FIRST PRINCIPLE STUDY ON THE ELECTRONIC STRUCTURE OF SUPERCONDUCTING LITHIUM IRON ARSENIDE (LiFeAs)

BY

TEKIL SHIFERAW

A THESIS SUBMITTE TO APPLIED PHYSICS PROGRAM

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Advisor: Mesfin Asfaw (PhD)

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Acronyms

BCS= John Barden, Leon Cooper, and Robert Schrieffer.

DFT= Density Functional theory.

DC= Direct current.

HTS= 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.

LDA= Local Density Approximation.

ARPES= Angle Resolved Photo Electric Spectroscopy.

Symbols

KB= Boltzmann constant.

I_C=Critical current.

J_c= Critical current Density.

B_c= Critical magnetic field.

= Coherence length.

Tc= critical Temperature.

W_D= Debye frequency.

$_D$= Debye Temperature.

= Energy gap.

H_{c1}= Lower critical field.

H_{c2}= Upper critical field.

= penetration depth.

LiFeAs = Lithium Iron Arsenide.

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Adama science and Technology University

Tekil shiferaw

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Abstract

Lithium Iron Arsenide (LiFeAs) had been placed to be a high-Tc superconductor following the discovery of superconductivity in this compound in 1908 at a critical temperature of 18k by Hosono group. The compound has a tetragonal structure as seen by XcrySden. We reproduced the electronic band structure of superconducting Lithium Iron Arsenide (LiFeAs) by employing a known quantum modeling approach that is density functional theory (DFT) as implemented by a computer code called quantum-ESPRESSO. We found that the band structure showed a multi band nature and an electronic DOS that decreases strongly with increasing energy in the vicinity of the Fermi energy. In addition to this the theoretical calculated values of the superconducting is compared to their experimental values. From equation 4.3 we understood that theoretically calculated value of critical temperature is 17.37k. This shows the theoretical result was approximately in agreement with the experimental value. We also found that the dispersion in different high point sets back the importance of

understanding on the effect of hole bands to increase the transition temperature.

Keywords; Density functional theory, Quantum ESPRESSO code, superconductivity, pseudo

Potential, Tc

Chapter 1

Introduction

1.1 Back ground of the Study

The beginning of the twentieth century was a revolution in theoretical physics. This new physics, and in particular quantum mechanics, met with success after success, it explained the ultraviolet catastrophe, the photoelectric effect, the Compton Effect, the structure of the atom and even made the prediction of antimatter [1-2]. This advance on all fronts has been challenged by the two phenomena of super fluidity of helium and superconductivity of metals. The emerging of superconductivity had date back 100 years. It was in 1908 where the Dutch physicist Heike Kamerlingh onnes initiated the field of low-temperature physics by liquefying helium in his laboratory at Leiden. Three years later he investigated that below 4.15k of the DC resistance of mercury dropped to zero [3]. With that investigation the concept of superconductivity was born.

Theoretical explanation on the set of superconductivity was forwarded in 1957 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)[1]. The

theory explains that the materials became superconductors when the electrons in side them joins forces to make cooper.

Experimentalists were intended to search more knowledge on the superconductivity after the declaration of the existence of new physics (superconductivity). Accordingly, in 1933, Meissner and Ochsen feld approved that: when a specimen is placed in a magnetic field and is then cooled below transition temperature for superconductivity, the magnetic flux originally present is ejected from the specimen [1-3]. This time a superconductor which is weak in magnetic field will act as a perfect diamagnetic, then, in the 1950s and 1960s, a remarkably complete and satisfactory theoretical picture of the classic superconductors was emerged [1-3].

