling corrections are reflected in deviations from the universal behavior predicted for weak-coupling systems. Second, the small characteristic energy $K_B T^*$, or, equivalently, the narrow width of the quasiparticle bands implies a small value of the Fermi velocity $v_F$. As a result, the size of the Cooper pairs in the HF systems, i.e., the coherence length ($\xi \propto v_F$) is much less than in a typical "ordinary" superconductor. Many of the systems can be considered as "clean" with the mean-free paths exceeding the coherence length. As a result, anisotropic pair states can form which are strongly suppressed by impurity scattering in "ordinary" superconductors with large coherence lengths.

Although we know the correlations which characterize the superconducting state we are still far from a complete theory of superconductivity in these materials. Major questions are still open. Among the prominent is the question of which order parameters characterize the superconducting states and what is the origin of the attraction between
the quasiparticles. The correct microscopic description of the interaction would yield, of course, the superconducting transition temperatures as well as the detailed form of the order parameter. To describe ordered phases, the determination of the type and the symmetry of the order parameter is of central importance. The latter restricts the possible excitations in the ordered phases and hence determines the low-temperature properties. Order parameters given in terms of expectation values of physical observables like spin- and charge densities can be directly measured by X-ray or neutron diffraction. The magnetic phases of the lanthanide and actinide compounds are therefore rather well characterized. Superconductivity, however, corresponds to an off-diagonal long-range order parameter which is not directly observable. The usual procedure to determine the symmetry of the superconducting order parameter is to select plausible candidate states corresponding to irreducible representations of the symmetry group, calculate expected behavior of physical quantities and compare the predictions with experiment.

The fact that HF superconductors can be considered as "clean" systems with the mean-free path exceeding the coherence length has rekindled speculations so as to find inhomogeneous superconductivity phases at sufficiently low temperatures in sufficiently high magnetic fields. In fact, the order of the phase transition in an applied magnetic field has been found to change from second to first order with decreasing temperature - in agreement with long-standing theoretical predictions.

An indispensable prerequisite to a microscopic theory of superconductivity is a microscopic theory of the normal state, of the quasiparticles and their interactions. The Landau theory does not make assumptions or predictions concerning the microscopic nature of the ground state and the low-lying excitations. It does not address the question how the latter emerge in an interacting electron system. During the past decade it became clear that there are different routes to heavy fermion behaviour.

In Ce-based compounds, the heavy quasiparticles with predominantly 4f-character arise through the Kondo effect in the periodic lattice. The Kondo picture for the Ce-based heavy fermion compounds is supported by the fact that the thermodynamic properties at
low temperatures (e. g., the specific heat & magnetic susceptibility) as well as the
temperature dependence of the spectroscopic data can be reproduced by an Anderson
model. This picture has been confirmed in detail by deHaas-vanAlphen and
photoemission studies. The strongly renormalized quasiparticles can be described by a
semi-phenomenological ansatz, the Renormalized Band Method which yields realistic
quasiparticle bands. The nesting features of the calculated Fermi surfaces can serve as a
useful guideline in the search for instabilities with respect to modulated structures. In
particular, the calculations provide realistic models for the study of the
competition/coexistence phase diagrams. Despite the efforts to implement modern
many-body methods for strong correlations into realistic electronic structure
calculations there is still no general concept for quantitative microscopic correlations.
In particular, the interplay between local and intersite effects continues to challenge
theorists. The latter may lead to long-range order while the former favor the formation
of a Fermi liquid state at low temperatures.

1.5.1.2 U-based HF Superconductors:

A microscopic picture for the heavy quasiparticles has finally emerged for the actinide
compounds. Increasing experimental evidence points towards a dual character of the 5f-
electrons with some of them being delocalized forming coherent bands while others
stay localized reducing the Coulomb repulsion by forming multiplets. The hypothesis of
the dual character is translated into a calculational scheme which reproduces both the
Fermi surfaces and the effective masses determined by deHaas-vanAlphen experiments
without adjustable parameter. The method yields a model for the residual interaction
leading to various instabilities of the normal phase. The dual model should also provide
insight into the mysterious hidden order phases of U compounds.

