2.1 SERVEY OF EXPERIMENTAL RESULTS

2.2 SERVEY OF THEORETICAL MODELS
2.1 SURVEY OF EXPERIMENTAL RESULTS:

This section includes critical review of experimental results related to binary intermetallic compound superconductors & high-temperature superconductors.

Some properties of magnesium diboride are similar to that of conventional superconductors. These properties include isotope effect ([Hinks et al. (2001); Bud'ko et al. (2001 a)]), the linear dependence of upper critical field [Bud'ko et al. (2001 b)]. Some other properties like temperature dependence of penetration depth [Panagopoulos et al.(2001); Klein et al.(2001); Pronin et al.(2001)] and sign reversal of Hall coefficient near transition temperature [Jin et al. (2001)] pointed out that MgB$_2$ is unconventional superconductor like cuprates.

Larbaletier et al. (2001) demonstrated that magnesium diboride (MgB$_2$) does not exhibit weak link behaviour unlike to HTSC’s. Weak link problems limit the use of HTSC’s, which is strongly reduced in magnesium diboride. In future, magnesium diboride may play a major role for various applications of superconductivity because of high critical temperature, the absence of a weak link, high values of critical field and currents, low cost and availability in abundance.

For above said reasons, theoretical and experimental studies of magnesium diboride and other intermetallic binary superconducting compounds are of great interest to researchers so far.

Bud’ko et al. (2001a & b) studied the effect of boron isotopes on superconductivity in Magnesium diboride (MgB$_2$). They found that the transition temperature of MgB$_2$ was increased by 1 K if B$^{11}$ was replaced by B$^{10}$ in it. They calculated boron isotope effect exponent $\alpha_B = 0.26$. 
Hinks et al. (2001) also calculated $\alpha_B = 0.3$. The transition temperature of MgB$_2$ was found to be increased by 0.1 K when substitution of Mg$^{24}$ with Mg$^{26}$ was made. $\alpha_{\text{Mg}}$ was found to be 0.02. These results of the isotope effect in MgB$_2$ gave direct evidence of phonon-mediated superconductivity mechanism with dominant boron phonons contribution to the overall pairing.

Xu et al. (2001) measured lower critical field for single crystal whereas Joshi et al. (2001); Li et al. (2001); Tokano et al.(2001) & Sharoni et al.(2001) measured lower critical field for bulk MgB$_2$. All these values are ranging between 25 and 48 mT. Using these results the values of the penetration depth ($\lambda$) for MgB$_2$ was found to vary from 85 to 203 nm. Jung et al. (2001) & Xu et al. (2001) reported the coherence length value $\xi_{ab}(0) = 6.1$-6.5nm (parallel to ab plane) & $\xi_c(0) = 2.5$-3.7nm (parallel to c direction) for single MgB$_2$ crystal.

The magnitude of superconducting energy gap ranging from 1.5 to 3.5 meV for small gap & 5.5 to 8.0 meV for larger gap Buzea and Yamashita (2001).

In Figure 2.1, the variation of superconducting energy gap of magnesium diboride for $\sigma$ and $\pi$ bonding states with temperature is shown. These energy gaps exhibit different temperature dependence. At low temperature, the larger energy gap of $\sigma$ bonding states changes slowly as compared to the smaller energy gap of $\pi$ bonding states. Near transition temperature 39K, we observe somewhat opposite nature of variation of the energy gap. The energy gap of both $\sigma$ and $\pi$ bonding states becomes zero at the transition temperature of MgB$_2$. 

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Figure 2.1: Temperature dependence of the superconducting gaps of magnesium diboride for $\sigma$ and $\pi$ bonding states {Buzea and Yamashita (2001)}
Rosova et al. (2015) analyzed the microstructure of dense pore-free undoped MgB\(_2\) single filament wire made by internal magnesium diffusion process (IMD). Electrical measurements have shown high critical current densities in MgB\(_2\) layer, which are encouraging for further improvements and possible applications.

Zhou et al. (2011) found that DC magnetization measurements indicate a high superconducting transition temperature (39 K) for non-doping MgB\(_2\) nanowires. On increasing the carbon content the transition broadens and shifts toward lower temperatures.

Agassi (2013) introduced a model for the critical current density in porous MgB\(_2\) powders in the presence of a low external magnetic field of less than 4T.

Gomes da Silva et al. (2014) studied a non-conventional superconducting system where the Cooper pairs are formed by fermions from different bands described via two band model with hybridization. They found a first-order phase transition at low temperatures. They observed a tricritical point in the phase diagram.

Higashikawa et al. (2014) developed a characterization method of local critical current in iron sheathed MgB\(_2\) wires. Their result suggested that MgB\(_2\) wires fabricated by internal Mg diffusion processes have much higher potential and larger longitudinal inhomogeneity than that predicted by the four probe transport method.

Jang et al. (2013) analyzed the effect of oxygen affinity additives on the superconducting properties of MgB\(_2\). Additives like elemental Y, Sm, Ca and Li compounds could not improve the critical current density. Additives like polyethylene and polyethylene glycol enhanced the critical current density.
Brunner et al. (2014) produced mono-core MgB$_2$ wires by in-situ powder-in-tube (PIT) and internal magnesium diffusion (IMD) technique. Using Bean’s critical state model they calculated critical current density, $J_c$. They concluded that $J_c$ for the PIT sample was lower and more field-dependent than $J_c$ of the IMD sample.

Fang et al. (2011) compared the temperature-dependent transmittance of Au films and MgB$_2$ films. They found that the experimental data are in agreement with analytical calculations.

Maeda et al. (2013) reported that both the high- and the low-field properties of magnesium diboride can be improved without doping by increasing the initial magnesium partial pressure or by reducing the size of the magnesium particles. They have shown that in situ processed bulk MgB$_2$ sintered with fine magnesium powders has superior superconducting properties compared with a bulk sample magnesium lumps. There was negligible change in the lattice parameters. It was found that the low-field critical current density was slightly increased for the fine magnesium powder sample.

Song et al. (2005) reported lower and upper critical field [$H_{c1}$ & $H_{c2}$] and the irreversibility field [$H_{irr}$] of a dense polycrystalline MgB$_2$ superconductor prepared by the spark plasma sintering. The upper critical field $H_{c2}$ (T) was well fit to BCS-type function. The $H_{irr}$ (T) was described by power-law relation. The $H_{c1}$ (T) followed linear temperature dependence.

