THE STUDY ON THE EFFECT OF CARBON ON THE ELECTRONIC STRUCTURE OF THE SUPERCONDUCTING MAGNESIUM DIBORIDE (MgB_2)

BY

KEBEDE BEKELE

A THESIS SUBMITTED TO THE DEPARTMENT OF APPLIED PHYSICS SCHOOL OF APPLIED NATURAL SCIENCE

OFFICE OF GRADUATE STUDIES
ADAMA SCIENCE AND TECHNOLOGY UNIVERSITY

PRESENTED IN PARTICIPIAL FULFILLMENT OF THE REQUIREMTS FOR THE DEGREE OF MASTERS OF SCIENCE IN PHYSICS

Adama

September, 2018

THE STUDY ON THE EFFECT OF CARBON ON THE ELECTRONIC STRUCTURE OFTHE SUPERCONDUCTING MAGNESIUM DIBORIDE (MgB_2)

BY;

KEBEDE BEKELE

ADVISOR; MESFIN ASFAW(PHD.)

A THESIS SUBMITTED TO THE DEPARTMENT OF APPLIED PHYSICS
SCHOOL OF APPLIED NATURAL SCIENCE

OFFICE OF GRADUATE STUDIES
ADAMA SCIENCE AND TECHNOLOGY UNIVERSITY

PRESENTED IN APARTIAL FULFILIMENT OF THE REQUIREMENTS FOR

THE DEGREE OF MASTERS OF SCIENCE IN PHYSICS

Adama
September 2018

Table of Contents page

List of figures

List of tables

Acronyms

BCS= John Barden,Leon Copper, and Robert Schrieffer

DFT=Density functional theory

LDA=Local density approximation

HTSc= High temperature superconductor

PWSCF=Plane wave Self consistent field

Quantum-ESPRESSO=open source package for research in electronic structure simulation and optimization

GGA=Generalized gradient approximation

Symbols

$K_{B=}$Boltzmann constant

$n_{s=}$carrier density

I_c= critical current

J_c=critical current density

$B_{c=}$ critical magnetic field

ζ=coherence length

$T_{C=}$ critical temperature

w_D = Debye frequency

θ_D= Debye temperature

Δ = Energy gap

H_{c1} = Lower critical field

H_{c2} Upper critical field

λ = penetration depth

MgB2C= carbon containing Magnesium diboride

MgBC= carbon substitution of boron in MgB_2

Acknowledgements

First and for most, I would like to give special thanks and glory to the almighty God for gave me the grace, this chance and good health to complete this thesis.

I would like to express my appreciation to my advisor; Dr. Mesfin Asfaw for his un limited and constructive guidance, valuable comments, friendly encouragement, suggestion and the support with his vast knowledge and experience and providing me in necessary equipments. My thanks extend to applied physics program (ASTU). I would like to thanks for the chair man of applied phys

cs program and w/r Yetnayet secretory of the department for their help through out my contact with the Department.

My heart felt thanks also go to My uncle Ato Boshora Jerbo fromWollega University for his moral, financial and writing material support through out my time of M.sc thesis accomplishment. I would like to express my deepest gratitude to my father and mother as well as my elder brother Teacher Tesfaye Bekele for their care love and help that enabled me to realize my long term dream.

Abstract

Experimental study results show an exceptionally large superconducting transition temperature of 39 K in MgB_2. In order to understand the unexpected superconducting behavior of this compound we have made electronic structure calculations for MgB_2 and closely related systems, MgB_2C and MgBC. The compounds have hexagonal structures as seen by Xcrysden. Were produced the electronic band structure of pure magnesium diboride and also its density of state. We also calculated and determined the crystal structure, electronic band structure and density of state by carbon substitution in the absence of one boron, that means MgBC and by adding carbon in the in the presence of two boron, MgB_2C. In both cases we determined the crystal structure, electronic band structure and density of state along high symmetry lines, using density functional theory as implemented by a code quantum –ESPRESSO. We found that, hole bands are changing around a Fermi level, except, $\Gamma - A$ points incase of MgB_2, the hole bands are drop around the Fermi level in case of MgBC, and the electron and the hole bands are cross each other around the Fermi level in case of MgB_2C. This dispersion in different high symmetric points enables us to know the effect of carbon on the electronic structure and density of state of hole bands to change the critical temperature of super conductors. Their crystal structure in case of the three compounds is the same to be hexagonal closed packed structures. We also calculated Tc using reasonable approximations, and we found that, T_c=27.07 K, 37.34 K, and 41.09k for MgB_2C, MgB_2 and MgBC respectively. In MgB, quite large number of bands are crossing the Fermi level.

Chapter 1

Introduction to superconductivity

1.1 Back ground of the study

Superconductivity was discovered in 1911 by the Dutch physicist Heike KamerlinghOnnes. Three years earlier, Onnes and colleagues had discovered how to liquefy Helium which they later used to cool mercury to below 4.2 K. At this temperature they found mercury lost its electrical resistance [1-4]. He received the Nobel Prize in 1913 for his work on helium liquefaction [5].

A classification of known superconducting compounds is carried out. One includes 13 types of compounds, namely organic superconductors, *A* 15 compounds, magnetic superconduct ors, heavy fermions, oxides without copper, pyrochlore oxides, ruther no curates, high temperatu re superconductors, rare earth boro carbides, silicon Superconductors, chalcogens, carbon superc onductors, MgB_2 and related compounds [7]. Heavily doped semiconductor can become superco nducting as Ge or Si.

Nor the noble metals (Cu, Ag, Au) neither the alkaline (Li, Na, K, Rb, Cs, Fr)present a superconducting phase transition at least above a few temperature superconductivity. In general, good conductors are not good superconductors (meaning that they do not have high critical temperatures). The number of conducting electrons in a metal is of the order of 10^{22}per cm^3. In a semiconductor at room temperature these are of the order of 10^{15}per $cm^3$and in a heavily doped semiconductor this number (in the same units) is around 10^{18}per cm^3. Un conventional superconductor is characterized first by its critical temperature, Tc.

For conventional superconductors it is very low. The highest Tc =23K) was found in Nb3Ge (a compound) which was fabricated for the first time in 1973. Superconductivity is characterized by three distinguishable properties, these being zero DC resistance, a fully diamagnetic Meissnereffect, and macroscopic quantum phenomena. In 1933 Walther Meissner and Robert Oc hsenifeld, discovered that superconducting materials expel magnetic fields from their interiors

[9]. In 1957, explanation of why the materials exhibit superconductivity was put forward by three physicists, John Bardeen, Leon Cooper and Robert Schrieffer in their theory known as BCS theory (named in the honor of its three discoverers)[6]. This theory explains that the materials become superconductors when the electrons inside them join forces to make Cooper pairs. Electrons generally are scattered due to the impurities, defects and vibrations of the material crystal lattice. All of these cause resistance to the flow of electricity. But at low temperatures, when the electrons pair up, they can freely move without being scattered, thus causing no resistance to the flow of electricity [7,11-12].

Superconductors are promising materials for power applications such as cables, generators and motors. Reducing their resistance and consequent power dissipation is essential for such applications [13]. MgB_2 is a black, inter metallic, polycrystalline material that had been known since 1953 and was used in the commercial preparation of elemental boron. It was not known to be Superconducting until this property was accidentally discovered by Akimitsu and colleagues in 2001[12]. Furthermore, MgB_2 had a critical temperature of 39K. The un aspected superconduc ting behavior of MgB_2 has been studied and reported [14-17, 31]. Unlike most known superconductors, MgB_2 is a metallic binary compound with a relatively simple layered hexagonal crystal structure. Its relatively high T_C coupled with its simple structure and high critical current density makes MgB_2 an attractive candidate for practical applications [18].Like conventional superconductors, MgB_2isa phonon-mediated superconductor with a relatively long coherence length [19].

The effects of carbon doping on superconductivity in MgB_2 compound has been extensively studied. The Jc(critical current density) of B(boron) performance can be greatly improvement by doping with various different carbon sources, such as carbon, diamond , graphite and carbon tubes [22 ,16 ,17,18]. T_c of MgB_2 also increased by hole doping [30]. The addition of small amount of-C causes substitution of boron by carbon, which decreases the critical temperature and increases the upper critical field as well as the current density in high magnetic fields. The transition temperature curves of tapes with different C doping levels determined by susceptibility measurements. The T_c decreases monotonically with increasing C doping level. The depression of T_c is caused by the carbon substitution for B.

1.2 Statement of the problem

Superconducting critical temperature is not yet raised to room temperature. Different experimental and theoretical methods have been employed in order to understand the onset of superconducting and to increase T_c. Electronic structural calculation can provide information on the properties of supper conducting materials.

Then, the main aim of this thesis is to understand the effect of carbon on the electronic structure of magnesium diboride supper conductor materials. Density functional theory (DFT) was employed to calculate the band structure of this compound by using experimental values. This mathematical simulation is believed to provide the desired information about the effect of carbon on the electronic structure of magnesium diboride in detail.

1.3 Objectives

1.3.1 General objective

The general objective of this work is to study the effect of carbon on electronic structure of Magnesium Di boride (MgB_2).

1.3.2 Specific objectives

The specific objectives of this study are:

- to obtain The DOS and band structure of carbon added Magnesium Diboride.
- to compare the band structure of MgB_2 with carbon(MgB_2c and MgBC) and without carbon.
- to analyze the general properties of carbon added superconducting Magnesium Diboride in depth.
- to calculate the superconducting critical temperature.

Chapter 2

Review of related literature

2.1 Over view of superconductivity

Superconductivity is characterized by three distinguishable properties, these being zero DC resistance, a fully diamagnetic Meissner effect, and macroscopic quantum phenomena. In 1933 Walther Meissner and Robert Ochsenfeld, discovered that superconducting materials expel magnetic fields from their interiors [9]. In 1957, explanation [10] of why the materials exhibit superconductivity was put forward by three physicists, John Bardeen, Leon Cooper and Robert Schrieffer in their theory known as BCS theory (named in the honor of its three discoverers).

This theory explains that the materials become superconductors when the electrons inside them join forces to make Cooper pairs. Electrons generally are scattered due to the impurities, defects and vibrations of the material crystal lattice. All of these cause resistance to the flow of electricity. But at low temperatures, when the electrons pair up, they can freely move without being scattered, thus causing no resistance to the flow of electricity [7, 11-12]. Superconductors are promising materials for power applications such as cables, generators and motors. Reducing their resistance and consequent power dissipation is essential for such applications [13].

As a compound magnesium diboride, (MgB_2) has been available since 1953[10]. Accidental discovery of superconductivity in this simple binary compound in 2001[10] generated a great deal of interest in both theoretical and experimental investigations worldwide. Several surprising properties of this material were revealed during intensive fundamental studies of this super conductor that were following its discoveries.