In both cases, i.e. in Ce and U-based HF compounds, the coherent heavy quasiparticles
are derived from the partially filled f-shells whose degrees of freedom have to be
(partially) included into the Fermi surface. The situation is different for the Pr
skutterudites where the quasiparticles are derived from the conduction states whose effective masses are strongly renormalized by low-energy excitations of the Pr 4f-shells. From a microscopic point of view we are dealing with three different classes of HF superconducting materials.

It is generally agreed that the pairing interaction in HF superconductors is of electronic origin. Theoretical models usually involve the exchange of a boson. It is therefore convenient to classify the various mechanisms according to the boson which is exchanged. The majority of models construct effective interactions based on the exchange of spin fluctuations. Neither these models nor their refined variants which account for the internal orbital f-electron structure are able to properly predict the symmetry of the order parameter, e.g., in UPt$_3$. In particular, the calculations do not reproduce a multicomponent order parameter as stable solution. Recently, a model based on the exchange of weakly damped propagating magnetic excitons was suggested for U-based HF compounds. First estimates of the transition temperature yield a value of the correct order of magnitude. Pairing due to intra-atomic excitations may also occur in the Pr-skutterudite HF superconductor. In this case, however, quadrupolar instead of magnetic excitons should be involved. Superconductivity in HF compounds is usually found to coexist or to compete with various cooperative phenomena. Of particular importance in this context is itinerant antiferromagnetism as realized in a spin density wave (SDW). Since both order parameters appear in the itinerant quasiparticle system the observed behavior results from a subtle interplay between Fermi surface geometry and gap structures.

Many HF systems are on the verge of magnetic instability. By application of pressure these materials may be tuned in their normal states through a quantum critical point (QCP) from an antiferromagnet to a paramagnetic metal. The theoretical picture, however, is at present still rather controversial and contentious.
1.5.1.3 RARE-EARTH SKUTTERUDITES:

The recently discovered heavy fermion superconductor PrOs$_4$Sb$_{12}$ is potentially of similar interest as UPt$_3$ because it represents the second example of multiphase superconductivity with a critical temperature $T_C = 1.85$ k. The skutterudites RT$_4$X$_{12}$ (R = alkaline earth, rare earth or actinide; $T =$ Fe, Ru or Os and X = P, As or Sb) show a cage structure where large voids formed by tilted T$_4$X$_{12}$ octahedrons can be filled with R atoms. They are however rather loosely bound and are therefore subject to large anharmonic oscillations in the cage. In addition, the presence of several equivalent equilibrium positions may give rise to tunneling split states. Both effects may lead to interesting low temperature elastic and transport phenomena, such as thermoelectric effects. Depending on the cage-filling atom this large class of compounds displays also a great variety of interesting effects of strong electron correlation. Mixed valent and HF behavior, magnetic and quadrupolar order, non-Fermi liquid and Kondo insulating behavior has been found. Recently the superconductivity in non-stoichiometric skutterudites Pr(Os$_{1-x}$Ru$_x$)Sb$_{12}$ has been investigated throughout the whole concentration range of $0 \leq x \leq 1$. While for $x = 0$ one has an unconventional HF superconductor, the $x = 1$ compound PrOs$_4$Sb$_{12}$ on the other hand is a conventional superconductor with $T_C \sim 1$ k. The type of superconductivity changes at $x \sim 0.6$ where the transition temperature $T_C (x)$ has a minimum value of 0.75 k.

In the HF multiphase superconductor PrOs$_4$Sb$_{12}$ ($x = 0$) the specific heat jump due to superconductivity is superposed on a Schottky anomaly due to the lowest CEF excitation. Nevertheless, its detailed analysis provides clear evidence for a split superconductivity transition at $T_{C_1} = 1.85$ k and $T_{C_2} = 1.75$ k. The total jump of both transitions $\sim 3$ which considerably exceeds the BCS value 1.43 for a single transition. It also proves that the SC state is formed from the heavy quasiparticles that cause the enhanced value of the electronic low-temperature specific heat contribution.
A $T_C$-splitting of similar size also was clearly seen in thermal expansion measurements. The two SC transitions are reminiscent of the split transition in UPt$_3$. There, a twofold orbitally degenerate SC state is split by weak AF order that reduces the hexagonal symmetry to an orthorhombic one.