As all previous (low- temperature) superconductors require expensive liquid helium to cool them to aroun4k (4). Also substantial skill and training is required to transfer liquid helium from one container to another without freezing the apparatus and the superconductors were rarely used in applications. More over the cost of the superconductor will always be substantially higher than that of a conventional conductor; it must bring over whelming cost effectiveness to the system [5]. This situation was over turned and the

subject was revitalized in 1986, when the new class of hightemperature superconductors was discovered by Bednorz and Miller, which was paving the way of a gradual proliferation of superconductivity and it was time at which people believed that superconductivity is a “mature” physics. Following this, for first time the very important category of compound known as iron based superconductor was observed in 2008 by Hideo Hosono(from the Tokyo institute of Technology in Japan) in LaOFFeAs(1111 family)[6,7].

These Iron based superconductors (FeSCs) divided in to six different structures of FeAs layer families and out of these the „111“ family consist Lithium Iron Arsenide which is under investigation of our work. This compound has been studied experimentally and theoretically whose Tc value reaches 18k [8]. As Lithium Iron Arsenide (LiFeAs) is apparently a key compound for the mechanism of superconducting in FeSCs, and it is a very remarkable member in the family of „111“. We are interested to study the superconductivity of Lithium Iron Arsenide (LiFeAs) from electronic structure point of view.

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.

1.2 Statement of the problem

In the recent work many researchers had been investigating the electronic structure of Lithium Iron Arsenide (LiFeAs) by using weak method of the local density approximation (LDA) and the mechanism of superconducting in this compound that they used were not yet understood well, In this work we have been interested to study the electronic structure of Lithium Iron Arsenide (LiFeAs) by applying density functional theory (DFT) mainly we looked at the structure and density of state (DOS).

1.3 Objectives of the study

❖General Objective

- The general objective of this thesis is to study superconducting properties and the electronic band structure of superconducting Lithium Iron Arsenide (LiFeAs). ❖**Specific Objective**

The specific objectives of this thesis are:-

- To calculate the electronic band structure of superconducting Lithium Iron Arsenide (LiFeAs) by implementing the density functional theory(DFT)
- To obtain the superconducting critical temperature.
- State the relation between lattices parameter, Fermi energy and temperature.
- Calculate electronic density of states for LiFeAs.

Chapter 2

Review of Literature

2.1 Existence of superconductivity

Superconductivity was widely regarded as one of the great scientific discoveries of the 20th century. This miraculous property causes certain materials, at low temperatures, to lose all resistance to the flow of electricity. This state of "loss less ness" enables a range of innovative technology applications. The era of low-temperature physics began in 1908 when the Dutch physicist Kamerlingh ones first liquefied helium, which boils at 4.2k at standard pressure. Three years later, in 1911, in the Leiden laboratory of Kamerlingh onnes and one of his assistants discovered the phenomenon of superconductivity while studying the resistivity of metals at low temperature. At that time it was noticed that the resistivity of Hg metal vanished suddenly at about 4.2k [9].

The macroscopic quantum phenomenon at which the electrical resistivity of many metals and alloys drops suddenly to zero at particular temperature called critical temperature (Tc) is known to be superconductivity [10]. At a critical temperature (Tc), the specimen under goes a phase

transition from a state of normal electrical resistivity to a superconducting state. According to onnes, mercury has passed in to a new state, which on account of its extra ordinary electrical properties which is called the superconductive state [11].

The typically experimental dependence of resistance on temperature in a superconductor is shown in figure 2.1 in which the resistivity of the superconductor suddenly falls to zero when the temperature reduces to a certain value below the critical temperature. The zero resistance Property of a superconductor is not the minimal resistance in the usual sense but is equal to zero. This is because carriers are not scattered by the crystal lattice, thus there is no energy dissipation in a superconductor carrying a DC current, which suggests that superconductivity is a kind of macroscopic quantum effect (11).