The critical temperature of (T_c) of MgB_2-39 K is the highest among conversional (BCS) binary compounds. For along time, the temperature of 23 K observed in Nb_3Ge, was the top values in this class of super conductors. Was discovered in 1911 by the Dutch physicist Heike Kamerlingh Onnes Similar to high T_c superconductor. MgB_2 has layered structure which leads to significantly an isotopic superconducting properties [21]. Interestingly, MgB_2 possesses two, gap

superconductivity. Phenomenon which was predicted theoretically in 1959[22],but was only obviously observed for the first time in this compound.

MgB_2 is a black, inter metallic, polycrystalline material that had been known since 1953 and was used in the commercial preparation of elemental boron. It was not known to be Superconducting until this property was accidentally discovered by Akimitsu and colleagues in 2001 [12]. Furthermore, MgB_2had a critical temperature of 39 K.MgB_2has been studied and reported [14-17, 31].

Unlike most known superconductors, MgB_2 is a metallic binary compound with a relatively simple layered hexagonal crystal structure. Its relatively high T_C coupled with its simple structure and high critical current density makes MgB_2 an attractive candidate for practical applic ations [18]. Like conventional superconductors, MgB_2 is a phonon mediated superconductor with a relatively long coherence length [19]. The effects of carbon doping on superconductivity in MgB_2compound has been extensively studied.

The Jc (critical current density) of B(boron) performance can be greatly improvement by doping with various different carbon sources, such as carbon, diamond graphite and carbon tubes [22 ,16 ,17,18]. T_c of MgB_2 also increased by hole doping [30]. The addition of small amount of-C causes substitution of boron by carbon, which decreases the critical temperature and increases the upper critical field as well as the current density in high magnetic fields. The transition temperature curves of tapes with different C doping levels doping level. The depression of T_c is caused by the carbon substitution for Bdetermined by susceptibility measurements. The $T_c$decreases monotonically with increasing C.

Table 2.1 Critical temperatures of Different Materials [4].

No	Material	Critical temperature (K)
1	Gallium	1.1
2	Aluminum	1.2
3	Indium	3.4
4	Tin	3.7
5	Mercury	4.2
6	Lead	7.2
7	Niobium	9.3
8	La-Ba-Cu-oxide	11.9
9	Y-Ba-Cu-oxide	92
10	TI-Ba-Cu-oxide	125

Table 2.1 shows list of some superconducting materialswith their corresponding critical temperatures.

The typical experimental dependence of resistance on temperature in a superconductor is shown in the **Figure 2.1** which the resistivity of the super conductor is suddenly falls to zero when the temperature reduces to a certain value below the critical temperature T_c.

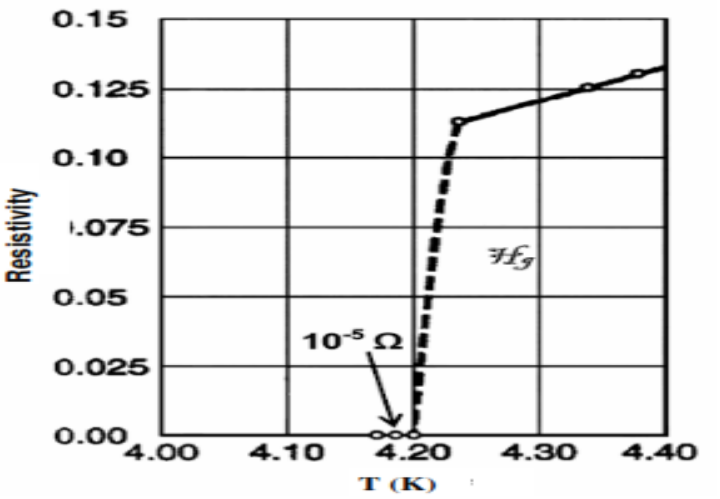
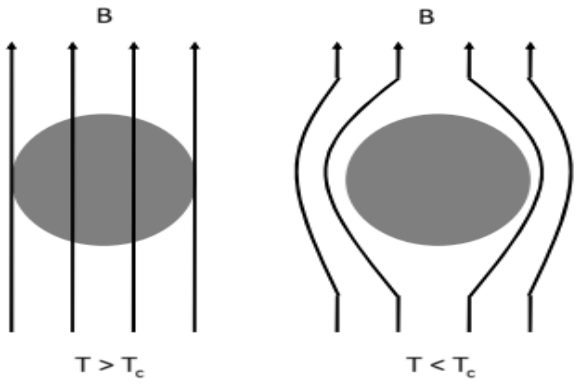


Figure 2.1: Resistance in ohms of a specimen of mercury versus absolute temperature by KamerlinghOnnes in 1911 [1].

2.1.1Meissner-Ochsenfeld effect

When the specimen is placed in a magnetic field, and then cooled, the magnetic flux is expelled from the specimen (**Figure 2.2**). This is known as Meissonier effect. If there would be any magnetic field in superconductor it would change.



T>T_c **T<**T_c

Figure 2.2: Meissonier effect in a superconducting sphere, which is cooled in a constant applied magnetic field; below critical temperature the lines of induction B are ejected from the sphere [3]. According to Lenz's law a current would be generated, which would oppose the flux, and eject any magnetic field from the superconductor. For the case, when magnetic field is expelled from the specimen.

2.1.2 BCS theory

BCS theory [15] was at its time a fantastic achievement of Bardeen [1,] Cooper and Schrieffer. The main result of the theory is to establish that the effect of the superconducting phase transition is to arrange the electronic system in such a way that an energy gap is introduced in the electronic band structures in both sides of the Fermi level. The general agreement of BCS theory with much of the experimental results leaves no doubt that the image of arrangement of the electrons into cooper pairs and the existence of the energy gaps in the main physical basis ,for adscription of the super conducting phase transition. In the superconducting state the electrons can reach states above the Fermi energy even at T= 0. The BCS theory to describe the super conducting distribution function can be seen as the equation.

$K_BT_C = 1.13W_D\hbar\exp(\frac{-1}{VNEF}$(2. 1)

Where, K_B is the Boltzmann constant $\hbar$ is the planks conistant divided by 2π, W_D is the Debye frequency, V is the strength of the coupling between the electron and the phonon s and $N(E_F)$ is the density of state at the Fermi level. The Debye frequency is the characteristic frequency of the lattice vibration that couples the electrons in the superconducting state. That lattice vibrations mediate, the cooper pairs it is not super conducting that T_C is directly proportional to this characteristic irrational frequency. we can consider the mechanical model of crystal that regards the atoms as masses that are coupled together with little springs. The characteristic frequency of this system is $\omega = \sqrt{\frac{k}{m}}$, where, k is the spring constant, m is the mass of the atom, using this relation, we can see that, T_c should be increase as the mass of the atom decreases. This tells us that, us that, compound containing lighter elements will have higher values of T_C, than those composed of heavier elements. The next parameter is V, the strength of coupling between the electron and the phonons. The high value of T_C can be achieved with large couplings as long as the crystal does not distort or lose stability.

When the electron phonon coupling becomes too strong, however, the structure of the crystal can distort to form a so-called charge density wave at low temperature. And for really, large value of v, a given crystal structure May simply cease to exist in favor of a different one. In other case, the new or distorted structure, tends not to be super conducting because, it generally has fewer

electrons available to participate in the super conducting ground state. For this reason, it was felt that, higher transition temperatures would be found that near structure phase transitions. Here the coupling is as strong as possible while suitable a crystal structure is maintained. The final therm in the BCS equation is $N(E_{F),}$ the density of state at the Fermi surface,simpliy speaking (E_F), is a measure the number of electrons that can take part in the super conducting ground state.

In general, compounds congaing transition metals elements that have a partially filled d shell hav e a larger density of states at the Fermi surface. And thus, a higher transition temperature than no n transition metal compounds, Before 2001 then reigning king of the inter metallic superconduct ors were niobium germicide, vanadium, silicide, niobium nitride and other transition- metal compounds this led to many physicists to believe that a high value for T_c could only be achieved in compounds that included transition metals to boost the density of states.

The BCS equation and, to some extent, these prejudices, have helped to define the search for new super conductor over the past decades. while physicists and chemists have a rough idea of how to control the Debye frequency and the density of states, the electron coupling has remained as somewhat elusive parameters .much of the search for new inter metallic super conductors has therefore, has focused on compounds that contain light elements or compounds will transition metals. However, the term for the electron phonon coupling remains important and by noting that lead has of the highest superconducting transition temperature of all the elements (7.2k).Even sough it is very heavy, and not a transition metals are forced to acknowledge that electron phonon coupling plays an important role [1-6,13,15,,16]. Super conducting materials are classified as type I and type II super conductors. That differ in their behavior has the magnetic field is increased.

2.1.3 TypeI super conductors

As shown in **Figure** 2.3a type I superconductors are in the Meissonier state over the whole sub-critical ranges of temperature<T_c, external Magnetic field B<B_c, and I<I_c,their critical parameters are quite law, however, which is the main problem for applications. The highest values are observed for lead; $T_c = 7.2$k, Critical magnetic field T_c = 0.055 Tesla at T = 0 K, and

surface(sheet)critical current density$J_c = \frac{B_c}{\mu}$ =4.4x10 ^{4}A/m in zero external magnetic field at T= 0(μ is the permeability of free space. Or Type I superconductors simply refuses to compromise with the applications in any way, shape or form. They always super conduct at magnetic field below some critical temperature H_c. Above this critical field, super conductivity destroyed. The magnitude of the critical magnetic field varies according to the relation (T) =$B_c(0)[1 -(\frac{T}{T_c})]$ where $B_c(T)$= the critical magnetic field at any temperatureBc(0) = the critical magnetic field at zero Kelvin ,T and T_c are temperature and critical temperature respectively.Some oftype I super conductors are; Al, Ga, Hg, In, Nb, Pb, Sn, Ta, Ti, V, W, and Zn.

2.1.4 Type II superconductors

Type II superconductors are characterized by two critical fields, Hc1 and Hc2, which are both temperature dependent. For fields 0 < H < Hc1 the substance is in the Meissonier phase with complete exclusion of the field from the interior. In the range Hc1 < H < Hc2 the substance enters the mixed phase, part of the magnetic flux penetrates the bulk of the sample[32]. Above Hc2, finally, the material is normal-conducting. They are made from alloys or complex oxide ceramics.

High temperatures superconductors are type II super conductors. Theyare harder and more complicated superconductors than type I super conductors. Unlike type I superconductors, type II superconductors have two supercritical fields,H_{c1} and H_{c2}. Due to scattering from the magnetic atoms, the transition temperature of the type one super conductors is lower than those of type twosuper conductors. For practical application in magnets, it would be rather unfortunate if only type two superconductors existed which permit no magnetic field and no current in the bulk mate rials. Alloys and the element niobium are so called type II superconductors. Their magnetization curves exhibit a more complicated dependence on magnetic field. Some of type II superconducto rs are Nb3Al, Nb3Sn, Nb3Ge, NbN, NbTi and Nb3(AlGe). In **Figure 2.3** magnetic field vs temperature graphs are described by type I and type II super conductors.