In this still rather early stage of investigation, various experiments gave inconclusive results on the question of the nature of gap anisotropy. As a preliminary conclusion, it seems clear that PrOS$_4$Sb$_{12}$ is a very unconventional multiphase HF superconductor of potentially the same interest as UPt$_3$. Since that heavy quasiparticles are presumably caused by coupling with virtual quadrupolar excitations from the nonmagnetic 5f ground state one is lead to speculate that superconductivity in PrOS$_4$Sb$_{12}$ might also result from an unprecedented pairing mechanism based on the exchange of quadrupolar fluctuations. At the moment, this quadrupolar superconductivity mechanism in PrOS$_4$Sb$_{12}$ as a third possibility for cooper pair formation in heavy fermion compounds in addition to the spin-fluctuation and magneticexciton exchange mechanisms is still a conjecture.

1.5.2 BORIDES AND BOROCARBIDES:

Rare-earth borocarbide superconductors have provided the first example of a homogeneous coexistence of superconductivity and ferromagnetism for all temperatures below $T_C$. The two antagonistic long-range orders are carried by different species of electrons that interact only weakly through contact exchange interaction leading to a small effect of the local moment molecular field on the SC conduction electrons. This allows a much better understanding of coexistence behavior as compared to the HF systems. Moreover, the nonmagnetic rare earth borocarbides have extremely large gap anisotropy ratios $\Delta_{\text{max}}/\Delta_{\text{min}} \geq 100$. Surely the standard electron-phonon mechanism has to be supplemented by something else, perhaps anisotropic Coulomb interactions to achieve this quasi-unconventional behavior in borocarbides.
The SC class of layered transition metal borocarbides RNi$_2$B$_2$C (nonmagnetic R = Y, Lu, Sc; magnetic R = lanthanide elements) was discovered in 1994. The crystal structure consists of R C rock salt type planes separated by Ni$_2$B$_2$ layers built from NiB$_4$ tetrahedra and stacked along the c-axis. More general structures with more than one R C layer are possible. The nonmagnetic borocarbides have relatively high $T_C$ values around 15 k. There is evidence that the SC mechanism is primarily of the electron-phonon type although this cannot explain the large anisotropy of the SC gap. At first sight the layered structure is similar to the HTS cuprates. However, unlike the copper oxide planes the NiB$_2$ planes show buckling. As a consequence, the electronic states at the Fermi level in the borocarbides do not have quasi-2-dimensional $d_{x^2-y^2}$ character and, therefore, have much weaker correlations excluding the possibility of AF spin-fluctuation mediated superconductivity.

However, the former have their own peculiarities, which are not yet completely understood. Foremost, despite their alleged electron-phonon nature, LuNi$_2$B$_2$C and YNi$_2$B$_2$C have strongly anisotropic gap functions and low energy quasiparticle states as is evident from specific heat and thermal conductivity. Furthermore, an anomalous upturn in $H_c^2$ has been observed.

The magnetic RNi$_2$B$_2$C are an excellent class of materials to study the effects of competition of magnetic order and superconductivity for the following reasons: The $T_C$ values are relatively high, and the $T_C / T_N$ ratio varies systematically across the R-series. Especially interesting are the cases of RNi$_2$B$_2$C with R = Dy, Ho and Er where $T_C$ and $T_N$ (or $T_C$) are not too different, leading to strong competition of the magnetic and superconductivity order parameters. Furthermore, the SC condensate and magnetic moments are carried by different types of electrons, namely itinerant 3d-electrons for the Ni$_2$B$_2$ layers and localized R$^{3+}$ 4f-electrons for the R C layers, respectively. Finally, they are well separated and their coupling which is of the local exchange type can be treated in a controlled perturbative way, somewhat akin to the situation in the well known classes of Chevrel phase and ternary compound magnetic superconductors. The
AF molecular field establishes a periodic perturbation characterized by a length scale of the order of the Fermi wavelength. This implies that the spatial extent of the Cooper pairs extends over many periods of the alternating molecular field. The latter is therefore effectively averaged to zero and does not suppress superconductivity via an orbital effect. The system is invariant under the combined operation of time inversion followed by a translation with a lattice vector which allows to form Cooper pairs in a spin singlet state with vanishing (crystal) momentum in the AF lattice. This pair-state can be considered as a natural generalization of the pairing in time-reversed states encountered in usual non-magnetic superconductors.