Ilonca et al. (2006) presented the transport properties of MgB$_2$ thin films up to magnetic field 9T. These thin films were fabricated on Al$_2$O$_3$ substrates. They calculated electron’s mean free path, coherence length, anisotropic coefficient and
penetration depth. In normal state, the Hall coefficient was found to be slightly temperature dependent and positive.

Tsuda et al. (2003) studied the superconducting gap of MgB$_2$ with the help of high-resolution angle-resolved photoemission spectroscopy [ARPES]. The ARPES spectra reveal that magnitude of the gaps to be 5.5meV and 2.2meV for $\sigma$ and $\pi$ bands respectively at 6K. Both these gaps closed at bulk transition temperature. It provided experimental evidence of two-band superconductivity of MgB$_2$. Experiments performed by them validated the role of k-dependent electron-phonon coupling as the origin of multiple gap superconductivity and high transition temperature in MgB$_2$.

Vajpayee et al. (2009) reported the effect of adipic acid [C$_6$H$_{10}$O$_4$] on various properties of MgB$_2$ superconductor. The doped samples show significant enhancement of current density ($J_c$) and irreversibility field (H$_{irr}$). They conclude that C$_6$H$_{10}$O$_4$ may be a promising material for MgB$_2$ for obtaining high $J_c$ under high magnetic fields.

Aswana et al. (2008) studied experimentally various physical properties of bulk polycrystalline MgB$_2$ superconductors. These physical properties included-resistivity under magnetic field, thermoelectric power, thermal conductivity and magnetization. They compared the obtained parameters with earlier reports available.

Yeoh et al. (2007) fabricated multiwalled carbon nanotube and nano-C doped MgB$_2$ bulk and wire. Both CNT and nano C substitution exhibited excellent magnetic $J_c$(H) (critical current density) and transport $I_c$ (critical current) at high temperature. Nano C-doped MgB$_2$ gave better improvement in flux pinning in comparison to CNT-doped MgB$_2$. They concluded that these variations could be explained by the reactivity of carbon source.
Yang et al. (2001) measured the low temperature specific heat for polycrystalline MgB$_2$ prepared by high-pressure synthesis. The electronic specific heat in the superconducting state is $C_{es}(T) = C(T,H) - C_{lattice}(T)$.

In Figure 2.2 $C_{es}(T)$ v/s $T_c/T$ for $H =0$ was plotted. Their results suggested that $C_{es}(T)$ vanished exponentially at low temperatures. They also suggested that magnetic field dependence of $\gamma(H)$ is non-linear as well as non-$H^{1/2}$. This behaviour of $\gamma(H)$ is associated with intrinsic electronic properties.
Figure 2.2: Variation of $C_{es}(T)$ v/s $T_c/T$ for $H=0$ (Yang et al. (2001))
Walti et al. (2001) measured the total specific heat of MgB$_2$ in the extended range of temperature. In Figure 2.3, Electronic specific heat $C_{\text{el}}(T)$ of MgB$_2$ is plotted as a function of temperature.

On the basis of the modified Debye -Einstein model, they determined the electronic contribution to the specific heat, obtained by subtracting the lattice specific heat from the total measured specific heat. They estimated the electron – phonon coupling constant $\lambda$, which is found to be the order of 2. It is sufficiently larger than the usual weak coupling values 0.4. Thus electronic specific heat of MgB$_2$ can be responsible for a conventional, $s$-wave type BCS model.
Figure 2.3:  Electronic specific heat $C_{el}(T)$ of MgB$_2$ as a function of temperature (Walti et al. (2001))
Jariwala et al. (2003) reported the comparative electronic structure of MgB$_2$ and ZrB$_2$ using X-ray photoemission spectroscopy. Their result reveals the higher density of states for MgB$_2$ in comparison to that of ZrB$_2$. They concluded that the high $T_c$ in MgB$_2$ is due to p- derived density of states.

Xu et al. (2006) synthesized MgB$_2$ bulk samples by solid reaction process in the high magnetic field. Their experimental results show that transition temperature remains unchanged whereas critical current density $J_c$ enhanced under application of the 8T magnetic field.

On the basis of experimental studies Orgiami et al. (2010) found that tilted magnesium diboride film gave new possibilities to investigate intrinsic fundamental properties of MgB$_2$.

Singh et al. (2008) synthesized Mg$_{1-x}$M$_x$B$_2$ (M= Cu, Ag; x=0, 0.5) using solid state reaction method. They studied the effect of these doping on transition temperature and grain size. They concluded that $T_c$ decreases by a small amount with Cu doping but remains almost same by Ag doping whereas the grain size remains unchanged with these doping.

Monteverde et al. (2001) studied pressure & temperature dependence of resistivity of MgB$_2$. It was found that $T_c$ of MgB$_2$ decreases with increase in pressure. The rate of decrease of $T_c$ with pressure is higher than that of conventional superconductors.

Okechukwu & Obinna (2015) investigated pressure dependence of transition temperature for a two-band superconductor based on two-band model with both phonon and non phonon induced interactions. They derived expressions for $T_c$ & $d(\log_e T_c) / dP$ within Bogoliubov – Valatin formalism for MgB$_2$ superconductor.
They have shown that any increase in electron – electron interband interaction causes reduction of $T_c$ at low pressure, whereas increasing electron - phonon interband interaction enhances $T_c$ at low pressure.

**Putti et al. (2003)** studied effects of Mg substitution by Al on the specific heat of polycrystalline $\text{Mg}_{1-x}\text{Al}_x\text{B}_2$ samples experimentally. They found that Sommerfield coefficient $\gamma$ decreases as Al concentration increases up to $x=0.4$. This decrease was due to change in DOS and electron-phonon coupling constant. They observed the excess of superconducting contribution $C_{sc}$ with respect to conventional BCS behaviour in $\text{Mg}_{1-x}\text{Al}_x\text{B}_2$ up to $x = 0.3$.

### 2.2 SURVEY OF THEORETICAL MODELS:

A comprehensive review of theoretical models developed so far to explain superconductivity and Green’s function technique are discussed in this section.