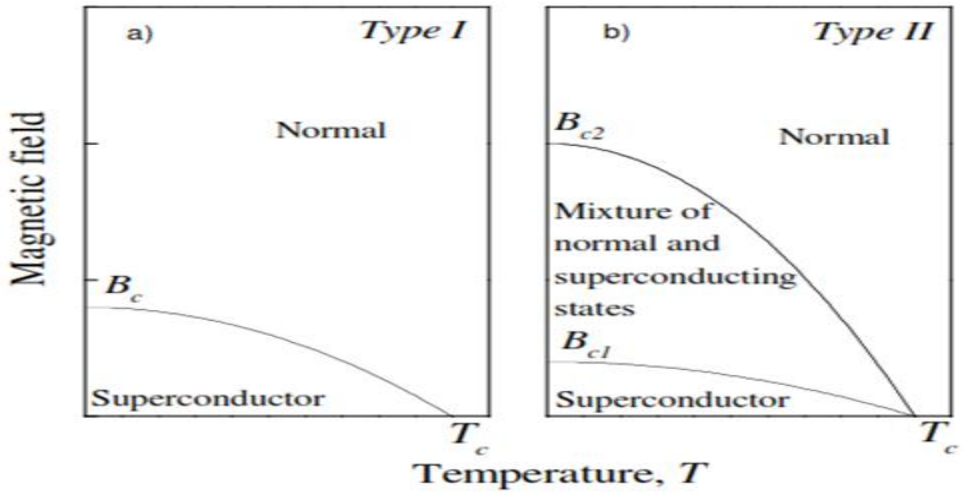


Figure 2.3 Type I and Type II super conductors

2.2 High temperature superconductivity

The high temperature superconductors represent a new class of materials which beaneath the extr aordinary superconducting and magnetic properties and great potential for wide ranging technolo gical applications. This class of materials not only showhightemperaturesuperconductivity but also shows properties that are different than classical superconductors. They offer a great challenge to understanding the basic phenomenon that causes superconductivity in these material s and to developing the appropriate preparation.

There has also been great progress in understanding the properties of materials developing differ ent methods of preparation and realizing superconducting devices which use these superconducto rs [20]. The first of the high temperature superconductors to be identified was Ba doped La2CuO4in 1986, which exhibited a transition temperature of T_c=30 K. This result was remarkable because the parent compound was anti ferromagnetic, insulating and because this transition temperature was much higher than what could be predicted by BCS theory [12]. High T_c superconductors are prepared in form of bulk, thick films, thin films, single crystals, tapes and wires[21]. Even a small change in oxygen content or action doping level can transform the material from a superconductor to a low carrier density of metaloreven to insulator. For thin films different techniques such as sputtering, evaporation, molecular beam epitaxial, laser

ablation, chemical vapor deposition and so forth have been used for thin film high temperature superconductors. Most of these techniques work in vacuum environment and the oxygen partial pressure near the substrate is controlled to obtain superconducting thin film. This can be done during film deposition or post deposition annealing. The substrate temperature during deposition is a crucial parameter that determines micro structural details such as texture and degree of epitaxial. It is desirable to develop low temperature process to maintain good quality films and prevent substrate film interaction. Some of high temperathre super conductors are shown in the

Table 2.2critical temperature of high T_c superconductor [1].

No	Material	Critical temperature(K)
1	$Ba_xLa(5x)Cu_5O_9$	30-35
2	$(La_o.9Ba_o.1)_2Cu_4$	52
3	$_{YB}a_{2C}u_{3O}(7-x)$	95
4	$Bi_2sr_2Ca_2CU_3O_1O$	110
5	$Tl_2Ba_2Ca_2CuO_1O$	125
6	$HgBa_2CuO(8+x)$	133
7	$HgBa_2Ca_2Cu_3O_1O$	147

Table 2.2 shows some of type II super conductors mostly, they are compounds.

2.3 Review of superconductivity of MgB_2

The discovery of superconductivity in magnesium diboride (MgB_2) with T_c=39K [1] is the highest value known for the non-cuprate phases, has renewed the interest to the simple non oxide compounds and stimulated the worldwide research activity on its fundamental physical properties and various aspects of material fabrications. The simple chemical composition and crystal structure, the relatively high T_c value and the “weak-link free grain boundaries make MgB_2 an attractive candidate for both of basic study and application [2]. Extensive theoretical

and experimental studies performed during last one-and-half year showed that despite of the chemical and structural simplicity, the band structure of MgB_2 is not simple, characterized by the four bands that could give two superconducting gaps with different characters [3, 6].

The layered crystal structure consisting of alternating layers of Mg and B atoms causes an appreciable an isotropy of superconducting parameters [7,8] that changes significantly with temperature [9,10]. Although MgB_2 can be synthesized by a straight forward method (from a low cost and non toxic reagents) the synthesis of high-quality (phase pure) samples is still quite challenging. It requires a heat treatment of reactant mixture in a closed reaction vessels or utilization of external pressure of inert gases to prevent evaporation and oxygenation of magnesium.

Different synthetic techniques and variation of processing parameters produce the polycrystalline samples with slightly different T_c, residual resistivity, flux pinning properties etc., which was attributed to the effect of impurities, structural defects (i.e. Mg vacancies) and lattice strains [11-18]. In addition to these problems, the low chemical stability of MgB_2 causes degradation at ambient atmosphere. All these facts are considered to be the reasons for the discrepancies of experimental data reported for polycrystalline samples.

The growth of high-quality single crystals of sub-millimeter size has opened a route for the various physical studies involving the X-ray structural analysis. The measurements of magnetism , electric transport [8,], thermal conductivity [9], Hall effect penetration depth , de Haas van Alphen effect [6] Raman scattering , angle-resolved photoemission and optical spectra which are important for understanding of the fundamental properties of MgB_2 superconductor.

Two different methods were developed for the crystal growth of MgB_2. One is heat treatment in sealed metal (Mo, Nb, stainless steel) containers and the other is the sintering at high-pressures and temperatures in BN [7, 10,] or Ta reaction cells. Although most single crystal data are in reasonable agreement, the apparent differences of crystal size, morphology, structural and superconducting properties are reported for different methods by several research groups .Superconductors as a function of the magnetic field, It is instructive to compare measured data on pure lead (type I) and lead-indium alloys (type II) of various composition.

Superconducting parameters of carbon subtitled MgB_2.

Table 2.3 super conducting parameters of MgB_2.

No	Parameters	Values
1	$CriticalTemperature$	$Tc = 39\text{k}$
2	**Hexagon lattice parameters**	**a = 0.3086nm. c = 0.3524nm**
3	**Theoretical density**	$\rho = 2.55\frac{g}{cm^3}$
4	**Pressure coefficient**	$\frac{dT_c}{dP}$**= -1.1 - 2**$\frac{K}{GPa}$
5	**Carrier density**	$\mathbf{n_s = 1.7 - 2.8x10^{23}}\frac{holes}{cm^3}$
6	**Isotope effect**	$Mg = \alpha_B + \alpha_c$**0.3+0.02**
7	**Resistivity near Tc**	$\rho(40K) = 0.4 - 16\mu\Omega c$
8	**Resistivity**	**RR=** $\frac{\rho(40k)}{\rho(300)}$**=127**
9	**Upper critical field**	$\mathbf{H_{c2}}$ **//ab(0) =14 -39T,** $\mathbf{H_{c2}}$**//c(0)=2-24T**
10	**Lower critical field**	$\mathbf{H_{c1}}$**(0)=27-48mT**
11	**Irreversibility field**	$\mathbf{H_{irr}}$**(0) =35T**
12	**Coherence lengths**	$ab(0) = \xi_c$**3.7-12nm,** $\mathbf{4}\xi c(0) = 1.6 - 3.6nm$
13	**Penetration depth**	$\lambda(0) = 85 - 180n\,m$
14	**Energy gap**	$\Delta(0) = 1.8 - 7.$
15	**Debye temperature**	$\theta_{D=750-880K}$
16	**Critical I density**	J_c**(4.2k,0T) > 10**^{7}**A/**cm^3

2.3.1 Two gap super conductivity in magnesium Diboride (MgB_2)

A crucial feature of the superconducting state is the existence of an energy gaps at the Fermi level region of the excitation spectrum of superconductors.

According to the BCS model the value of the super conducting gap is given by

$\Delta = 1.76K_BT_C$ (2.2)

In this material, the E_2g phonon couples to both the σ and π bands resulting in two distinct super conducting gaps. In a two gap superconductor a strong change of Tc with impurity concentration should be expected [15]. A very good answer to this question has been given by

Mazzinetal [16]. Due to the particular electronic structure of MgB_2 the electronic wave functions on π bands and σ bands possess different parity symmetry. The π bands deriving from the Boron p_z orbitals are mainly ant symmetric with respect to the Boron plane, while the σ bands deriving from both Boron p_x and py orbitals are mainly symmetric.

The π bands deriving from the Boron p_z orbitals are mainly ant symmetric with respect to the Boron plane, while the σ bands deriving from both Boron p_x and py orbitals are mainly symmetric. This disparity of σ and π bands makes the impurity scattering matrix element between these two types of bands exceptionally small as compared with the impurity scattering matrix element within each of these bands. Using density functional super cell calculations for various impurities Mazzini etal were able to show that the inter band scattering rate appears to be one to two orders of magnitude smaller than the inter band scattering rates due to this band disparity. This means that impurity scattering will equalize the gaps within each of the two types of bands, but not very much between them.

This makes the two gaps in MgB_2 exceptionally stable against impurity scattering. Only a very large amount of impurity scattering is expected to lead to a reduction of Tc due to inter band scattering and an accompanied merging of the two gaps. While signatures of the two gaps have been observed in several different experiments, so far direct experimental confirmation of the important role of the E_2g phonon for the pairing is still lacking. In principle, such a strong coupling phonon could produce observable structures in the tunneling density of states. However, there are difficulties in the case of MgB_2 has been discussed [17]. on one hand the high frequency of the phonon mode leads to a strong reduction of the structures produced in the tunneling spectrum, on the other hand tunneling spectroscopy is mostly dominated by theπband phonons, which are not so important for the pairing interaction. This makes observation of the E2gphonon and its coupling strengthens tunneling spectroscopy difficult. Concluding this section we can say that we seem to have a consistent and quantitative picture of [26].

The two gaps arised due to a strongly an isotropic electron phonon interaction of the E2g phono n mode, which couples more strongly to the electrons on the σ bands than to the ones on the π bands. Due to the disparity of the two types of bands these two gaps appear to be very stable against impurity scattering, allowing $T_c$to remain large even in samples with large residual resistivity.

2.3.2 Crystal structure of MgB_2

MgB_2 possesses simple hexagonal AlB_2 –type structure (space group$\frac{p_6}{mmm}$), which is common among borides. The MgB_2 structure contains graphite –type (graphite the same carbon layer structure has boron has in MgB_2 boron layers which are separated by hexagonal closed- packed layers of magnesium. The magnesium atoms are located at the center of hexagons formed by barons and donate their electrons to the boron planes. Similar to graphite,MgB_2 exhibits an isotropy in the B-B lengths. The distance between the planes is significantly longer than in-plane B-B distance [22, 24].