The nonmagnetic YNi$_2$B$_2$C and LuNi$_2$B$_2$C compounds with comparatively high $T_C$ values of 16.5 k and 15.5 k serve as reference systems for the more difficult systems RNi$_2$B$_2$C with both magnetic and SC phases. The electron-phonon nature of superconductivity in YNi$_2$B$_2$C and LuNi$_2$B$_2$C is inferred from a substantial s-wave character of the order parameter.

On the other hand, the gap function is strongly anisotropic as can be seen both from temperature and field dependence of thermodynamic and transport quantities indicating the presence of gap nodes. More precisely, within experimental accuracy, there must be at least a gap anisotropy $\Delta_{\text{max}}/\Delta_{\text{min}} \geq 100$. For an electron-phonon superconductor this would be the largest anisotropy ever observed. This conjecture is also supported by the field dependence of the low temperature specific heat and of the thermal conductivity along (001). Since in the latter case the heat current is perpendicular to the vortices this proves that quasiparticles must be present in the inter-vortex region.

The discovery of superconductivity in MgB$_2$ in early 2001 with $T_C \sim 40$ k, almost twice the record value before HTS brought back a bit of the HTS bonanza spirit of the late 1980s. The fact that such a simple material which was known since the early 1950s had been missed in the systematic research for superconductivity on this class of compounds was as amazing as the "materials preparation" that was usually practiced immediately after the discovery by most of the research groups for reestablishing this
high $T_C$ value. They simply ordered MgB$_2$ powder from chemicals wholesale where it was commercially available in quantities of metric tons already for years.

Isotopically pure Mg$_{11}$B$_2$ and Mg$_{10}$B$_2$ show sharp superconducting transitions in resistivity with $T_C$ (Mg$_{11}$B$_2$) = 39.2 k and $T_C$ (Mg$_{10}$B$_2$) = 40.2 k. No strong Coulomb correlation effects can be expected in MgB$_2$. No atomic d- or f-shells are involved in the conduction electron system of this binary compound of light elements. In addition, the simple crystal structure consisting of graphite-like B-layers with intercalated Mg clearly favors conduction along these layers and a respective superconductive and normal state anisotropy, but it does not introduce a reduction of the effective dimensionality, as in the case of organic superconductors due to the stacking of isolated aromatic rings. The coupling of the conduction electrons to a particular boron phonon mode was hence identified right from the start as basic origin of superconductivity in MgB$_2$. The observation of two energy gaps (at 1.8 and 6.8 meV) and the considerable superconductive anisotropy as large as 6.9 challenged a more thorough theoretical investigation which tries at present to explain these findings in terms of two-band superconductivity on the basis of the large anharmonicity of the involved phonon mode and a refined treatment of its coupling with the different sheets of the electronic conduction band.

MgB$_2$ has already been fabricated in the form of bulk, single crystals, thin films, tapes and wires. Serious difficulties in depositing MgB$_2$ films, such as the volatility of Mg, the phase stability of MgB$_2$, the low sticking coefficients of Mg at elevated temperatures, and the reactivity of Mg with oxygen have meanwhile been overcome. Epitaxial MgB$_2$ films with superior superconducting properties have been produced. MgB$_2$ wires are already used in first real applications. MgB$_2$ is hence a further excellent example for the progress and excitement of the research on superconductors. Superconductivity with its wide range from the most fundamental aspects of physics to hands-on applications is, one century after its discovery, still one of the most fascinating topics of modern science.
1.6 HIGH $T_C$ SUPERCONDUCTORS:

1.6.1 High $T_C$ Cuprate Superconductors:

Mercury ($T_c = 4.2$ k) was the first superconductor discovered in 1911 by Kamerliengh Onnes. But for many years, scientists were not able to push $T_C$ above 23 k (for Nb$_3$Ge).