Review of various theoretical studies having been done by different groups of researchers e.g. Rice (1987); Khurana (1987); Pines (1988); Verma (1988); Fulde (1988); Kakani (1990); Sinha and Kakani (1995); Kakani and Kakani (1996).

The mechanism of superconductivity can broadly be classified as phononic (lattice base) and non-phononic [electronic]. BCS theory, Eliashberg strong coupling theory, John-teller mechanism, bipolaronic mechanism etc. are some examples of phononic mechanism.
The non-phononic or electronic mechanism is further divided into two broad categories as described below:

Non-phononic Mechanism

- Electronic excitation exchange mechanism
- Magnetic origin mechanism
(a) Electronic excitation exchange mechanism:

It includes Ginzburg excitons exchange theory, interlayer model, Rice model or charge transfer and fluctuation theory, Acoustic plasmons exchange theory, etc.

(b) Magnetic origin mechanism:

It includes Hubbard model, resonating valence bond theory, anti-ferromagnetic spin fluctuation theory, spin bag model, d-wave pairing symmetry, etc.

All theoretical models to explain various characteristics of binary intermetallic superconductors have a broad agreement that the electron correlation plays a vital role. The main difficulty is to see the origin of binding energy of the pairing interaction.

Here we present a concise discussion of some novel mechanisms proposed so far:

The BCS theory has two basic concepts-

(a) attractive interaction occurring between two electrons through phonon exchange and

(b) The wave function pairing, minimizing the energy gain due to the attractive interaction.

Frohlich et al. (1950) were first to notice the importance of the first concept.
Isotope effect changes transition temperature supports the idea that electron-phonon interaction plays an essential role in superconductivity Maxwell (1950). Dependence of transition temperature on the mass of the constituting atom suggests that the lattice modes must be responsible for superconductivity.

Three American physicists J. Barden, L.N. Cooper and R. Schrieffer (BCS) {Bardeen et al. (1957)} gave a microscopic theory of superconductivity in 1957. According to them, superconductivity is due to the interaction between electrons and the surrounding ions in the crystals.

Kruchinin & Nagao (2006) and Kruchinin et al. (2011) investigated two band model for the explanation of multi gap superconductivity of MgB$_2$.

They applied their model to –

(i) An electron - phonon mechanism for the traditional BCS method

(ii) An electron - electron interaction mechanism for high – T$_c$ superconductors (HTSC)

(iii) a cooperative mechanism to multiband superconductors.

They started from the Hamiltonian having two-bands i & j.

$$H = H_0 + H_{\text{int.}}$$

where

$$H_0 = \sum_{k,\sigma} \left[ \epsilon_i - \mu \right] a_{ik\sigma}^+ a_{ik\sigma} + \sum_{j, \sigma} \left[ \epsilon_j - \mu \right] a_{jk\sigma}^+ a_{jk\sigma}$$
\[
H_{\text{int}} = \frac{1}{4} \sum \sum \left[ \Gamma_{\alpha \beta \gamma \delta}^{i \rightarrow i} a^{\dagger}_{\alpha p \sigma} a^{\dagger}_{\beta p \sigma} a_{\gamma p \sigma} a_{\delta p \sigma} + (i \leftrightarrow j) \right]
\]

Here \( \Gamma \) is the bare vertex part,

\[
\Gamma_{\alpha \beta \gamma \delta}^{i \rightarrow j} = \langle ip_{\alpha} j p_{\beta} | k p_{\gamma} l p_{\delta} \rangle \partial_{\alpha} \partial_{\gamma} - \langle ip_{\alpha} j p_{\beta} | l p_{\delta} k p_{\gamma} \rangle \partial_{\gamma} \partial_{\delta}
\]

With \( a^{\dagger}_{p \sigma} (a_{p \sigma}) \) is the creation (annihilation) operator corresponding to excitation of electrons (or holes) in \( i \)-th band with momentum \( p \) & spin \( \sigma \). \( \mu \) is chemical potential and \( \phi \) is a single-particle wave function. They focused on three electron scattering processes.

\[
g_{i1} = < ii | ii >
\]

\[
g_{j1} = < jj | jj >
\]

\[
g_{2} = < ii | jj >
\]

\[
g_{3} = < ij | ij > = < ji | ji >
\]

\[
g_{4} = < ij | ji > = < ji | ij >
\]

Here \( g_{i1} \) & \( g_{j1} \) represent \( i \)-th & \( j \)-th intra band two particle normal scattering processes respectively, \( g_{2} \) intra band two particle umklapp scattering.

To describe superconductivity in MgB\(_2\), they considered \( g_{i1} \& g_{j1} \), \( g_{2} \neq 0 \) and others equal to 0.
The proposed Hamiltonian now reads as

\[ H = H_0 + H_{\text{int}} \]

\[ H = \sum_{i\sigma} \left[ (\epsilon_i - \mu) a_{i\sigma}^+ a_{i\sigma} + (\epsilon_j - \mu) a_{j\sigma}^+ a_{j\sigma} \right] \]

+ \sum g_{ij} a_{i\sigma}^+ a_{i-\sigma}^+ a_{j\sigma} a_{j\sigma} + \sum_i \to j + \sum g_{2i} a_{i\sigma}^+ a_{i-\sigma}^+ a_{j\sigma} a_{j\sigma}

Order parameters are defined as

\[ \Delta_i = \sum_p < a_{ip\uparrow}^+ a_{i-p\downarrow}^+ > \]

\[ \Delta_j = \sum_p < a_{jp\uparrow}^+ a_{j-p\downarrow}^+ > \]

The relation between two superconducting order parameters is

\[ \Delta_j = \frac{1 - g_{ii} \rho_i f_i}{g_{jj} \rho_j f_j} \Delta_j \]

where

\[ f_i = \int_{\mu}^{E_c} d\xi \frac{d\xi}{(\xi^2 + \Delta_i^2)^{1/2}} \tanh \left( \frac{(\xi^2 + \Delta_i^2)^{1/2}}{2T} \right) \]

\[ & f_j = \int_{\mu-E_j}^{\mu} d\xi \frac{d\xi}{(\xi^2 + \Delta_j^2)^{1/2}} \tanh \left( \frac{(\xi^2 + \Delta_j^2)^{1/2}}{2T} \right) \]

with the coupled gap equation

\[ (1 - g_{ii} \rho_i f_i)(1 - g_{jj} \rho_j f_j) = g_{jj}^2 f_i f_j \]
They estimated $g_2$ coupling parameter of pair electron scattering process as

$$g_2 = \sum_{k_1,k_2} V^{1,2}_{k_1,k_2}$$

$$V^{1,2}_{k_1,k_2} = \sum_{r,s,t,u} u^*_{1,r}(k_1)u^*_{1,t}(k_1)V_{r,s}u_{2,t}(k_2)u_{2,u}(k_2)$$

Here label 1 is for $\pi$-band, label 2 is for $\sigma$ band $u_{ir}(k_i)$ is the LCAO coefficient with i band $k_i$ momentum. The index $k_1$ & $k_2$ are summed over each Fermi surface. The coupling constant $g_2$ is found to be 0.025 eV. They used density of states of $\pi$ & $\sigma$ bands.