The bonding between boron atoms is much stronger than, that between magnesium. And therefore the disordering appears to be much easier than the boron layers). Each Mg atom located at the center of the hexagon formed by B donates its electron to the B planes; hence the B-B bonding is strongly an isotropic. Since this plane has a two dimensional structure the material is expected to exhibit two dimensional superconductivity, as a result of its crystalline structure. The in plane B-B distance is almost half that of the inter plane B-B distance [19, 22, 2].

Table2.4 the crystal structure parameters of MgB_2

No	Parameter	Values
1	Atomic position of Mg	(000)
2	Atomic position of B	(0.3300, 0,6700, 0.5000)
3	Atomic position of B	(0.6700, 0.3300, 0.5000)
4	B-B inter layer distance	0.1780nm
5	Mg-Mg inter layer distance	0.3084nm
6	Mg-Mg interlayer distance	0.3584
7	Mg –B interlayer distance	0.25nm

Figure-2.4 shows, MgB_2 has AlB_2-type structure and lattice parameters, a =3.084°Aand c = 3.522°A. It is a simple hexagonal lattice of close-packed Mg layers alternating with graphite-like B layers. B atoms arranged at the corners of a hexagon with three nearest neighbor B atoms in each plane.

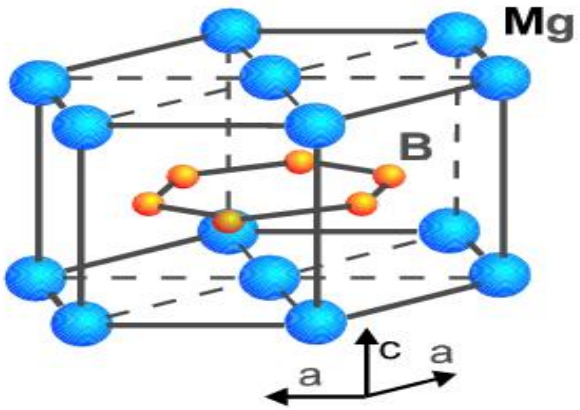


Figure 2.4. The crystal structure of MgB_2 containing graphite-type B layers separated by hexagonal close-packed layers of MgB_2 [19, 23].

2.3.3 Al– substitution of MgB_2

Al substitutes for Mg and donates electrons reducing the number of holes in MgB_2, thus suppressing. The decrease in Tc is very significant in loss of superconductivity [36]. Increasing the Al doping level causes a slight increase in the superconducting gap. This effect was very weak, and enhancement of $Bc_2$was not observed [38]. Further increasing the Al content results in the reduction of super conducting gap. [23]. As a result, superconductivity decreases.

2.3.4 C-substitution of MgB_2

It was experimentally found that C-based doping leads to significant enhancement in the superconducting properties of MgB_2conductor-based doping results in C substitution into B sites in the MgB_2crystal lattice. In addition, C donates electrons and reduces the number of holes in MgB_2. According to the configuration of the superconducting gaps in the MgB_2For preparation of C-substituted crystals a precursor with graphite used as a source ofcarbon has Selected studied single crystals of MgB_2.since C forms strong covalent-bonded layered structures, it may be that

in $Mg(B1\text{-}xCx)_2$ is the chemical formula of carbon doped Magnesium Di boride. This experimental value claims that high concentration of carbon decreases the critical temperature of MgB_2.

2.3.5 Band structure of MgB_2

Band structures are a representation of the allowed electronic energy levels of solid materials and are used to better inform their electrical properties. A band structure is a 2D representation of the energies of the crystal orbitals in a crystalline material. Additionally, the curvature of the bands can reflect the carrier mobility through those bands [24]. Band structure calculations on MgB_2 suggest that the bands at the Fermi level (E_F) mainly originate from the orbital of boron due to substantially ionized Mg, and there are four conduction bands, namely, two σ bands delivered from the σ bonding orbital's and two π bands delivered from the π- bonding and the anti-bonding orbital.

Some experimental results verifying that, in MgB_2 the holes bands couple very strongly to the optical E_g phonon mode[2427]. And hence a change in the px_a, py_b bands directly affects the sup erconducting properties of MgB_2 [7].Thus, to get a more detailed picture of how the changes in D OS and E_F affects the super conducting properties of MgB_2 we have to analyze the changes in the B contributions to N and E_F. In addition,the result shows that the DOS near the Fermi surface is unchanged. The Fermi energy increases and it moves out ward as a result of the increase in the n umber of valence electron [24,25]. It was noted that, the valence bands of MgB_2 and graphite are similar to each other. The inter atomic interactions in MgB_2 were analyzed and compared with th ose in Iso structural diborites AlB2 and TiB2. Among the known metal diborides, titanium dibori de TiB_2 possesses extreme thermal and strength characteristics [7]. It was noted the valence bands of MgB_2 and graphite are similar to each other. The main contribution to the valence band of magnesium diboride is made by a combination of boron. Fig 2.5 shows the electronic band structure of MgB2.

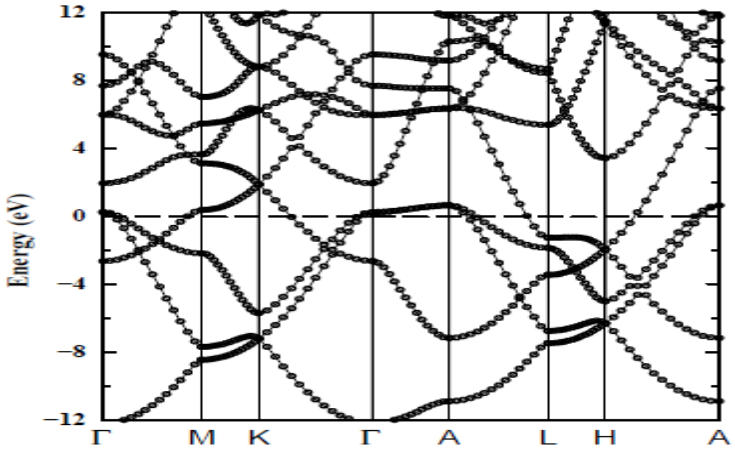


Figure 2.5 Band structure of pure MgB_2

2.3.6 Potential Application of MgB_2 [2,25]

For super conducting magnets, Magnetic resonance imaging [MRI],Nuclear magnetic resonance[NMR],For energy storage magnets, Transformer, Rotors, Transmission cables

2.3.7 Fermi surface of MgB_2

Fermi surface of MgB_2 was reported long before the discovery of superconductivity in this comp ound. The smaller cylindrical σ sheets (shown in red) have superconducting energy gap of about 7.2 meV. With small deviation which is less than 0.1 meV. The wider cylindrical σsheets (shown in orange) have superconducting energy gap which ranges from 6.4 to 6.8 meV. They have a maximum near Γ and a minimum near A.

On the πsheets (superconducting energy gap ranges from 1.2 to 3.7 meV. The temperature dependence of the superconducting energy gaps for The Fermi surface consist of four separated sheets, as shown in **Fig. 2.6** [28]. Two them (colored in red and orange), which look like cylinders, are originated from the σ-bonding px,orbitalsofboronand formed around the four Γ Aliens. Other two(colored in blue and blue green), which look like webbed tunnels, are originated from the π-bonding pzorbital's of boron and formed around K –Mand H -L lines.

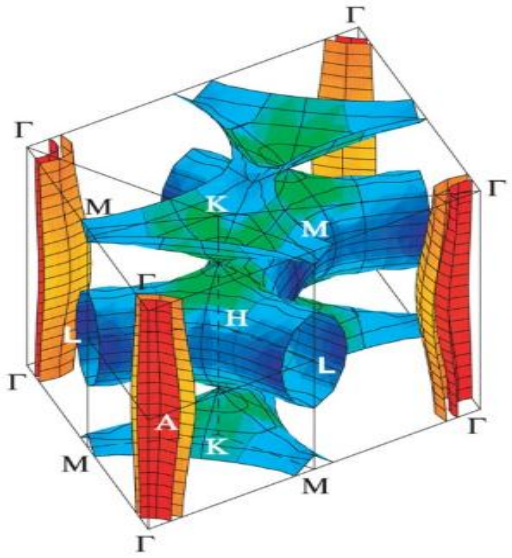


Figure 2.6 Fermi surface of MgB_2 [27]

2.4 Density functional theory (DFT)

Density Functional Theory is a phenomenally successful approach to finding solutions to the fundamental equation for the quantum behavior of atoms and molecules, the Schrodinger equation, in settings of practical value. So the quantity of physical interest is instead the probability that N electrons in any order have specific coordinates. modeling method used in , and to investigate the (principally the) of , in particular atoms, molecules, and the .

Using this theory, the properties of a many-electron system can be determined by using , i.e. functions ofanother which in this case is the spatially dependent . Hence the name density functional theory comes from the use of functional of the electron density. The development of new DFT methods designed to overcome this problem, by alterations to the functional 44] or by the inclusion of additive terms, is a current research topic Overview of method In the context of computational , (from first principles) DFT calculations allow the prediction and calculation of material behavior on the basis of quantum mechanical considerations, without requiring higher order parameters such as fundamental material properties.

In contemporary DFT techniques the electronic structure is evaluated using a potential acting on the system's electrons. This DFT potential is constructed as the sum of external potentials V_{ext}, which is determined solely by the structure and the elemental composition of the system, and an effective potential V_{eff}, which represents inter electronic interactions. Material with *n* electrons can be stud ied as a set of *n*one electron , which are also known as . Electron densities in molecules and soli ds also show relatively small departures from the over laped densities of the constituent atoms. T he starting point is the stationary Schrödingerequation for a N- electron system in a given external potential [42 -43].

$$[\frac{-\hbar^2}{2m}\sum_i^N \nabla_i^2+\sum_i^N v_{ext}\, r_i+\frac{1}{2}\sum \frac{e^2}{|\, r_i-r_j\,|}][\psi(r_i-r_j]=E\psi(r_i \ldots . r_N) \quad (2.3)$$

The first term in equation gives the electronic kinetic energy, the second gives, the effect of the external potential, and the last gives, the electron-electron interaction.

2.4.1 Hohenberg– Kohn theorems

Although density functional theory has its roots in the for the electronic structure of materials, DFT was first put on a firm theoretical footing by and in the framework of the two Hohenberg–theorems (H–K)]. The original H–K theorems held only for non-degenerate ground states in the absence of a , although they have since been generalized to encompass these,. In ground-state DFT one is interested in systems of N interacting electrons described by the Hamiltonian,

$$\hat{H}=\hat{T}+\hat{V}+V_{ee} \quad (2.4)$$

where, T is the kinetic energy, V is the external potential and $V_{ee}$is electron- electron interactions.