After a large gap of 70 years Bednoz & Muller in 1983 discovered a high $T_C$ Cuprate superconductor LaBaCuO$_2$ having transition temperature $T_C$ equal to 30 k. These cupper oxide superconductors are based on the structure with square planner CuO$_2$ layers. It is believed that CuO$_2$ layers are responsible for conduction and increase in their number, increases transition temperature $T_C$ of the superconductors. The highest transition temperature reached till date is 160 k under externally applied pressure for HgBaCaCuO$_2$. We are still 136 k behind from room temperature superconductivity. To achieve this, first we should know the reason for high $T_C$ of cuprate superconductors.

![Fig. 1.2: Superconductivity over the years.](image)
The structural element of high $T_C$ cuprates related to the location of mobile charge carriers are stacks of a certain number $n = 1, 2, 3, \ldots$ of CuO$_2$ layers which are "glued" on top of each other by means of intermediate Cu layers (Fig. 1.3).

Counterpart of these "active blocks" of \((\text{CuO}_2/\text{Ca})_{n-1}\text{CuO}_2\) stacks are "charge reservoir blocks" \(\text{EO}/(\text{AO}_x)_m/\text{EO}\) with \(m = 1, 2\) monolayers of a quite arbitrary oxide \(\text{AO}_x\) (\(A = \text{Bi, Pb, Tl, Hg, Au, Cu, Ca, B, Al, Ga}\)) "wrapped" on each side by a monolayer of alkaline earth oxide \(\text{EO}\) with \(E = \text{Ba, Sr}\). The HTS structure results from alternating stacking of these two block units. The choice of BaO or SrO as "wrapping" layer is not arbitrary but depends on the involved \(\text{AO}_x\) since it has to provide a good spatial adjustment of the CuO$_2$ to the AO$_x$ layers.

The general chemical formula \(A_m\text{E}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+m+2+y}\) [see Fig. 1.3 (b)] is conveniently abbreviated as \(A\text{-m2(n-1)n}\) (e.g. \(\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}\): Bi-2223) neglecting the indication of the alkaline earth element. The family of all \(n = 1, 2, 3,\ldots\) representatives with common \(\text{AO}_x\) are often referred to as \(A\)-HTS., e.g. Bi-HTS. The most prominent compound \(\text{YBa}_2\text{Cu}_3\text{O}_7\), the first HTS discovered with a critical temperature \(T_C\) for the onset of superconductivity above the boiling point of liquid nitrogen, is traditionally
abbreviated as "YBCO" or "Y-123" (Y\textsubscript{1}Ba\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7-δ}). It also fits into the general HTS classification scheme as a modification of Cu-1212 where Ca is completely substituted by Y. This substitution introduces extra negative charge in the CuO\textsubscript{2} layers due to the higher valence of Y (+3) compared to Ca (+2). The HTS compounds REBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7-δ} ("RBCO", "RE-123") where RE can be La or any rare earth element except for Ce or Tb can be regarded as a generalization of this substitution scheme. The lanthanide contraction of the RE ions provides an experimental handle on the distance between the two CuO\textsubscript{2} layers of the active block of the doped Cu-1212 compound. Y\textsubscript{1}Ba\textsubscript{2}Cu\textsubscript{4}O\textsubscript{8} ("Y-124") is the m = 2 counterpart Cu-2212 of YBCO.

The CuO\textsubscript{2} layers are believed to be the location of the mobile charge carriers in the cuprate HTS compounds. This is in agreement with band structure calculations. However, in contrast to these results based on the independent electron approximation the stoichiometric compounds are actually antiferromagnetic (AF) insulators due to strong correlation effects. In HTS cuprates, the copper 3d-shells are filled with nine electrons, resulting in Cu\textsuperscript{2+} ions in d\textsuperscript{9} configuration which are subject to a strong Jahn-Teller effect. The deformation of the oxygen octahedra which surround each Cu ion make the \(d_{x^2-y^2}\) orbital the only unoccupied Cu - 3d orbital, i.e., it accommodates the single hole. This copper \(d_{x^2-y^2}\) state hybridizes with the \(p\sigma\)-orbitals of the surrounding four oxygen atoms. Due to the strong Coulomb repulsion for adding another hole at a Cu site these holes cannot move to neighboring Cu sites. This Coulomb correlation effect prevents a metallic behavior and turns the stoichiometric HTS compounds into insulators. Virtual charge fluctuations generate a "superexchange" interaction, which favors antiparallel alignment of neighboring spins. The result is long-range AF order up to rather high Néel temperatures \(T_N = 250 - 400\) k.