They used $\rho_i = 0.2/\text{eV}$, $\rho_j = 0.14/\text{eV}$, chemical potential $\mu = -2.0$, $E_j = -1.0$, $g_{i1} = -0.4$ eV, $g_{j1} = -0.6$ eV to find the temperature dependence of two gap parameters. This dependence is shown in figure 2.4.
Fig. 2.4: Temperature dependence of two superconducting gap of MgB$_2$ (Kruchinin and Nagao (2006)).
They obtained the temperature dependence of the two gap parameters which have qualitative agreement with experiments. They derived the expression for transition temperature as

\[ T_{c_1} = 1.13(\zeta - E_j) e^{(-\sqrt{g_j})} \]

Here

\[ g_1 = \frac{1}{24}
\left( B + \sqrt{B^2 - 4A} \right) \]

\[ A = g_{1i}g_{1j} - g_2^2 \]

\[ B = g_{1i} + g_{1j} \]

\[ \zeta = -\mu \]

They observed the change in \( T_{C_1} \) due to enhanced interband pairing scattering (\( g_2 \)). Figure (2.5) shows the mechanism of pairing for two gaps.

\[ \text{Fig. 2.5: Diagram of mechanism of pairing for two gaps of MgB}_2 \]

\{Kruchinin and Nagao (2006)\}
They proposed two channel scenario of superconductivity

(i) Conventional channel (intraband $g_1$)

(ii) Unconventional channel (inter band $g_2$).

First- conventional channel (intraband) is connected with BCS mechanism in different zone. The second one explains the tunneling of a Cooper pair between two bands. This tunneling stabilizes superconducting order parameters & increases critical temperature.

Macocian (2006) presented study of two band Eliashberg model. This model was applied to deduce temperature dependence of the two energy gaps in the superconducting state. He started his analysis with Eliashberg equations for a two band superconductor. He adopted the approach to solve these equations on the imaginary axis, summing on Matsubara frequencies. This method needed four equations two for the gaps and two for the renormalization functions one each corresponding to $\sigma$ and $\pi$ bands:

$$
Z_i(i\omega_n) = 1 + \frac{1}{\omega_n} \pi T \sum_{\nu_n} \sum_{j=\sigma,\pi} \left[ \lambda_{ij}(i\omega_n - i\nu_n) - \mu_{ij}^* \right] \times \frac{V_m}{\sqrt{V_m^2 + \Delta_j^2(i\nu_m)}}
$$

$$
\Delta_i(i\omega_n) Z_i(i\omega_n) = \pi T \sum_{\nu_n} \sum_{j=\sigma,\pi} \left[ \lambda_{ij}(i\omega_n - i\nu_n) - \mu_{ij}^* \right] \times \frac{\Delta_j(i\nu_m)}{\sqrt{\nu_m^2 + \Delta_j^2(i\nu_m)}}
$$

Here $\Delta_i(i\omega_n)$ are the superconducting order parameters of $\sigma$ (i = $\sigma$) & $\pi$ (i = $\pi$) bands, $Z_i(i\omega_n)$ are the corresponding mass renormalization functions, $\mu_{ij}^*$ are the Coulombian pseudo potentials and $\lambda_{ij}$ is electron-phonon coupling matrix element.
The summation is over the fermionic Matsubara frequencies and over the indices \( j = \sigma, \pi \) to include both intra and interband processes.

Frequency dependence of the gap function \( \Delta_\sigma \) & \( \Delta_\pi \) at \( T = 4.2 \) K is shown in figures 2.6 and 2.7.

The dependencies of real \( \Delta \) for both \( \sigma \) and \( \pi \) bands present a maximum with a sharp slope at chosen frequency 64 meV phononic \( E_{2g} \) mode. The curve reverses its sign above this frequency. It may be due to the over screened pairing interaction. The imaginary part of the gap function starts to increase above the peak value of the \( E_{2g} \) mode due to phonon generation.

The dependencies of \( \Delta_\sigma \) & \( \Delta_\pi \) are very similar. \( \Delta_\sigma \) is found to be three times greater than \( \Delta_\pi \) which confirms the weaker coupling in \( \pi \) band comparing with \( \sigma \) band. The frequency dependencies of real & imaginary part of the mass renormalization function lead to the same conclusion as evident from figures 2.8 & 2.9.
Fig. 2.6: Frequency dependence of the gap $\Delta_\sigma$ of MgB$_2$ (Macocian (2006))

Fig. 2.7: Frequency dependence of the gap $\Delta_\pi$ of MgB$_2$ (Macocian (2006))
Fig. 2.8: Frequency dependence of the mass renormalization function $Z_\sigma$ of MgB$_2$ [Macocian (2006)]

Fig. 2.9: Frequency dependence of the mass renormalization function $Z_\pi$ of MgB$_2$ [Macocian (2006)]
The study suggests that superconductivity mainly occurs in $\sigma$ band. In $\pi$-band, it is induced from $\sigma$-band through interband scattering. The ratio $\frac{2\Delta(0)}{T_c}$ obtained in both $\pi$ & $\sigma$ band is in fairly good agreement with experimental data. It is higher in the $\sigma$ band & lower in the $\pi$-band in comparison to weak coupling BCS –type value. His results confirmed the correctness of assumption that electron-phonon coupling is mainly due to phonons of $E_{2g}$ mode for both bands.

One can apply this strong electron-phonon coupling approximation for magnesium diboride.