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	17.9
9	Y-Ba-Cu-Oxide	92
10	Ti-Ba-Cu-Oxide	125

Table 2.1 critical temperatures of different materials [11]

Table 2.1 shows list of some superconducting materials with their corresponding critical

Temperature

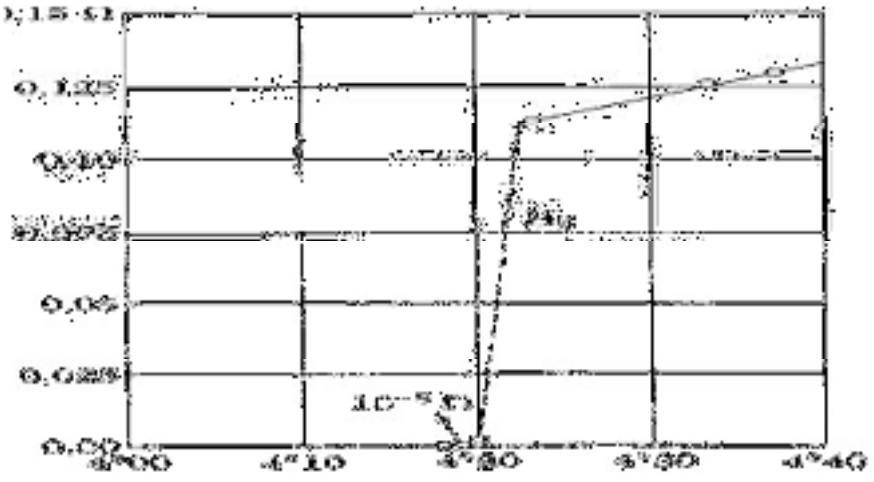

Figure 2.1: Onnes graph plotting electrical resistance of a mercury sample versus Temperature in Kelvin‟s [12,13].

2.1.1 Meissner Effect

One of the most unusual properties of superconducting materials is what happens when they are placed near a magnetic field. At high temperatures and field strengths, the magnetic field lines pass straight through the material as expected. But as Walther Meissner and Robert Ochsen feld discovered in 1933, when a superconducting material is cooled below the transition temperature, Tc, at which current can flow without resistance the field lines are expelled from the material(as shown in the figure 2.2) and have to pass around the sample what is known as the Meissner effect[1-6,8-9,14,15].

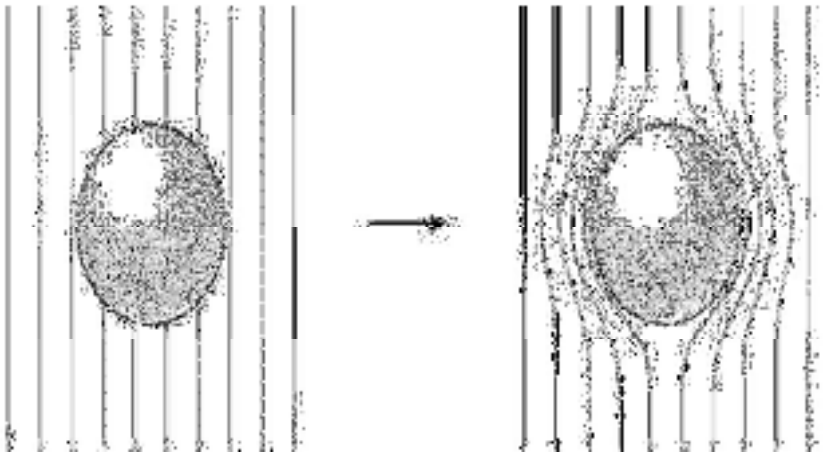

Figure 2.2; Meissner effect in conducting at sphere cooled in a constant applied Magnetic field; on passing below the transition temperature the lines of induction **B** are ejected from the sphere[15].