Adding charge carriers by variation of the oxygen content or by suitable substitution of cations relaxes the restrictions of spin alignment due to the interaction of these additional spin-1/2 particles with the spin lattice. \(T_N\) decreases and the insulator turns into a bad metal. The room-temperature mobility of the charge carriers increases
gradually, in direct inverse proportionality to the AF correlation length. At low
temperature, however, the electric transport shows a dramatic change within a small
doping range from an insulating behavior with an divergent upturn of the resistivity on
decreasing temperature, to a superconducting behavior with a respective sudden
downturn of resistivity next to $T_C$. For La$_{2-x}$Sr$_x$CuO$_4$ this happens at a critical hole
concentration $x = 0.05$ in the CuO$_2$ planes (see Fig. 1.4).

Fig. 1.4: Schematic HTS temperature-doping phase diagram dominated by the
interplay of antiferromagnetism (AF) and superconductivity.

On stronger doping, superconductivity can be observed up to an increasingly higher
critical temperature until for "optimal doping" ($x \approx 0.16$ for La$_{2-x}$Sr$_x$CuO$_4$) the
maximum $T_C$ is achieved. On further doping, the critical temperature decreases again
until finally ($x \geq 0.27$ for La$_{2-x}$Sr$_x$CuO$_4$) only normal conducting behavior is observed.
The rise and fall of $T_C$ as a function of doping leads to the classification of the
 corresponding regions of the chemical phase diagram as "underdoped" and "overdoped"
 regimes, respectively. At a first glance, the physical properties of these two regimes
 seem to be not so different for the SC state, but they are dramatically different for the
normal state. In the underdoped regime for temperatures far above $T_C$, even up to room temperature, a peculiar redistribution of electronic states in the energy spectrum is observed in the vicinity of the Fermi energy resembling the features of a SC energy gap. The critical temperature associated with this "pseudogap" energy decreases monotonically on doping, in stark contrast to the monotonic increase of $T_C$ in this doping regime. In the overdoped regime, in electron spectroscopy only a regular SC gap is identified. This is widely interpreted as coincidence of the SC gap and the pseudogap, which is hence regarded as a precursor of the SC gap.

The charges introduced by doping into the AF spin lattice may align in equidistant rows to form parallel "stripes" in transversal orientation to the spin wave, thus forming a charge density wave running in the same direction but with half the spatial period of the corresponding spin wave. This construction results in perfect commensurate AF spin domains extending over half a spin wave period, enclosed by charge stripes. Here a phase jump occurs so that the spin pattern of the neighboring AF domains appears to be spatially shifted by one lattice position. Stripes have been suggested to constitute a fundamental structural element of the ground state of all doped AF insulators arising from a competition between phase separation (the tendency of an AF insulator to expel doped holes) and the long-range part of the Coulomb interaction. The incommensurability $\varepsilon$ increases monotonically with doping up to optimal doping where it saturates at $\varepsilon \sim \pi/4$. A quantitative description of this experimental incommensurability-doping relation was given by the concept of "metallic stripes" where only every other spin, i.e., hole along with its spin, is removed from the stripe positions. The remaining spins delocalize along the stripe forming metallic zone separating the AF domains.

These recent findings and speculations show that there is strong co-relation between magnetism and superconductivity in high $T_C$ cuprate superconductors. So in this present work it is try to understand the mechanism behind co-existence between superconductivity with magnetism in these high $T_C$ cuprates.
1.6.2 Iron Pnictide Superconductors:

Recently in 2008, Yoichi Kamihara found a new class of high $T_C$ superconductors LaFeAs(O, F) with the remarkable $T_C$ of 26 k. This new class of high $T_C$ superconductors compound is known as Iron Pnictide Superconductors or Oxypnictides. Similar to high- $T_C$ cuprates, the superconductivity in iron arsenide compounds is related to a layered structure. But the presence of Fe atoms in these components creates a mystery which is trying to solve. The highest transition temperature in these compounds reached till date is 55 k for SmFeAsO$_{0.80}$F$_{0.11}$. Many researches are going to understand the mechanism in these High $T_C$ compounds and try to increase the transition temperature $T_C$.