**Kristoffel et al. (2003)** developed a two-band model of MgB$_2$ superconductivity. Using the scheme developed by Ord T. & Kristoffel N. in 2002, they calculated superconducting characteristics of MgB$_2$. They started with linearised Hamiltonian for the effective $\sigma$-band & $\pi$-band ($\alpha=1$ for $\sigma$ band & $\alpha=2$ for $\pi$ band).

$$H = \sum_{\alpha k} \tilde{\varepsilon}_{\alpha}(k) a_{\alpha k}^+ a_{\alpha k} - \sum_{\alpha k} \Delta_{\alpha k} <a_{\alpha k \uparrow}^+ a_{\alpha -k \downarrow}>$$

$$+ \sum_{\alpha k} \Delta_{\alpha k} a_{\alpha k \uparrow}^+ a_{\alpha -k \downarrow} + \Delta_{\alpha k}^* a_{\alpha -k \downarrow} a_{\alpha k \uparrow}$$

where superconductivity gap order parameters are

$$\Delta_{\alpha k} = 2 \sum_{p' k' } W_{\alpha \beta}(k', k) \gamma_{\beta \mu} <a_{\beta \mu \downarrow} a_{\alpha \mu \uparrow}^* >$$

Here the band energy $\varepsilon_{\mu} = \tilde{\varepsilon}_{\mu} - \mu$ and $\mu$ is chemical potential.

The Free energy of the system is given by
\[ F = \sum_{\alpha k} \left[ \varepsilon_{\alpha}(\vec{k}) - 2k_B T \log_e \left( \frac{E_{\alpha}(\vec{k})}{2k_B T} \right) + \frac{1}{2} \Delta_{\alpha k}^2 \right] \]

The quasi particle energy is \( E_\alpha(\vec{k}) = \sqrt{\varepsilon_{\alpha}^2(\vec{k}) + \Delta_{\alpha}^2} \)

\[ & \xi_{\alpha k} = \frac{1}{E_\alpha(\vec{k})} \tanh \frac{E_\alpha(\vec{k})}{2k_B T} \]

Similarly, they obtained the expression for heat capacity jump. With the help of calculations & comparison with available experimental data, they concluded that, a two band model with \( \sigma \) intra band and \( \sigma-\pi \) inter band interactions allows one to describe the basic superconducting characteristics of MgB\(_2\) satisfactorily.

Lagos & Cabera (2003) presented two band model for superconductivity based on standard BCS like pairing mechanism. They followed with Hamiltonian

\[ H = \sum_{k,m} E_{k,m} \left( C_{k,m}^+ C_{k,m} - C_{-k,m}^+ C_{-k,m} \right) \]

\[ -\frac{1}{N} \sum_{k,q,m} V_{n,m} C_{k,n}^+ C_{-k,n}^+ C_{-q,m} C_{q,m} \]

Here \( C_{k,n}^+ \)'s are usual creation operators, \( E_{k,m} \) are the bands dispersion \((m = 1, 2)\), \( V_{n,m} \) are the positive pairing coefficients \( V_{12} = V_{21} \) and \( D = V_{11} V_{22} - V_{12}^2 \neq 0 \)

We have defined \( k = (k, \uparrow) \) & \( -k = (-k, \downarrow) \), \( N \) is the number of sites. They defined order parameters \( \Delta_n \) as

\[ \Delta_n = \frac{1}{N} \sum_{k,m} V_{n,m} < C_{k,m}^+ C_{-k,m}^+ > \]
The Free energy per site $F$ is

$$ F = E_0 + \frac{T}{N} \sum_{k,m} \ln f_{k,m} (1 - f_{k,m}) $$

Here $f(\omega) = \frac{1}{\beta \omega}, \omega_{k,m} = \sqrt{E_{k,m}^2 + \Delta_m^2}$ and $f_{k,m} = f(\omega_{k,m})$

The Thermodynamic critical field $H_c$ is

$$ \delta F(T) = -\frac{1}{8\pi} H_c^2 $$

Specific heat is $C_V = T \left( \frac{\delta S}{\delta T} \right)_V$

$$ C_V = \frac{2\beta^2}{N} \sum_{k,m} f_{k,m} (1 - f_{k,m}) \left( \omega_{k,m}^2 + \frac{1}{2} \beta \frac{\delta \Delta_m^2}{\delta \beta} \right) $$

Entropy (per site)

$$ S = -\frac{2}{N} \sum_{k,m} \left( (1 - f_{k,m}) \ln (1 - f_{k,m}) + f_{k,m} \ln f_{k,m} \right) $$

They computed the gaps equations at zero temperature. They also computed specific heat, entropy, critical field & conductance as the function of temperature considering interband scattering mechanism & two planar symmetrical bands. The results obtained are found to be in good agreement with experimental results on MgB$_2$ which indicated that interband pairing is somehow relevant for this compound.

Nuwal & Kakani (2013) considered canonical two band BCS Hamiltonian having free surfaces of $\sigma$ & $\pi$ - bands. They considered the Hamiltonian given by Chakraverty (1993) as
\[
H = H_0^p + H_0^d + H_{pd}
\]
\[
H = \sum_p \varepsilon_p \left(C_{p\uparrow}^+ C_{p\downarrow} + C_{-p\downarrow}^+ C_{-p\uparrow}\right) + \Delta_{pp} \sum_p C_{-p\downarrow} C_{p\uparrow}
\]
\[
+ \Delta_{pd} \sum_p C_{p\uparrow}^+ C_{-p\downarrow} + \sum_d \varepsilon_d \left(C_{d\uparrow}^+ C_{d\downarrow} + C_{-d\downarrow}^+ C_{-d\uparrow}\right)
\]
\[
+ \Delta_{dd} \sum_d C_{-d\downarrow} C_{d\uparrow} + \Delta_{ad} \sum_d C_{d\uparrow}^+ C_{-d\downarrow} + \Delta_1 \sum_d C_{-d\uparrow} C_{d\downarrow}
\]
\[
+ \Delta_2 \sum_p C_{-p\downarrow} C_{p\uparrow}^+ + \Delta_2' \sum_p C_{-p\downarrow} C_{p\uparrow}^+ + \Delta_2' \sum_d C_{d\uparrow}^+ C_{d\downarrow}^+
\]

where

\[
\Delta_1 = V_{pd} < C_{p\uparrow}^+ C_{-p\downarrow} >,
\]
\[
\Delta_2 = V_{pd} < C_{d\uparrow}^+ C_{-d\downarrow} >,
\]
\[
\Delta_{pp} = V_{pp} < C_{p\uparrow}^+ C_{-p\downarrow} > &
\]
\[
\Delta_{dd} = V_{dd} < C_{d\uparrow}^+ C_{-d\downarrow} >
\]

Where \( p \) & \( d \) are momentum labels in the \( \pi \) & \( \sigma \) bands respectively with energies \( \varepsilon_p \) & \( \varepsilon_d \). Each band has its proper pairing interaction \( V_{pp} \) and \( V_{dd} \).