The first H–K theorem demonstrates that the ground state properties of a many-electron system are uniquely determined by an that depends on only three spatial coordinates. It set down the groundwork for reducing the many-body problem of *N* electrons with 3*N* spatial coordinates to

three spatial coordinates, through the use of of the electron density $n_o(r)$. (TDDFT), which can be used to describe excitedstates[35].

The second H K theorem defines an energy functional for the system and proves that the correct ground state electron density minimizes this energy functional E[n(r)].Energy functional given as;

E[n(r)]= $\left\langle \psi \vee \left| T + U + V \right| \right| \vee \psi \right\rangle = \left\langle \psi \left| \vee T + U \right| \right| \vee \psi \right\rangle + \left\langle \psi \left| \vee V \vee \right| \psi \right\rangle$ =F[n(r)]+ $\int n(r)V(r)$ dr (2.5)

Where [n(r)] is a universal functional of a charge density n(r) and not of (r).For this functional, a vibrational principle holes as the ground state energy is minimized by the ground state charge density. As a result, DFT Exactly reduces the N body problems. In work that later won them the , The H–K theorem was further developed by and to produce (KS DFT). Within this framework, the intractable of interacting electrons in a static external potential is reduced to a tractable problem of non-interacting electrons moving in an effective [43] The effective potential includes the external potential and the effects of the between the electrons, e.g., the and interactions.

Modeling the latter two interactions becomes the difficulty within KS DFT. The simplest approximation is the (LDA), which is based upon exact exchange energy for a uniform , which can be obtained from the , and from fits to the correlation energy for a uniform electron gas. Non-interacting systems are relatively easy to solve as the wave function can be represented as a of . Further, the functional of such a system is known exactly. The exchange–correlation part of the total energy functional remains unknown and must be approximated [44].

Another approach, less popular than KS DFT but arguably more closely related to the spirit of the original H–K theorems, is (OFDFT), in which approximate functional are also used for the kinetic energy of the none interacting system.

2.4.2 The self-consistent Kohn-Sham Equations

In 1965, Khon and Sham showed that it is possible to reduce the many- body quantum problem to an exactly equivalent set of one-electron equations, solved self consistently. The Khon-sham

total energy functional of an electron gas subject to an external potential (including kinetic, Hartree, exchange-correlation energy) for asset of doubly occupied orbitals ψ_i(a single slater determinant) is writtenas[48].

$$\mathbf{E[\psi]=2[\frac{\hbar^2}{2m}]\sum_i \int \psi_i \nabla^2 \psi dr + E_H[n] + \int \nu_{ext} n(r) dr} \quad \mathbf{(2.6)}$$

Where the kinetic energy, has been replaced by its exact analytical expression on the set of orbitalsψ. The ground state electron density is given by

$$\mathbf{n(r)=2\sum |\psi(r)|^2} \quad \mathbf{(2.7)}$$

Like that of DFT, that is only the minimum values of theKhon-sham energy functional has physical meaning, and in order to determine the ground state total energy of the electronic system, one then needs to determine the set of orbitals $\psi(r)$ that minimizes it.This is done by self-consistent solvingtheKhonshamequations[50].

$$\mathbf{[\frac{-\hbar^2}{2m}\nabla^2 + V_{ion}(r) + V_H(r) + V_{xc}(r)]\psi_i(r) = \varepsilon_i \psi_i} \quad \mathbf{(2.8)}$$

Where, ε_i is the Kohn-Sham eigenvalue associated with electronic state is the Hartree potential given by;

$$\boldsymbol{V_H(r) = e^2 \int \frac{n(r')}{|r-r'|} d^3} \quad \mathbf{(2.9)}$$

$\mathbf{V}_{\text{ion}}$ is the ionic potential describing the attractive interaction between electrons and nuclei. And V_{xc} the exchange correlation potential is given by the functional derivatives. Under an effective potential, due to the other electrons and their interaction with the nuclei The Khon-Sham equations are in fact a reformulation of theorem berg Khon problem where one map the many electron system onto a system of non-interacting particles**[42, 43, 45, 53, 54].**

2.4.3 Exchange-correlation approximations

Which is no doubt one reason why LD approximations and The LD. After spending several years developing functional forms based on everexpanding amounts of experimental data noted that some simpler functional allow us to separate different types of correlation in molecules and

concluded the simplest parameter-free GGA functional are the best functional to use with DFT, because they offer thesimplest interpretation and have greater globalpredictivepower. In fact, the bondingpatternsare correct in most cases.

2.4.4 Local density approximation(LDA)

Local density approximation is the simplest class of approximation in exchange correlation functional. It is derived from homogenous electron gas model.

Generally, for a spin un polarized system, the local density approximation for the x_c energy is expressed as,

E_{xc}^{LDEA}**=** $\int n(r)\, E_{xc}$**[n(r),r]dr** **(2.10)**

Where E_{xc} is the exchange correlation energy density of the homogenous electron gas. The local density approximation, originally proposed by Kohn and Sham because of its formal simplicity, is clearly wrong due to the simple fact that the electron density around an atom cannot be assumed to homogenous. Nevertheless, it is amazing how much success the method has had in describing condensed phase systems. Also for spin polarized system local density approximation s gives more satisfactory result of fDFT calculation. In such a case E_{xc} is given by Taking spin into account.

2.4.5 Generalized Gradient Approximation (GGA)

The gradient –correlated approximation is one in which the functional depends on local density and its gradient. The knowledge of the density makes use of point r in LDA. That is the density varies in space. For the rapidly varying electron densities of many materials, areasonableapproximation has to be considered. And the gradient of the density (n(r)).In GGA, the densities of the surrounding infinitesimal volumes are considered. Which means the gradient of the density plays a role. Numerically it is defined **as,**

E_{XC}^{GGA}**=** $\int f^{GGA}$**[n(r),**∇n**(r)dr.** **(2.10)**

2.5 Quantum- ESPRESSO

Quantum – ESPRESSO stands for Quantum open- source package for research Materials and Method needs to be included. QUANTUM ESPRESSO is an integrated suite of computer codes for electronic-structure calculations and materials modeling, based on density-functional theory, plane waves, and pseudo potentials (norm-conserving, ultra soft, and projector-augmented wave). The acronym ESPRESSO stands for open Source Package for Research in Electronic Structure, Simulation, and Optimization [51,52]. It is freely available to researchers around the world under the terms of the GNU General Public License. QUANTUM ESPRESSO builds upon newly-restructured electronic-structure codes that have been developed and tested by some of the original authors of novel electronic-structure algorithms and applied in the last twenty years by some of the leading materials modeling groups worldwide.

Innovation and efficiency are still its main focus, with special attention paid to massively parallel architectures, and a great effort being devoted to user friendliness. QUANTUM ESPRESSO is evolving towards a distribution of independent and interoperable codes in the spirit of an open-source project, where researchers active in the field of electronic-structure calculations are encouraged to participate in the project by contributing their own codes or by implementing their own ideas into existing codes. PWscf, implements an iterative approach to reach self-consistency, using at each step iterative diagonalization techniques, in the framework of the plane-wave pseudo potential method. An early version of PWsc fis described in [51].
Both separable NC PPs and US PPs are implemented; recently, also the projector-augmented wave method [53]has been added, largely following the lines of [52] for its implementation. In the case of US PPs, the electronic wave functions can be made smoother at the price of having to augment their square modulus with additional contributions to recover the actual physical charge densities. For this reason, the charge density has much finer spatial variations around the nuclei The augmentation terms can be added either in reciprocal space (using an exact but expensive algorithm) or directly in real space (using an approximate but faster algorithm that exploits the local character of the augmentation charges).

PWscf, can use the well-established LDA and GGA exchange–correlation functional, including spin-polarization within the scheme proposed in [58] and can treat no collinear magnetism [59, 60]. Other advanced functional, include TPSS meta-GGA [62], functional with finite-size corrections [66], and the PBE0 and B3LYP [64, 65] hybrids. Self-consistency is achieved via the modified Broyden method of [65], with some further refinements that are detailed in appendix A.1. The sampling of the Brillouin zone (BZ) can be performed using either special [66, 64] **k**-points provided in input or those automatically calculated starting from a uniform grid. Crystal symmetries are automatically detected and exploited to reduce computational costs, by restricting the sampling of the BZ to the irreducible wedge alone. Some of the most important points on the input file of PWSCF are ;

CONTROL is the control block describing how the calculations starts, what will be done in the calculation, and where output will go.

i . calculation =csf specifies as elf consistent field calculations (DFT).

We know that in DFT, the electron is determined by the charge density, which is determined by their wave functions. This needs to be self-consistent.

ii. res tart-mode=from scratch declare s that, we will be generating a new structure, and not reading in charge densities or wave functions from a file.

iii. prefix prefix =MgB2, MgB2C and MgBC are the file name prefix to be used for temporary files.

iv. stress= .true. turns on the calculations of the stress tensor.

v. tprnfor=.tru.turns on the calculation of forces.

vi. pseudo-dir=specifies the location of the directory, where we store the pseudo potentials.

vii. out-dir=defines the location of the temporary files.

SYSTEM = is the system block that describes the geometry of the calculate

Chapter 3

Methodology

In this study we apply the known mathematical tool Density functional theory (DFT) as implemented in QUANTUM ESPRESSO to calculate the electronic band structure, Crystal structure and density of state for superconducting MgB2, MgBC, and MgB_2C. We used one of the quantum -espresso package, PWSCF code. We applied different pseudo potentials from QUANTUM ESPRESSO home page. We prepared input files based on parameters, for MgB_2, MgBC and MgB_2C. There are a number of pseudo potentials, presented in the quantum espresso website. Then, we tried different calculations of the electronic structures of MgB_2, MgB2C and MgBC using the various pseudo potential inputs for each of the elements. Among them, we used the following, that provide us a good results. The pseudo potentials of those parameters are; Mg.Pz-n-Vbc.UPF, B.Pz-Vbc.UPF and C.Pzy.-n-Vbc.UPF. for Mg, B and C respectively.

The PWSCF code uses different input parameters for the electronic structure simulation. In this thesis we used the input parameters which are unique for MgB2,MgBC and MgB2C. We did nonmagnetic calculations. The other soft ware required to implement this work was, xmgrace, XcrysDen and fortran. That means, we usedxcrysdon software; to obtain crystal structure, xmgrace software; to obtain band structure and density of state and fort run is install quantum espresso package. Not only the above input parameters but also we have made a lot of changes in the quantum –ESPRESSO code. For example, in density of state calculation we use tetrahedral calculation. In the input file we make use of explained lattice parameters for example, for MgB_2, a=0.3084 nm, b=c=0.3524 nm.

Figure 3.1 shows the ireduce able brillioun zone for the hexagonal closed packed structure.