Iron-based superconductors (sometimes misleadingly called iron superconductors) are chemical compounds (containing iron) with superconducting properties. In 2008, led by recently discovered iron pnictide compounds (originally known as oxypnictides), they were in the first stages of experimentation and implementation. (Previously most high-temperature superconductors were cuprates and being based on layers of copper and oxygen sandwiched between other (typically non-metal?) substances. This new type of superconductors is based instead on conducting layers of iron and a pnictide (typically arsenic) and seems to show promise as the next generation of high temperature superconductors. Much of the interest is because the new compounds are very different from the cuprates and may help lead to a theory of non-BCS-theory superconductivity. More recently these have been called the ferropnictides. The first ones found belong to the group of oxypnictides. Some of the compounds have been known since 1995 and their semiconductive properties have been known and patented since 2006. It has also been found that some iron chalcogens superconduct; for example, doped FeSe can have a transition temperature ($T_C$) of 8 k at normal pressure, and 27 k under high pressure. A subset of iron-based superconductors with properties similar to the oxypnictides, known
as the 122 Iron Arsenides, attracted attention in 2008 due to their relative ease of synthesis.

The Oxypnictides such as LaOFeAs are often referred to as the '1111' pnictides. The discovery of the high- $T_C$ superconductor LaFeAsO:F ($T_C = 26$ k) has caused a recurrence of a new superconductivity boom similar to that caused by the finding of layered copper oxides. By either applying an external pressure of $\sim 3$ GPa or replacing La with other rare-earth elements such as Sm, it has been possible to achieve $T_C$ beyond 55 k. The undoped LaFeAsO, which is the parent compound of the superconductor, is a member of the large LnTMPnO family, where Ln represents a 4f rare-earth element, M a transition-metal element with a more than half-filled 3d shell, and Pn a pnictogen element. These have a common ZrCuSiAs-type crystal structure, belonging to the tetragonal P4/nmm space group. The crystal is formed by an alternating stack of electrically charged LnO and TMPn layers, and can also be represented as $(\text{LnO})^{+\delta}(\text{TMPn})^{-\delta}$ as reported by T. Nomura et al. (fig. 1.5).

Several high-$T_C$ superconductors have also been discovered in other Fe-based analogous compounds including AFe$_2$As$_2$ (A is an alkali-earth-metal element such as Sr and Ba) and LiFeAs. This, together with the observed lower $T_C$ in LaFePO and
LaNiP(As)O ($T_C = 2–4\, \text{k}$), strongly suggests that the FeAs layers play a leading role in the appearance of the high $T_C$. This view is supported in part by theoretical analysis of the energy band structure based on density functional theory, revealing that five Fe 3d orbitals hybridized with As 4p contribute to the Fermi surface whereas the LaO, A and Li layers are blocking or spacer layers which act as a charge reservoir. By changing the M element, the electronic and magnetic properties of the LnTMPnO compounds vary such that it is an antiferromagnetic insulator for $M = \text{Mn}$, a superconductor for $M = \text{Fe}$, a ferromagnetic metal for $M = \text{Co}$, and again a superconductor for $M = \text{Ni}$. Further, the replacement of La with other 4f rare-earth elements having spin magnetic moments provides an additional magnetic interaction and facilitates antiferromagnetic ordering of the spins at low temperatures, which results in the coexistence of the superconductivity with antiferromagnetism for $\text{Ln} = \text{Ce, Nd, Pr and Sm}$, for instance. More importantly, the substitution of rare-earth elements with smaller ionic radii makes the lattice constants smaller and enables raising $T_C$ up to 56 k. High - $T_C$ superconductivity in LnFeAsO materials is realized upon doping with electrons; this can be achieved either by replacing O$^{2-}$ ions in the reservoir layers by F$^-$ ions or by forming oxygen vacancies. The doping can also be achieved by partially substituting Co for Fe in the FeAs layer. In contrast, AFe$_2$As$_2$ compounds can undergo the superconducting transition only after hole doping, which is achieved through the replacement of A elements with potassium. Parent compounds of the high - $T_C$ superconductors show a rapid decrease in their electrical resistivity, which is clearly seen in the resistivity–temperature curves with a kink at $\sim 160\, \text{k}$. This anomaly has been attributed to the combined effect of a crystallographic phase transition at $\sim 160\, \text{k}$, and an antiferromagnetic ordering of the Fe spins at a slightly lower temperature of $\sim 140\, \text{k}$. Both transitions can be simultaneously suppressed by electron or hole doping, suggesting a close association of these phase transitions with the superconductivity observed in the doped compounds. The Fe-based and the Cu-based superconductors have a common feature in that superconductivity is attained by providing itinerant electron or hole carriers to the two dimensional transport layers containing 3d
transition-metal elements. However, they differ distinctly from each other in that nine 3d electrons (one hole) are involved for Cu$^{2+}$, which forms an ionic bond with oxide ions, whereas six 3d electrons participate in the more complex interplay of Fe–Fe and Fe–As bonding.