\( V_{pd} \) is pair interchange between \( p \) & \( d \) bands & \( V_{pd} = V_{dp} \).

Considering the above Hamiltonian and following Green's function technique & equation of motion method, they found that MgB\(_2\) possess two gaps.

\[
\bar{\Delta}_p = \Delta_{pp} + \Delta_2 \quad \text{and} \quad \bar{\Delta}_d = \Delta_{dd} + \Delta_1.
\]
The two gap structure is found in agreement with experimental observations. The specific heat $C_{es}$ versus $T$ is found in satisfactory agreement with experimental results. The theoretical values obtained are higher than the experimental values. The density of states behavior is similar to BCS weak coupling superconductors corresponding to $\pi$ & $\sigma$ band.

The theories of superconductivity in binary intermetallic compounds presented above provide a basic understanding of the new phenomenon in these systems, but a microscopic theory and satisfactory mechanism seems still lacking.

**High-Temperature Superconductivity**

The discovery of superconductivity in Cu-oxide compounds of lanthanum and barium at $T_c \approx 35K$ by Muller and Bednorz [1986] gave an additional push to the intensification of the scientific activity in the field of superconductivity. Over the last 29 years, $T_c$ has been increased to 134K. Recently, the high $T_c$ of new MgB$_2$ ($T_c = 39K$) LnO$_{(1-x)}$F$_x$FeAs (50 K) were registered. After the discovery of HTSCs, the problem of clarifying mechanisms of high-$T_c$ superconductivity became urgent.

To explain high-temperature superconductivity, a lot of models and mechanisms of this unique phenomenon have been proposed. The key question is the nature of the mechanism of the pairing of carriers.

Several mechanisms have been proposed to explain superconductivity in HTSC’s. Apart from ordinary BCS mechanism based on electron-phonon interaction, there are so many models or mechanisms of superconductivity, i.e. magnon model, exciton model, anharmonic model, plasmon model, bipolaronic model, resonance valence bond (RVB) etc.

**Brusov (1999)** gave the classification of the mechanisms of the pairing of high-temperature superconductors as shown in table 2.1.
<table>
<thead>
<tr>
<th>Density fluctuations</th>
<th>Charge fluctuations</th>
<th>Spin fluctuations</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Anharmonic Phonons</td>
<td>(a) Plasmons</td>
<td>(a) RVB</td>
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<tr>
<td>(b) JahnTeller effect</td>
<td>(b) Exciton</td>
<td>(b) Anyon superconductivity</td>
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<tr>
<td>(c) Bipolarons</td>
<td>(c) Chemical mechanism</td>
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<td>(d) vH’s</td>
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<tr>
<td></td>
<td></td>
<td>(g) Spin bag mechanism</td>
</tr>
</tbody>
</table>

Table 2.1: Classification of the mechanisms of pairing of HTSCs  
{Brusov (1999)}
All these models use the concept of pairing with a subsequent formation of a Bose condensate at transition temperature regardless of the reasons for the attraction. Here we present a brief discussion of some important mechanisms of the pairing of HTSCs.

(a) BCS mechanism:

BCS mechanism is based on the weak electron - phonon interaction. The expression for $T_c$, the critical temperature from BCS theory

$$T_c = 1.14\Theta e^{-\left(\frac{1}{N(0)v}\right)}$$

Here $\Theta = \frac{\eta \Omega_D}{k_B}$ $\eta \Omega_D$ is Debye energy, $N(0)$ is the density of states of the Fermi level & $V$ is attractive pairing potential acting between electrons. The maximum transition temperature suggested by the BCS theory is about 40 K.

The general scheme for interaction of electrons through transfer system $X$ is

$$e_1 + X = e_{1}^{i} + X^*$$

$$e_2 + X^* = e_{2}^{i} + X$$

Here $e_i$ corresponds to electron having momentum $p_i$, $X$ is ground state & $X^*$ is excited state of the transfer system. Due to the result of the above reaction –

(i) The electron makes an exchange by moment,

(ii) The system returns to the initial state.

Such interaction leads to attraction & critical temperature is given by
$T_c \approx \Delta E e^{-\frac{1}{\lambda}}$

Where $\Delta E$ is energy difference of ground & excited state. $\lambda$ is a term which depends upon the interaction of electrons with the system. However, the BCS theory seems to be inadequate to fully explain how superconductivity works, because it does not take the quantum entanglement of the electronic system into account.

(b) Magnetic mechanism of pairing:

Various studies on the magnetic mechanism of pairing used an assumption that pairing arises due to the exchange of spin excitations – magnons. Akhiezer and Pomeranchuk (1959) considered that interaction between conduction electrons due to exchange by acoustic phonons & magnons (spin waves).

One knows that superconductivity and ferromagnetism can coexist in the same spatial regions. In the case of triplet pairing, an increase in the concentration of ferromagnetic components increases critical temperature ($T_c$) at sufficiently low concentration. The pairing happens in a singlet state in phonon mechanism. Here $T_c$ decreases with increase in the concentration of ferromagnetic component.

(c) RVB mechanism:

Anderson (1987) moved forward the model of resonance valance bonds (RVB’s) to understand Cooper pairing in HTSC’s by the participation of magnetic excitations. This model is based on the idea of magnetic ordering.

In RVB model, the pairing of carriers exists due to exchange by magnons. The RVB model was successful in drawing the attention of researchers to the study of Anti-ferromagnetism in high-temperature superconductors.
(d) Exciton mechanism of pairing:

Little (1964) proposed the first exciton model for organic superconductors whereas Ginzburg & Kirshnitz (1982) proposed the same for layered systems.