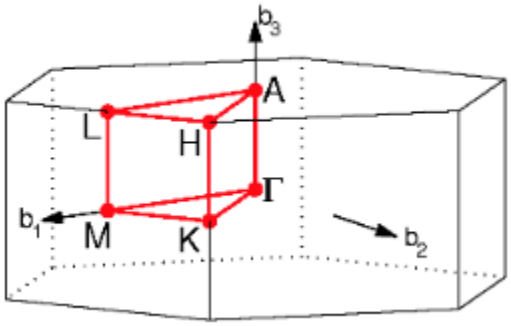


Figure 3.8:Brillouin zone of HEX lattice. Path:Γ-M-K-Γ-A-L-H-A|L-M|K-H [67]

Based on this structure we used to calculate the electronic structure of the superconducting compounds by determining thir k-points.

Chapter 4

Result and discussion

By employing the the QUANTUM ESPRESSO and using the super conducting parameter of MgB_2, the calculated band structures, crystal structures and density of states of the super conducting compounds, MgB_2, MgB_2C, and MgBC are presented in Figures (4.1-4.9). Thus, we can consider one by one figuratively.

As shown in the **Figure 4.1** the crystal structure of MgB_2 which is obtained by x crysden. It is hexagonal closed packed in structure.

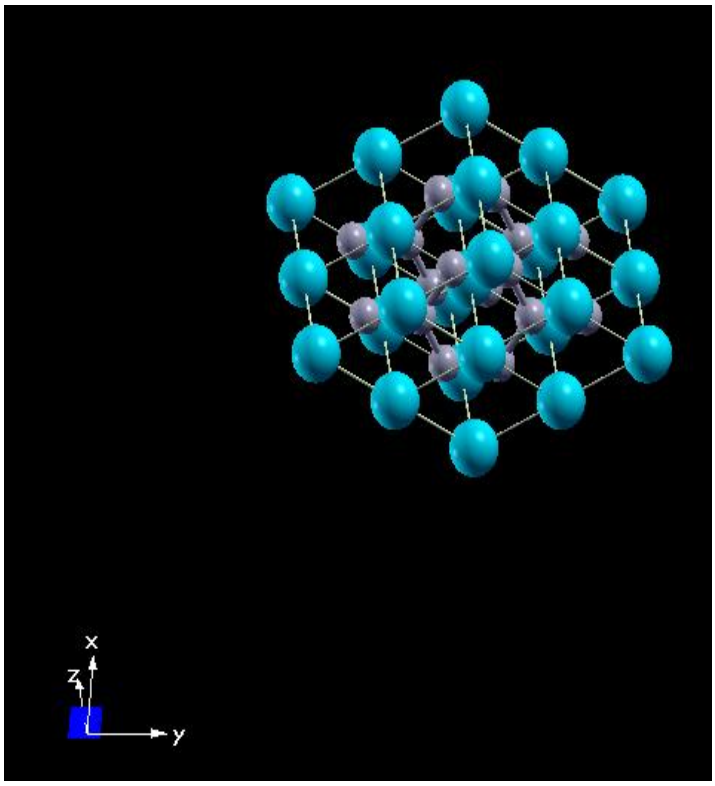


Figure 4.1 The calculated crystal structure of super conducting pure Magnesium di boride (MgB_2)

The crystal structure (Fig4.1) is in agreement with the known structure of MgB2. Our initial file provide us the right structure.

Figure 4.2 shows the calculated electronic band structure of super conducting Magnesium diboride(MgB_2) it is obtained by xmgrace software along the high symmetry of $\Gamma - M - K - A - L - H - A$ direction of the Brillouin zone. There fore we have the following findings concerning the hole and electron bands respectively. Hole bands originated from the sigma p_x and p_y orbitals of the boron atom and lie a little above the Fermi level of the brilounzone. Furthermore the hole bands have the greatest dispersion along Γ- K in the (k_x and K_Y) direction. These hole bands nearly flat band was, seen above the Fermi surface in the direction of $\Gamma - A$. For πbands consists of both the electron and hole bands the maximum dispersion along k_z ($\Gamma - A$ directions.

Here the electron bands crosses the Fermi level along L-H and the hole band along M-K direction.

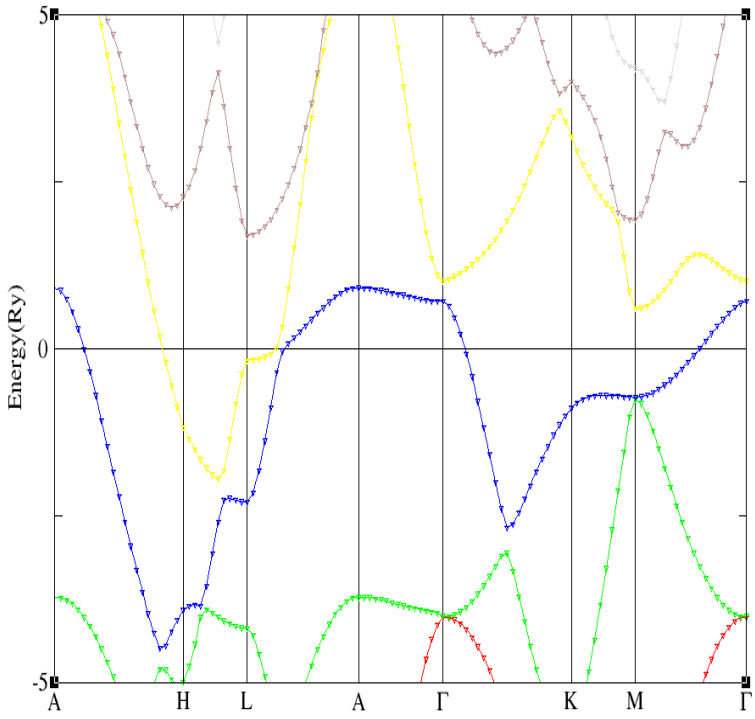


Figure 4.2. Band structure of superconducting pure Magnesium di boride along high symmetry lines.

Figure 4.3 is the density of state of of super conducting the graph ploted N(∈) versus band width. It is peacked down ward around the Fermi level. The zero point is the Fermi level. comparing with the other three, this density of state is the smallest one. Because, the top value is around 1.5 state/cell/eV. Using our theoretical value of DOS equation (2.1) we calculated the super conducting critical temperature of MgB_2 as follows,

$T_C = \theta_D \exp(\frac{-1}{VNE_F})$ (4.1)

Where, θ_D is the debye temperature taken from Table 2.3 with its corresponding value 750k $N(E_F)$=0.7540(our calculated density of state), λ =0.3, I,e λ<0.5 , then from $\lambda = VN(E_F)$ V=0.40491513, using equation 4.1 above, T_c ofMgB_2 becomes, T_c=37.34 k.

This result is compared to the experimental value.

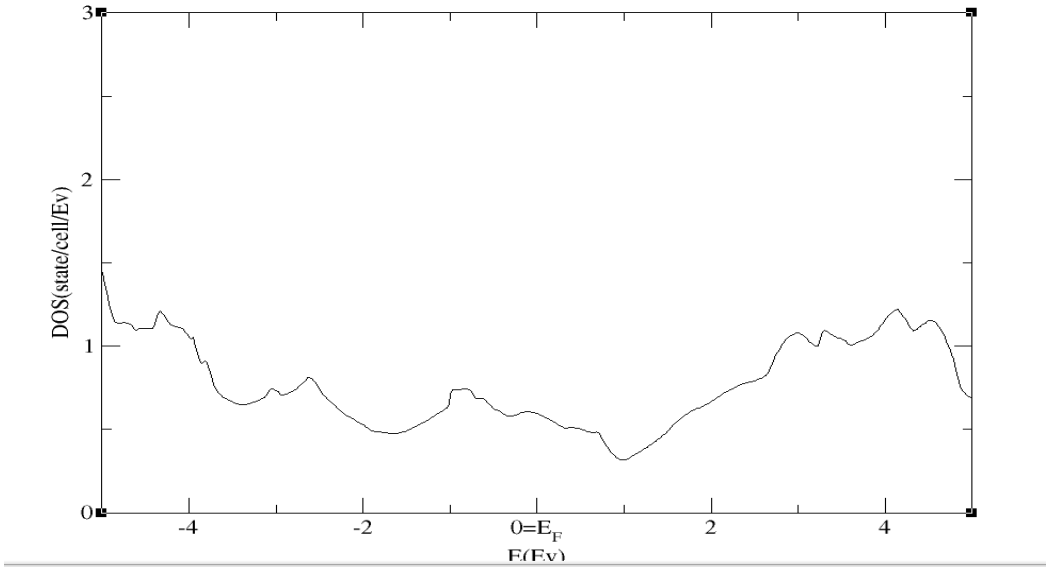


Figure 4.3 Density of state of super conducting pure magnesium diboride.

The crystal structure of MgB_2C is as shown in the **Figure 4.4**. It is obtained by, X crysdenandis a hexagonal closed packed structure similarto that of MgB2. Its defference from the other two is the number of boron atom in the unit cell as expected.

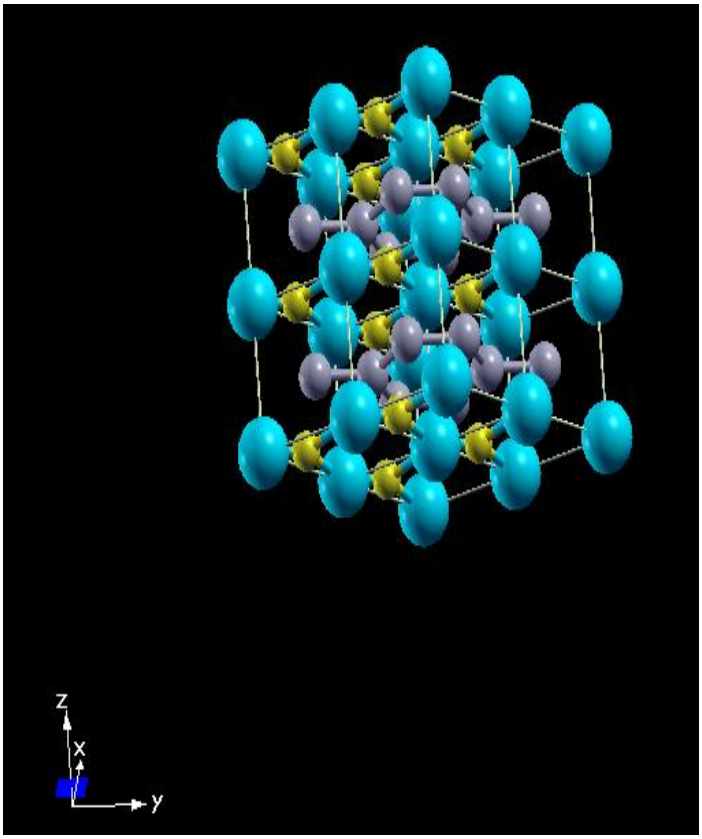


Figure 4.4 Crystal structure of (MgB_2C).

In this system, we added one carbon atom to study the effect on the electronic structure.