However, these materials have strong magnetic properties, these materials also shows superconducting phase with high transition temperature. So the presence of superconducting phase in these materials raises a question that “Is magnetism helping to achieve superconductivity in these materials?” To understand this question first we should understand properties of these materials and also the role of magnetism in these materials.

In this present study for oxypnictides LnFeAsO, we consider stripe phase of Fe spins, with stripe $a$ having spin direction opposite to the spin direction of stripe $b$ as shown in fig. 1.6.

![Diagram showing exchange coupling in FeAs layers of LnFeAsO system.](image)

**Fig 1.6: Four types exchange coupling in FeAs layers of LnFeAsO system.**

We have considered three types of in plane spin exchange interaction ($J_1$, $J_2$ and $J_3$) between the Fe-Fe atoms and one out of plane spin exchange interaction ($J_\perp$) of Fe atoms with the As atoms. $J_1$ is the antiferromagnetic spin exchange interaction between nearest Fe – Fe atoms of stripe $a$ and $b$. $J_3$ is the spin exchange interaction between first
nearest Fe – Fe atoms of stripe $a$ and $b$, which is antiferromagnetic in nature. $J_2$ is the spin exchange interaction between nearest Fe – Fe atom of the same stripe, which is ferromagnetic in nature.

Using only three interactions between Fe-Fe atoms i.e. $J_1$, $J_2$ and $J_3$, we found by our calculation that Neel temperature $T_N$ for these compounds is always less than experimental value of $T_N$. As suggested by T. Yildirim that Fe spin is always present in oxyptinitide, interaction between Fe and As atoms is important and can not be ignored. However yildirim had not considered this interaction and above model is an improvement of his model. By including $J_\perp$ in our model we will study the magnetic properties and will make compression with the experimental results. Although these As-As atom have a strong attraction between them but due to presence of magnetic moments in Fe atoms, this interaction is reduced. Fe atoms has a magnetic moment and also these are much closer to As atoms, so there is an spin exchange interaction ($J_\perp$) exist between As and Fe atoms. This interaction reduces the As – As interaction and helps to reach at Neel temperature. This interaction also helps to understand magnetic properties in these compounds.

In view of above, study of interplay of magnetism & superconductivity in high $T_C$ superconductors can give some novel physics, which is turn give some insight into the mechanism responsible for superconductivity in high $T_C$ cuprates, which still remains elusive. The mechanism for superconductivity can pave path for the search of other high $T_C$ superconductors having $T_C \approx 300$ k (i.e. room temperature). Models suggesting strong superconducting fluctuations, antiferromagnetic correlations or separation of spin & charge are forwarded but there is no general consensus. This study has explained two problems taking in two different compounds, high $T_C$ cuprate superconductors and high $T_C$ Iron-pnictide superconductors to explore interplay of magnetism & superconductivity in high $T_C$ superconductors. The model Hamiltonian for the present situation in these two compounds are defined separately and expressions for superconducting and magnetic order parameters, sublattice magnetization and Néel temperature are derived and numerically solved in the forward section (Chapter 3).
OBJECTIVES

1. Study of variation of transition temperature $T_C$ as a function of magnetic & superconducting correlations.

2. Study of superconducting & magnetic order parameter.

3. To study the role of magnetism in high $T_C$ superconductors.

4. To stabilize the various limiting condition for coexistence of magnetism & superconductivity in high $T_C$ cuprate superconductors.