In this model, one has to assume two groups of electrons.

(i) One is related to the conduction band

(ii) Second group is related to almost localized electrons.

We should expect a high value of transition temperature \( T_c \approx \frac{1}{\sqrt{M}} \) because mass \( M \) of such excitonic excitations is small. Since high energy excitonic excitations do not ensure the binding of electrons in pair and therefore the above model was not realized practically. Experimental proof of the excitonic mechanism is not available so far.

(e) Anharmonic model:

We know that superconductivity is preceded by structural transformations in a crystal. Davyvov (1990) found that structural transformation arises prior to the appearance of superconductivity. It decreases the frequencies of phonons & so increasing the electron-phonon interaction parameter.
(f) Van Hove singularities:

Two decades ago vH’s (Van Hove singularity) in the density of states (DOS) $N(E)$ was put forwarded as a $T_c$ enhancement mechanism for intermetallic superconductors. It is very important to understand the specific features of the dispersion $E(k)$ and the behaviour of DOS $N(E)$. The DOS is independent of energy for a two-dimensional problem. $N(E)$ is constant & we have dispersion less band.

The presence of almost- flat band near the Fermi surface for cuprate superconductors was indicated by photoemission experiments. The existence of vH’s in the DOS near Fermi surface is due to the presence of its energetic surface & flat band. In this model,

$$T_c = 1.14 e^{-\frac{1}{\lambda}}$$

Here $\lambda = VN(E)$. If $N(E)$ is replaced by $N(E_f)$, it will be related to the vH’s.

In 2-D, $N(E) \approx \log \left| \frac{D}{E - E_f} \right|$.

So transition temperature has the form $T_c \approx De^{-\frac{1}{\lambda^2}}$. Here $D$ is characteristic energy cut off.

(g) Plasmon mechanism of pairing:

Many attempts have been made to explain high $T_c$ superconductivity on the basis of the idea of pairing as a result of the exchange of plasmons. Plasmons - longitudinal plasma waves are formed in solids in frequency region at which permeability of the
medium becomes zero. We can say that the exchange by plasmons will increase the pre-exponential factor in the expression for

\[ T_c = \Theta e^{\left(\frac{1}{x_0}\right)} \]

by 2-3 orders if \( \Theta = \frac{\eta \sigma_p}{k_B} \).

However, this increase does not grow \( T_c \) by a significant amount. Here \( \sigma_p = \frac{4\pi e^2 N}{m} \),

\( N \) is the concentration of electrons, \( e \) & \( m \) - charge and mass of electron respectively.

**Bipolaronic mechanism of superconductivity:**

The Bipolaronic theory is an important attempt to explain the phenomenon of high \( T_c \) superconductivity. Like cooper pairs, bipolarons are bose particles. **Alexandrov and Ranninger [1981 b]** were first to use the idea of bipolarons to explain the origin of high \( T_c \) superconductivity.

A dimensionless parameter ‘g’ characterizes the efficiency of the interaction of an electron with long wave longitudinal optical vibrations having frequency \( \Omega \) in the medium as

\[ g = \frac{e^2}{\varepsilon} \sqrt{\frac{m}{2\Omega \eta^2}} \]

Where \( \varepsilon \) is the dielectric permeability of the inertial polarization, \( m \) & \( e \) are mass and charge of electron respectively. The interaction is assumed to be small when \( g<1 \).

In bipolaronic model
\[ \lambda = \frac{2z^2 \eta \Omega z - V_c}{D} \]

where \( \lambda = V.N \left( E_f \right) \)

\( N(E_f) \) is the density of states of electrons at the Fermi surface and quantity \( V \) is inversely proportional to the coefficient of elasticity of the crystal. \( Z \) is the number of nearest neighbors. \( D \) is the width of the conduction band of free quasi particles.

The effective mass of a bipolaron is given by

\[ \tilde{m} = m \frac{\Delta}{D} e^{b^2} \]

The superconducting transition temperature \( T_c \) for ideal Bose gas is calculated by

\[ T_c = \frac{3.3 \eta^2 N^{2/3}}{\tilde{m} k_B} \]

Advances in experimental research have yielded a detailed consistent picture of phase behaviour and spin dynamics of HTSCs over a wide range of doping levels. Although our knowledge is far from complete, further experimental work is required especially in the over doped regime - the data now at hand are already an excellent basis for the assessment of said models and particularly spin-fluctuation pairing models.

**GREEN’S FUNCTION TECHNIQUE**

Various methods of modern quantum field theory have been penetrated into statistical mechanics. Fundamental problems in both the fields are very much same. Green’s function is one of the important aspects of quantum field theory. Green’s
functions are appropriate for the study of the properties of interacting quantized fields \{Falicov and Kimball (1969)\}

There are various types of Green’s functions. One of them is the causal Green’s function. It has been proved that the causal Green’s function is especially useful for making calculations based on the equation of motion method for the operators of interest, to solve the Hamiltonian \{Economou (1983); Inkson (1984); Rickayzen (1980); Lovesey (1986)\}. An important feature of the causal Green’s function is, its ability to obtain approximate results for non-linear systems, which are difficult to obtain by other alternative methods.

The application of Green’s function makes it possible, to obtain for the energy regularized expansions which do not contain higher powers of volume \text{Schwinger} (1951) therefore one can apply the perturbation theory to large systems. The application of Green’s functions is useful when combined with spectral representation - like Lehmann- Kallen relation \text{Klein} (1958).

The publication for the review of the properties of causal Green’s functions by \text{Zubarev (1960 a)} and \text{Ambegaoker (1963)} was an important step for the acceptance and development of this method.

Some other types of Green’s functions which we frequently used are

(i) Double time –temperature dependent (retarded and advanced) Green’s functions \text{Matsubara (1955)},

(ii) Temperature dependent Green’s functions.
These Green’s functions are defined as the expectation value of time ordered product of field operators. These Green’s functions are suitable for the development of diagrammatic perturbational expansions Dyson (1956). Green’s function in statistical mechanics is the proper simplification of the concept of correlation functions. They are closely linked with the evaluation of observed quantities. We can find the observed quantities by formulating the equation of motion and after that solving them for Green’s functions Lovesey (1986).