In 1935, the London brothers(London and London,1935) were able to mathematically describe the Meissner effect by assuming that the current density J in the superconducting state is directly proportional to the vector potential A of the local magnetic field B, where

$$B=\nabla \times A \quad (2.1)$$

(In the London gauge,$\nabla . A=0$). The London equation is given by

$$J = \frac{-1}{4\pi L}$$

(2.2)

Where L has the dimensions of length, under static conditions, one of Maxwell‟s equations (Amperes law) reduces to

$$\nabla \times B = 4\pi J \qquad (2.3)$$

.By taking the curl of both sides, this equation reduces to

$$\nabla^2 B = 4\pi \nabla \times J \qquad (2.4)$$

By combining this equation with the curl of the London equation, we obtain

$$\nabla^2 B = \frac{B}{\lambda^2} \qquad (2.5)$$

The solution of this equation is a flux density B, which decays exponentially with distance from the external superconductor surface. In a one dimensional semi-infinite superconducting medium occupying the positive side of the x-axis the solution to this equation for the magnetic flux density in side this medium would be

$$B(x) = -\frac{-x}{\lambda}$$

(2.6)

Where $B_o = \mu \times H$ is the parallel field at the plane boundary. In this example L measures the distance at which B(x) has fallen

to 1/e of its initial value, which is known as the magnetic or London penetration depth [16].

2.1.2 The BCS theory of superconductivity

Our basic understanding of the mechanism of superconductivity came over 40 years later thanks to a theory devised by John Bardeen, Leon Cooper and Robert Schrieffer in 1957. They described superconductivity to an attractive interaction between two electrons through electron-phonon interaction in BCS theory of superconductivity. One electron interacts with a positive ion in the lattice and deforms the lattice: a second electron of compatible momentum value interacts with the ion in distorted lattice so as minimize the energy. The interacting electrons are said to form a pair.

The electrons of a pair have equal and opposite momentum: one in spin up state and the other in spin down state, so that the total spin of a pair is zero. The electron pairs are called cooper pairs. The important feature of cooper pair is that excitation can take place in only pairs of electrons: i.e., if the state with $+K$ and spin up (↑) is occupied, the corresponding state with K and spin down (↓) is also occupied and if the state with $+K$ is vacant, the state with K is also vacant.

The BCS theory, as it became known, explains how electrons form pairs, known as cooper pairs. That acts as the building blocks of the superconducting state. This pairing takes place through an intermediary, namely a lattice vibration known as a phonon. The BCS theory has essentially three parameters as can be seen in the equation for the superconducting transition temperature

$$K_B T_c = 1.13 W_D \hbar \exp\left(\frac{-1}{VN(E_f)}\right)$$

(2.7)

Where KB is the Boltzmann constant, ħ is the Planck divided by 2π. W_D is the Debye frequency, V is the strength of the coupling between the electrons and the phonons and N (Ef) is the density of states at the Fermi level.

The Debye frequency is the characteristic frequency of the lattice vibrations that couple the electrons in the superconducting state. Given that lattice vibrations mediate the cooper pairs it is not surprising that Tc is directly proportional to this characteristic vibration frequency. Now let us invoke a grossly simplified, mechanical model of a 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 and m is the mass of the atom. Using this simplification we can see that the value of Tc should increase as the mass decreases. This gives rise to a prejudice that compounds containing lighter elements will have higher values of Tc than those composed of heavier elements.

The next parameter is V, the strength of coupling between the electrons and the phonons. A high value of T_C can be achieved with large couplings as long as the crystal does not distort or loose 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 temperatures. And for really large values of V, a given crystal structure may simply cease to exist in favor of a different one. In either case the new or distorted structure tends not to be superconducting because it generally has fewer electrons available to participate in the superconducting ground state. For this reason, it was felt that high transition temperatures would be found near structural phase transitions. Here the coupling is as strong as possible while a suitable crystal structure is maintained.