The band structure of MgB_2C is as shown in **the Figure 4.5** which was obtained by xmgracex along the high symmetry of $\Gamma - M - K - A - L - H - A$ direction of the Brillouin zone. the researcher observed that unlike for MgB_2 From Γ to M, thre are one electron and one hole in between 0eV to 2.5eV. Also, there is a flat band above a Fermi level in between 5evto 10 ev from fromΓ to Z. There is acurvature above and below the Fermi surface. From M - A.

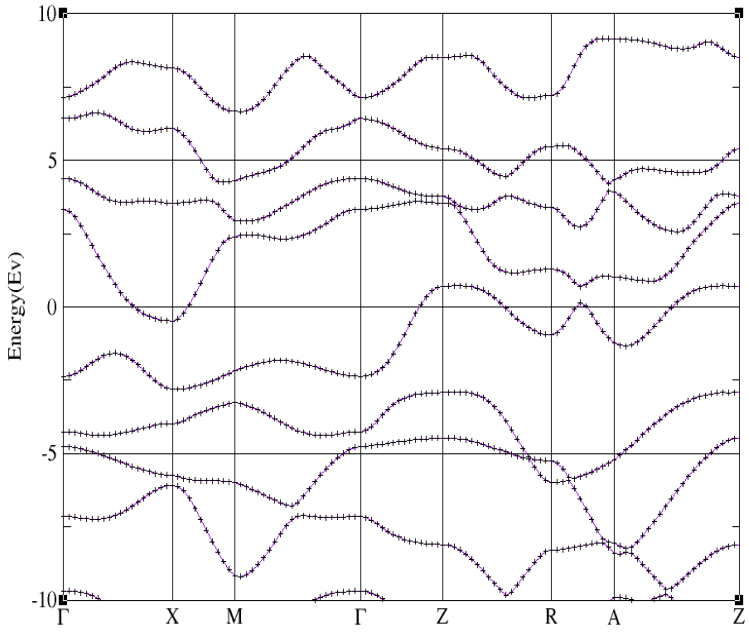


Figure 4.5 Band structure of (MgB_2C)

In this system due to the flatness of the bands, there are only a few numbers of bands cross the Fermi level.

The density of state(DOS) of super conducting MgB_2C is as shown in the **Figure 4.6** By observing this figure a researcher summarized that the density of stat at aFermi level for MgB_2C is approximately 0.6897state/cell/ev. Where as; the highestst peak up ward on the graph is aroun d 2state/ell/eV uunitwhere aste lowest peak down ward is around zero.

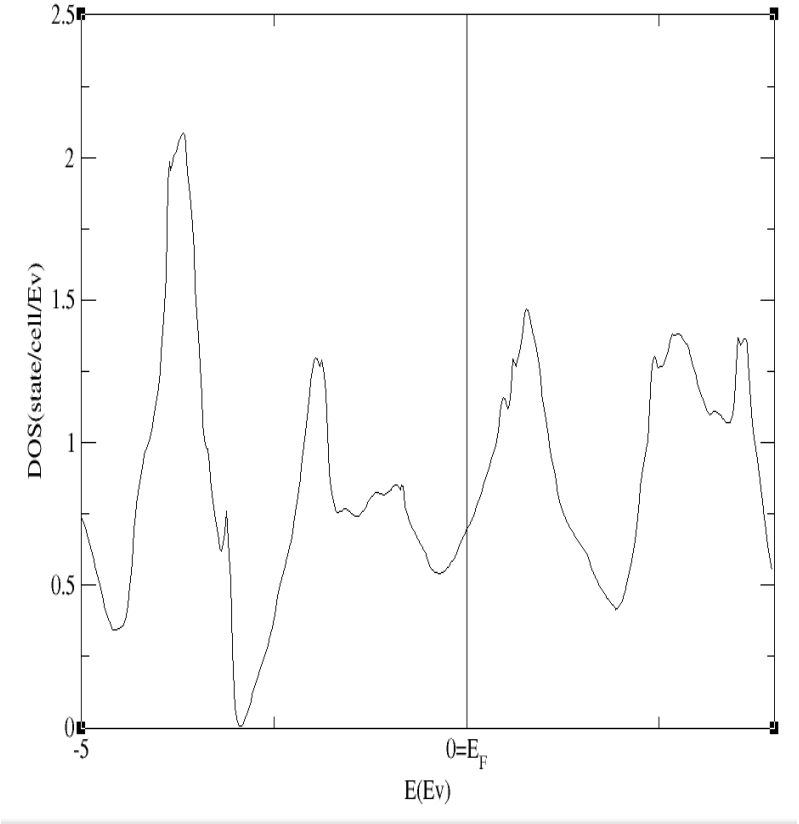


Figure 4.6 Density of state of super conducting carbon containing Magnesium diboride (MgB_2C) With variable approximations. We calculated the T_c value and it is Tc=27.07 k.

The crystal structure of carbon substitution of Boron in MgB_2 that is of MgBC as shown in the **Figure 4.7** which is hexagonal closed packed structure similar to that of **Figure** 4.1 and 4.4It is obtained by, X crysden There is no difference among the three structures, except the number of boron on unit cell.

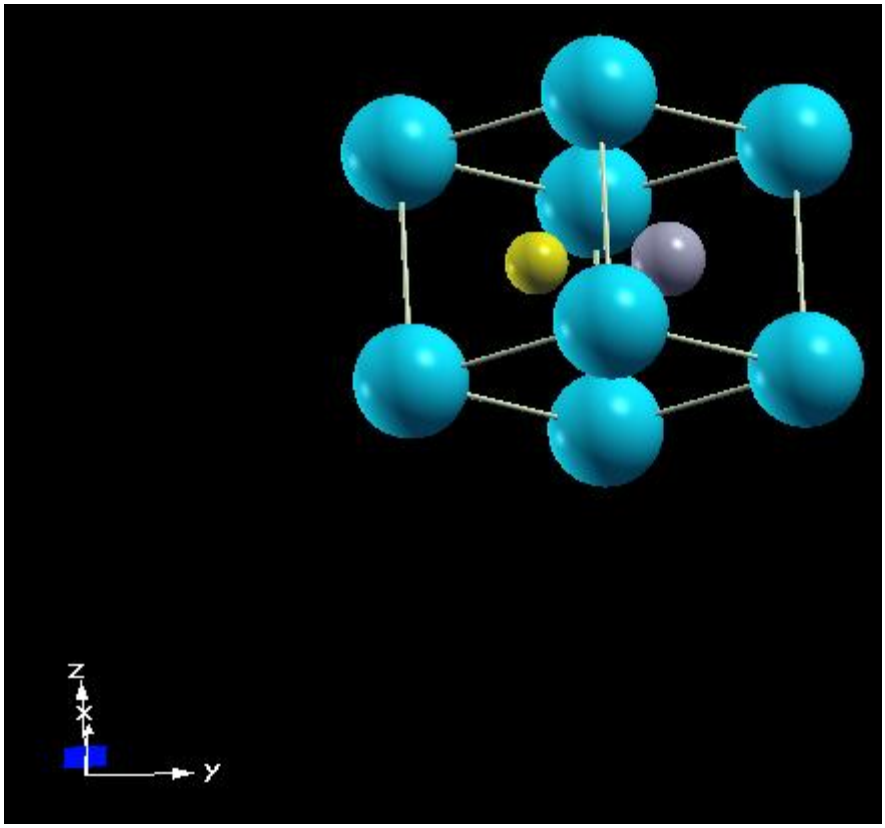


Figure 4.7 Crystal structure of super conducting carbon substituted Magnesium di boride MgBC

The electronic band structure of MgBC (carbon substitution in place of one Boron) is as shown on the **Figure 4.8** which is obtained from the xmgracealong the high symmetry of $\Gamma - M - K - A - L - H - A$ direction of the Brillouin zone.There is a band break from X-M, due to the absence of one Boron and replaced by one carbon do pant. This character is around the Fermi energy of -10 eV. There is the appearance of band gap and flat band properties from $\Gamma - Z$ in between the Fermi energies of 5eV and 10eV. There is also a band dispersion (overlap) above a Fermi level in between 0eV and 5eV, from $\Gamma - Z$.and also aband curvature in similar band widths, in between the Fermi energy of -10eV and 0eV. When we compare it with the structure on the other two there are quite bands crossing the Fermi level. Also with compared to the other, there is amulti band nature in case of this structure.

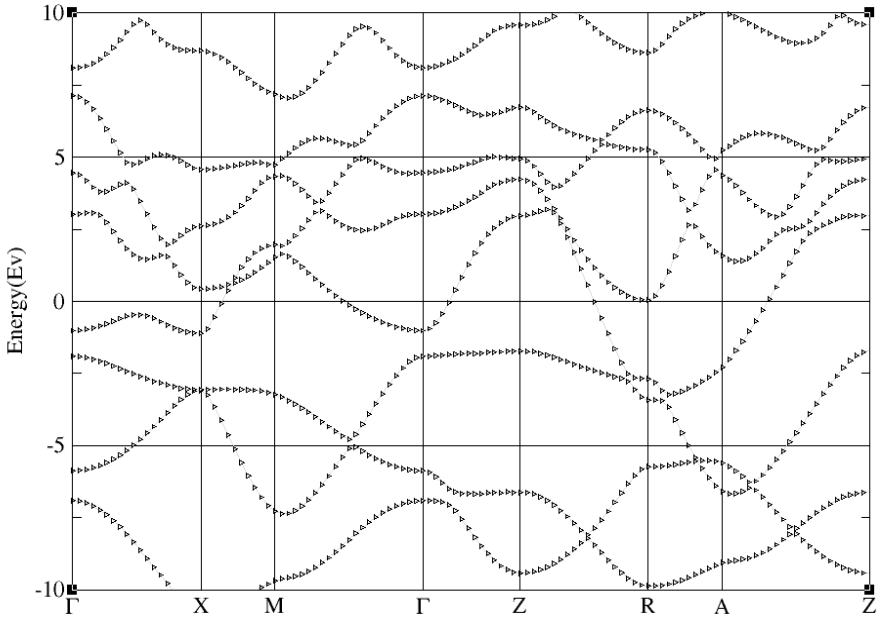


Figure 4.8 Band structure of carbon substituted Magnesium dboride (MgBC)

In this system because of the dispersion of the band and the fluctuation of critical temperature, there are more of bands crossing the Fermi level.

The density of state of carbon substitution of Boron in MgB2 or MgBC is as shown in the **Figure 4.9.** It was obtained by xmgrace. In this figure, the highest peak is found nearer to the Fermi surface and it shows the highest electron dope.Whereas the lowest peak is found around the Fermi surface, and it is found at the left of the Fermi surface. The density of state at the Fermi surface is calculated to be 0.9424 state/cell/eV. This DOS is the highest of the three compounds.