In order to study the superconducting properties of the binary intermetallic compounds using multi-band model, we follow the procedure of calculations based upon the Green’s functions technique as described by Zubarev (1960 a) and that of Bogolyubov (1958), the mean field decoupling procedure with pairing approximation. We are reviewing in short the principal definitions and fundamental equations of Green’s functions technique.

One can describe the average of an operator “A” over grand canonical ensemble as,

\[
\langle A \rangle = Q^{-1} \left[ \exp \left( - \frac{gA}{q} \right) \right]
\]

with \( Q = \text{trace} \left[ \exp \left( - \frac{gA}{q} \right) \right] = e^{-\Omega/\theta} \)

Here “Q” is partition function for grand canonical ensemble, \( \theta \) is equal to \( k_B T \) and “\( \Omega \)” is thermodynamic potential.

In the above equation, the operator \( gA \) is defined as,

\[
gA = H - \mu N
\]
where $\mu$ is chemical potential.

One can write Heisenberg representation of operator “A” and “B” as “$A(t)$” and “$B(t)$”, then the T-product of operator is written as,

$$TA(t) B(t') = \theta(t-t') A(t) B(t') + \eta \theta(t'-t) B(t') A(t)$$

Here $\theta(t-t')$ is a unit step function which is defined as,

$$\theta(t) = \begin{cases} 1 & \text{for } t > 0 \\ 0 & \text{for } t < 0 \end{cases}$$

and $\eta$ is defined from the following commutation relation of particles,

$$[A, B] = AB - \eta BA \quad \text{having } \eta = \pm 1$$

If both “A” and “B” are boson operators, then the value of $\eta$ is chosen as $+1$.

Whereas if they are Fermi operators then the value of $\eta$ is chosen as $-1$.

One may define double time Green’s functions as

$$G_c(t, t') = \langle \langle A(t) | B(t') \rangle \rangle_c = i \langle A(t), B(t') \rangle \theta(t-t') - i \eta \theta(t'-t) \langle B(t'), A(t) \rangle$$

$$G_r(t, t') = \langle \langle A(t) | B(t') \rangle \rangle_r = -i \theta(t-t') \langle A(t), B(t') \rangle - \eta \langle B(t'), A(t) \rangle$$

$$G_a(t, t') = \langle \langle A(t) | B(t') \rangle \rangle_a = i \theta(t'-t) \langle A(t), B(t') \rangle - \eta \langle B(t'), A(t) \rangle$$

Above equations represent causal ($G_c$), retarded ($G_r$) and advanced ($G_a$), Green's functions respectively. These Green’s functions in statistical mechanics are different
from the field theory. In Green’s functions, instead of taking averages over the
 lowest state of the system, one can find averages over the grand canonical ensemble.

The equation of motion for Green’s function can be written as,

\[
i \frac{dG}{dt} = i \frac{d}{dt} \langle \langle A | B \rangle \rangle = \frac{d\theta(t-t')}{dt} \langle [A(t), B(t')] \rangle + \langle [A(t), H], B(t') \rangle
\]

It has the same form for all the Green’s functions. The double-time Green’s function
 on the right-hand side of above equation is, of the higher order than the initial one.
 One can construct the equation of kind-retarded (\(G_r\)) for them and get a chain of
coupled equations for the Green’s functions. An infinite chain of equations is
available in this way. Using the decoupling procedure one can make a finite set.

The other chains for Green’s functions can also be obtained e.g. “Schwinger type”
for which multiple-time Green’s functions could be used. These chains have
quantities in the nature of vertex parts, depending on three-time arguments, for which
there is no spectral theorem. One can use some approximations to decouple the chain
of equations, reducing the chain of equations to a finite set of equations.

**CORRELATION FUNCTIONS**

The average over the statistical ensemble of the product of operators in Heisenberg
representation,

\[
F_{Ab}(t, t') = \langle A(t), B(t') \rangle
\]

or

\[
F_{Ba}(t, t') = \langle B(t'), A(t) \rangle
\]
are of enormous importance in statistical mechanics. One can see them as time correlation functions. When the times are different, i.e. \( t \neq t' \), these averages yield the time correlation functions, necessary for transport properties. Unlike the Green’s functions, the time correlation function does not contain the discontinuous factor \( Q(t - t') \), and are defined only when the times are same i.e. \( t = t' \).

The time correlation functions follow the equations,

\[
i \frac{d}{dt} (F_{AB}) = \left\langle \left[ A(t) H(t) - H(t) A(t) \right], B(t') \right\rangle
\]

or \[
i \frac{d}{dt} (F_{aa}) = \left\langle B(t'), [A(t) H(t) - H(t) A(t)] \right\rangle
\]

The correlation functions can be evaluated by direct integration of above equations. One can define the correlation functions related with the Green’s functions as,

\[
\left\langle B(t'), A(t) \right\rangle = \lim_{\epsilon \to 0} \frac{i}{2\pi} \int_{-\infty}^{\infty} \frac{d\omega}{e^{\beta\omega} + 1} \left[ \left\langle \langle A(t) | B(t') \rangle \right\rangle_{\omega+i\epsilon} - \left\langle \langle A(t) | B(t') \rangle \right\rangle_{\omega-i\epsilon} \right] e^{-i\omega(t-t')}
\]

One can obtain the correlation function using the identity,

\[
Lt_{\epsilon \to 0} \frac{i}{2\pi N} \left[ \frac{1}{(\omega + i \in -E_p)} - \frac{1}{(\omega - i \in -E_p)} \right] = \delta(\omega - E_p)
\]

and Dirac delta property,

\[
\int_{-\infty}^{\infty} f(y) \delta(w-x) dx = f(x)
\]

Above equations jointly with decoupling approximation offer an important method of calculation with Green’s functions technique.
In the present study, we propose to develop a simple microscopic theory of superconductivity in binary intermetallic compounds and study the various superconducting properties of the binary intermetallic superconductor MgB\(_2\) following Green’s function technique and equation of motion method. Using this model, we propose to derive the expression for superconducting order parameter, electronic specific heat, and density of states, free energy difference and critical field.

We will apply the theory developed to study magnesium diboride (MgB\(_2\)) system because it has remarkably highest transition temperature (\(T_c = 39\) K) for any binary intermetallic compound.