The final term in the BCS equation is N (Ef), the density of states at the Fermi-surface. Simply spackling, N (Ef) is a measure of the number of electrons that can take part in the superconducting ground state. In general compounds containing transition metallic elements that have a partially filled d-shell have a larger density of states at the Fermi-surface and thus a higher transition temperature than non-transition metal compounds. Before 2001 then reigning kings of the intermetallic superconductors were niobium germicide, vanadium suicide, niobium nitride and 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 superconductors 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-phonon coupling has remained a somewhat elusive parameter. Much of the search for new inter metallic superconductors has therefore focused on compounds that contain light elements and/or compounds with transition metals. However, the term for the electron-phonon coupling remains important, and by noting that lead has one of the highest superconducting transition temperatures of all the elements(7.2k)even though

it is very heavy and not a transition metal we are forced to acknowledge that electron phonon coupling plays an important role[1-6,17,18-20].

Superconducting materials are classified as type I and II superconductors that differ in their behavior as the magnetic field is increased.

2.1.3 Type I superconductors

As shown in figure 2.3 Type I superconductors are in the Meissner state over the whole sub-critical ranges of temperature T<Tc, external magnetic field Bo<Bc and current I<IC. Their critical parameters are quite low, however, which is the main problem for applications. The highest values are observed for lead: Tc=7.2k, critical magnetic field BC = 0.055Tesla at T=0k and surface (sheet) critical current density Jc=$\frac{Bc}{\mu}$ =4.4×10^{5} A/m in zero external magnetic fields at T=0(μ is the free space permeability). Or type I superconductors simply refuse to compromise with the applied field in any way, shape and form.

They only super conduct in magnetic fields below a certain critical value Hc. Above this critical field Superconductivity is destroyed and the sample returns to its normal state. Figure 2.3 illustrates this fact. They are mainly metals or metalloids

that display superconductivity. Identifying characteristics for this type are zero electrical resistivity below a critical temperature, zero internal magnetic fields (Meissner effect) and a critical magnetic field above which superconductivity ceases. The magnitude of the critical *magnetic f*ield varies with temperature according to the approximate expression:

$$B_C \qquad (T) = Bc\,(0)\,[1-(\frac{T}{T_c})] \qquad (2.8)$$

Where Bc (T) =the critical magnetic field at any temperature, Bc (0) = The critical magnetic field at zero Kelvin, T and Tc are the temperature and critical temperature respectively.

N0	Superconductor	Tc(K)	Bc(0)Tesla
1	Al	1.196	0.0105
2	Ga	1.083	0.0058
3	Hg	4.153	0.0411
4	In	3.408	0.0281
5	Pb	7.193	0.0803
6	Sn	3.722	0.0305
7	Ta	4.47	0.0829
8	Ti	0.39	0.010
9	V	5.30	0.1023
10	W	0.015	0.0000154
11	Zn	0.85	0.005

Table.2. 2 enumerates some of type I superconductors together with their Corresponding critical temperature and magnetic field [21]

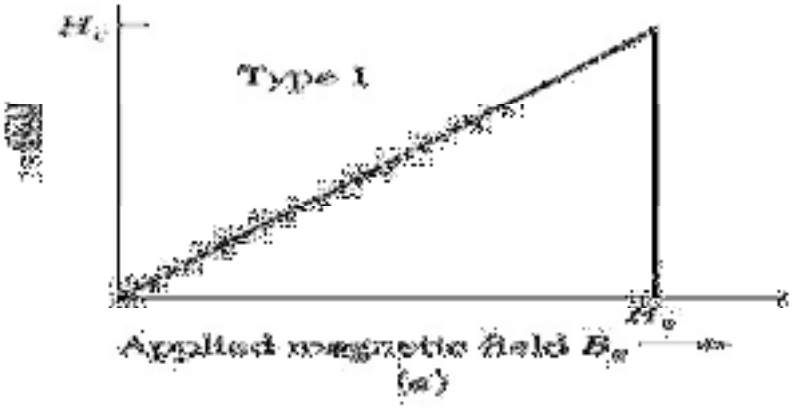

Figure 2.3: Type superconductors expel the magnetic field totally, but if the field is too big the superconductivity is destroyed [21]