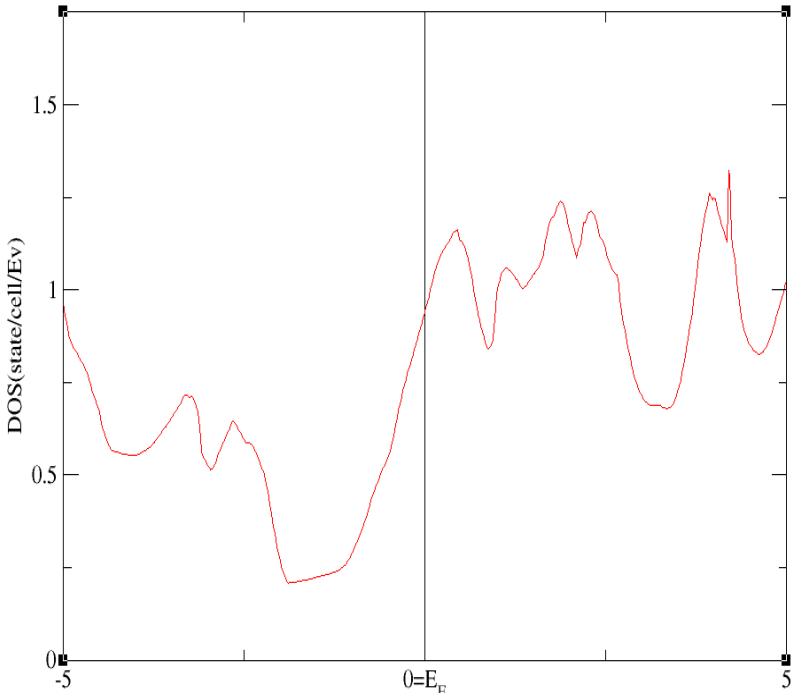


Figure 4.9 Density of state of super conducting carbon substituted magnesiumdiboride (MgBC)With similar approximation for Bcs Type supper conductor, we found that Tc=41.09k.

Chapter 5

Conclusion

In this work we calculated and arrived at a certain value of electronic band structure, crystal structure and density of state of super conducting magnesium diboride, carbon containing magnesium diboride (MgB_2C) and carbon substituted magnesium diboride (substitution of one boron by carbon) By using mathematical model called density functional theory. In fact, DFT is implemented by the computer programming called quantum –ESPRESSO, package called PWSCF. From the calculation, we observed that, using different pseudo- potentials, since the input causes, a great difference on the electronic band structure, we found that, the pseudo – potentials are: Mg.Pz-n-Vbc.UPF, B.Pz-n-Vbc.UPF and C.Pz-n-Vbc.UPF for Mg, B and C respectively. Those are the most convenient input, that resulted as the same structure as the experimental value [32].

Furthermore, from the structures, we learned that their Fermi surfaces are, made up two hole bands. For MgB_2 those bands are originated from, Boron or carbon sigma p_x and $p_y$bands. It was, seen that those hole bands are nearly flat above the Fermi surface. In the direction of ($\Gamma - A$). And its maximum dispersion is observed along $\Gamma - K$. The other type of bands is made up of both hole an electron bands which are supposed to be which are originated from boron bonding and unti bonding p_z orbital is π –band. It is seen that the electron bands are found along L-H line and the hole type is found along M-K direction. We observed that electron bands are far from the Fermi level . In case of Figure 4.5 and it is more of flat below the Femilevel. This shows us that the Fermi energy shows variation in both directions.

And also we conclude that there is also the variation of critical temperature Tc. The important point that we conclude is that, after carbon is added to MgB2 there was the change in Tc, DOS and band structure of the compounds.

In such a way that, In case of their increasing their density of state, MgB2C< MgB2<MgBC.

A cording to our result of study, among the three compounds, MgB2C is characterized by law density of state and law critical temperature. Also among the three studied compounds, we observed that, MgBC is characterized by highest density of state and its critical temperature is the highest of all the three. MgB_2C has the smallest critical temperature and has the smallest

density of state than the other two. From this we conclude that, after carbon is added to the super conducting MgB_2, the band structure, the density of state and the critical temperature are all changed. And the most important finding of the researcher was that, carbon has a great contribution than boron in case of increasing critical temperature and density of state and MgBC can be another compound having high critical temperature. Also the researcher concluded that, as the density of state increases, the critical temperature becomes increase.

Bibliography

[1] Tinkham M.(1996)introduction to supper conductivity.2nd eddition.McGaw Hill,inc.United state of America.

[2] P.C and Sergey et al physics world**,**vol**.31** January, 2002.

[3] Bardeen, L. N. et al. Schrieffer, Phys. **Rev. 108,** 1175(1957)

[4] P. M. Grant, physrev, **381**, 559 (1996).

[5] J.Hatton, Physics rev.1**03** 1167(1956)

[6] V.M et al ;physicsRev.Lett**102 ,**pp 117-106(2009).

[7] Valenzula et al;Am .J physics.**67 ,**11(1999).

[8] PouliMichailGirant,physics world v **24** Nov.4(2011).

[9] H.C and M.C.N et al , physics V **80,**No 2(2012).

[10] PModak et al ;Pramana-J.Phys.Vol**.58,**No 5 and (6,(2009)

[1] V.Dikovskyetal ,Eur.phys.J.D **51** ,247-259,(2009).

[12] D.Dew-Hughes,Lowtemp. Physics**.27** ,99-102(2001).

[13] S.Souma et al,Nature,Vol,**423,1,**(2003).

[14] B.K.Godwal et al;current.science.vol**85 ,**NO 7,10,(2003) .

[15] Jun Nagamatsu et al,Nature,Vol**,410,**(2001)

[16] Y. W. Maz,l. Phys. Lett. ,vol**. 88,** p. 505(2009)

[17] W.K.Yeohetal supper. SciTeechl V **19,**196- 5949(2006).

[18] Y. Zhao, s" Appl. Phys.Lett.Vol**.83**, p.2916 (2003).

[19] H. L. Xu,"Chin.Phys.Lett.**Vol.21** ,25 -113**,(**2004).

[20] Y. W. Ma" Supercond.Sci.Technol.Vol**.20** p.L5, 2007.

[21] X. P. Zhang ,"et al, Supercond.Sci.Technol.Vol**.20,**pp.117.[21] 2007.

[22] J. H. Kim nanotubes,et al" Appl. Phys. Lettv**89 ,** 122510 (2006)**.**

[23] E. C. Park, J. H. Shim, , et al v**19**pp2702-2705,2009.

[24] Y. Kong, O.V. Dolgov, et al Phys. Rev**.B 64**(2001) 20501.

[25] P. P. Singh, Solid State Commun.**125** (2003) 323.

[26] C. Lee W. Yang ,et al Rev. **B 37**, 785 (1988)

[27] C. Adamo, M. et al Phys., **112**, 2643 (2006)

[28] A. L. Ivanovskii, Russ. Chem. **Rev**. **70** (2001),717

[29] A. D. Becke, Phys. Rev. A **38**, 3098 ,(1988)

[30] Dan hao et al;physica C **497**, 43-48(2014).

[31] Sergy L. et al; arXiv;.150106948 v**1** [cond-mat.suppr-con] 27 Jan 2015

[32]J.G. Bednorz, K.A.Mueller, Possible high Tcsuperconductivity in Ba-la-Cu-O system,Z.Phys, B. Condensed Matter 64:189-193, 1986

[33] NeerajKhare, Ray Radenbaugh, V.I.Shnyrkov, Shoji Tanaka, A.Ya.Tzalenchuk,

[34] Becke, A. D., 2014,"Perspective: Fifty years of density-functionaltheory in chemical physics,

[35] M. Soler, E. Artacho, J. D. Gale, A. Garc. Matterıa, C**168(**2011)

[36] T. Dahmand N. Schopohl, Phys. **Rev. Lett. 91** (2003) 01700

[37] D. M. Ceperley and B. J. Alder,Phys.**Rev.Lett.45**,566(1980).

[38] N. Troullier and J. L. Martins,Phys. Rev. **B43**,1993(1991).

[39] L. Kleinman and D. M. Bylander,Phys. Rev. Lett.48,1425(1982).

[40] S. G. Louie, S. Froyen, and M. L. Cohen,Phys.Rev.**B26**,1738(1982).

[41] H. J. Monkhorst and J. D. Pack,Phys.Rev.**B13**,5188(1976).

[42] A. Gurevich, Phys. Rev. **B 67** (2003) 184515.

[43] J. Tersoff and D. R. Hamann,Phys. Rev**. B31**,805(1985).

[44] T. Ekino, T. Takasaki, R. Ribeiro, T. Muranaka, and J. Akimitsu,**63**,410 (2011)

[45] Yu. Eltsev, Physica C **385**, 162 (2003).

[46] J. M. Rowell, Supercond. Sci. Technol. **16**, R17 (2003).

[47] A. A. Golubov and A. E. Koshelev, Phys. Rev. **B 68** (2003) 10
4503.

[48] Baus, M., 1990,"The present status of the density-functional theory ofthe liquid-solid.

[49] Becke, A. D., 2014Perspective: Fifty years of density-functionaltheory in Jones, R. O., 1984b.

[50] Density functional calculations for ozone striking results for an important molecule,"Phys. Rev. **Lett.52**,.chemical physics,"J. Chem. Phys, (2002−2005).

[51] Dal Corso A 1996 A pseudopotential plane waves program(pwscf) and some case studies *Lecture Notes in Chemistry*vol 67, ed C Pisani (Berlin: Springer.

[53] Bl¨ochl P E 1994 *Phys. Rev.* B **50** 1795352].Kresse G and JoubertD(1999).

[54] Dovesi R, Civalleri B, Orlando R, Roetti C andSaunders**V R, (2005)** *Reviews in Computational Chemistry*vol 21, ed K B Lipkowitz, R Larter and T R Cundari.

(New York: Wiley) chapter 1.

[55] Spartan,Wavefunction, Inc. http://www.wavefun.com/products/spartan.html

[56] Laasonen K, et al D *Phys. Rev.* B **47** 10142, (1993).

[57] Giannozzi P, de Angelis, et al *Chem. Phys.***120** 5903,(2009).

[58] White J A , et al *Phys. Rev.* B **50** 4954, (2004).

[59] Oda T, Pasquarello A and Car R *Phys. Rev. Lett.***80** 3622, (1998).

[60] Gebauer R and BaroniS*Phys. Rev.* B **61** R645, (2000).

[61] Anisimov V I, Zaanen J and Andersen O K *Phys. Rev.* B**44** 943, (1991).

[62] Tao J, Perdew J P, Staroverov V N and Scuseria G E Phys. Rev. Lett. **91** 146401,(2003).

[63] Cococcioni M and de GironcoliS*Phys. Rev.* B**71** 035105, (2005).

[64] Becke A D *J. Chem. Phys.* **98** 1372, (1993).

[65] Stephens P J, Devlin F J, Chabalowski C F and Frisch M J *J. Phys. Chem.* **98** 1162, (1994)

[66] Kwee H, Zhang S and KrakauerH*Phys. Rev. Lett.***100** 126404, (2008)

[67] A. N. Kolmogorov, S. Curtarolo, Phys. Rev. **B 73** 180501(R), (2006).