2.1.4 Type II superconductors

They are made from alloys or complex oxide ceramics. High temperature superconductors are type I superconductors. Besides being mechanically harder than type superconductors, they exhibit higher critical magnetic fields. The situation is quite different for type- superconductors,

which can still conduct without resistance in relatively large applied magnetic fields. In this case there are two important field scales: a lower critical field, Hc1, below which the material behaves just like a type I super conductor, and an upper critical field, Hc_2, above which the sample is a normal conductor. For fields between Hc1 and Hc2, magnetic field lines, known as vortices" penetrate the sample to produce a mixed state that can still conduct. At the core of these vortices", the material reverts to its normal conducting state at Hc1 the vortices" are few and far between, while at Hc2 they overlap to such an extent that the whole sample becomes normal. They usually exist in a mixed state of normal and superconducting regions. This is called the vortex state, because filaments or cores of normal material are surrounded by vortices of superconducting currents.

In order to distinguish between type I and II superconductors, one has to know the two important characteristics length scales, the coherence length ξ and the magnetic penetration depth λ which measures the depth of penetration of the magnetic field: it is known as the London penetration depth. The coherence length is a measure of the characteristic scale for variations in the magnitude of the

macroscopic quantum wave function. Like the penetration depth, it is a microscopic quantity at low temperatures and diverges as the critical temperature is approached from below.

The ratio of these two length scales, the Ginsburg-Landau parameter k=, is approximately temperature in dependent, and distinguishes type-I superconductors (k< $\frac{1}{\sqrt{2}}$) from type- II superconductors (k> $\frac{1}{\sqrt{2}}$) [1-6, 22, 23, 24].

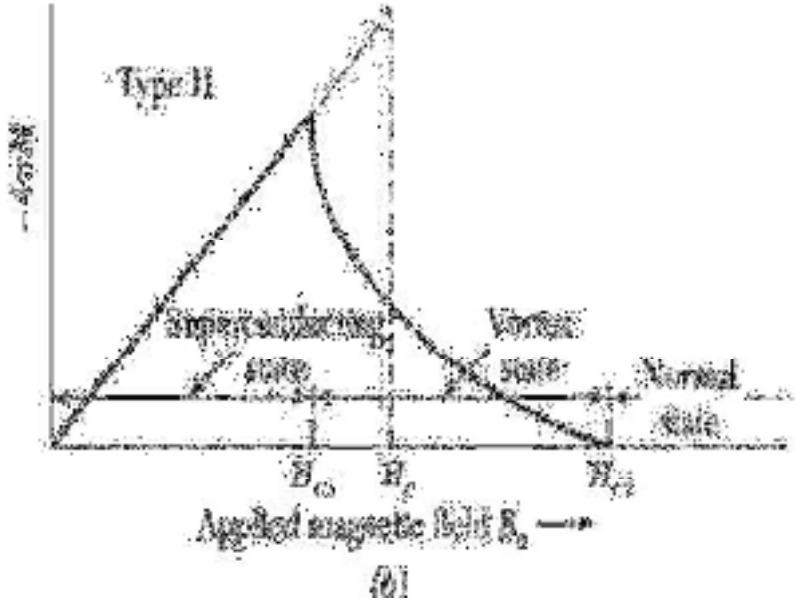

Figure 2.4: type II super conductors [25].

Above figure shows us below the critical temperature the field is totally expelled from the material. But as the strength of the field is increased the field passes partially and lastly

beyond its second critical value it penetrates all in all and the material changes to normal state

NO	Superconductor	Critical temperature(k)	Upper critical magnetic field(0)T
1	Nb_3Al	18.7	32.4
2	Nb_3Sn	18.0	24.5
3	Nb_3Ge	23	38
4	NbN	15.7	15.3
5	NbTi	9.3	15
6	Nb_3	21	44
7	V_3Si	16.9	23.5
8	V_3Ga	14.8	20.8
9	AlGe	21	44

Table 2.3: critical Temperatures and upper critical magnetic fields (at of some T=0k) Type II superconductors

have two values of critical magnetic field, for B< Bc1 the magnetic field is completely expelled (Type-I behavior), where as for Bc1< B< Bc2 the magnetic field partially penetrate through the material [26, 27].

2.1.5 High temperature superconductivity

April 1986, the term high-temperature superconductor was first used to designate the new family of Cup rate-perovskite ceramic materials discovered by Johannes George Bednorz and Karl Alexander miller [28] for which they won the Nobel Prize in physics in the year (1986). Their discovery of the first high temperature superconductor, LaBaCuO, with a transition temperature of 30k generated great excitement.

High-temperaturesuperconductors(abbreviated high-***T*c** or HTS) are materials that have a superconducting transition temperature (*T*c) above 30 K. From 1960 to 1980, 30K was thought to be the highest theoretically possible *T*c.

The first high-*T*c superconductor [29] was discovered in 1986 by IBM researchers Karl Miller and Johannes Bednorz, for which they were awarded the Nobel Prize in Physics in 1987. Until Febased superconductors were discovered in 2008[30-31] the term high-temperature superconductor was used interchangeably with cup rate superconductorfor

compounds such as bismuth strontium calcium copper oxide (BSCCO) and yttrium barium copper oxide (YBCO). "High-temperature" has two common definitions in the context of superconductivity:

1. above the temperature of 30K that had historically been taken as the upper limit allowed by BCS theory. This is also above the 1973 record of 23K that had lasted until copper-oxide materials were discovered in 1986.

2. Having a transition temperature that is a larger fraction of the Fermi temperature than for conventional Super conductors such as elemental mercury or lead. This definition encompasses a wider variety of unconventional superconductors and is used in the context of theoretical models.

The label high-Tc may be rebating in the high-Tc class[32-33] Technological applications benefit from both the higher critical temperature being above the boiling point of liquid nitrogen and also the higher critical magnetic field (and critical current density) at which superconductivity is destroyed. In magnet applications the high critical magnetic field may be more valuable than the high *T*c itself. However, cup rate materials are brittle ceramics which are expensive to

manufacture and not easily turned into wires or other useful shapes. Two decades of intense experimental and theoretical research, with over 100,000 published papers on the subject [34] have discovered many common features in the properties of high-temperature superconductors [35] but as of 2009, there is no widely accepted theory to explain their properties. Cup rate superconductors (and other conventional superconductors) differ in many important ways from conventional superconductors, such as elemental mercury or lead, which are adequately explained by the BCS theory. There also has been much debate as to high-temperature superconductivity coexisting with magnetic ordering in YBCO [36] iron-based superconductors, several ruthenium cup rates and other exotic

Superconductors, and the search continues for other families of materials.

HTSC are Type-II superconductors, which allow magnetic fields to penetrate their interior in quantized units of flux, meaning that much higher magnetic fields are required to suppress superconductivity.

2.1.6 Iron based superconductors

Iron-based superconductors are iron-containing chemical compounds. The study on the iron based superconductors has got a great attention following the report on $LaFeAsO_{1-x}F_x$ [36]. The highest superconducting critical temperature Tc reaches 56k [37] by replacing La with other rare earth elements Ce, Pr, Nd, Sm, and Gd. The class of material provides a large number of superconducting compounds that are grouped in general stoichiometric of LnFeAsO(„1111“) family(e.g.Ln=La),$MF_{e2}As_2$(„122““)family(eg.M=Ba),MFeAs(„111““)family(eg.M=Li),&Fe M(„11“)family(e.g. M=Se)[38-40]. Both families of iron pnictides have a quasi-two-dimensional (2D) tetragonal crystal structure. The parent compound LaFeAsO contains FeAs layers sandwiched by LaO layers. Each FeAs layer consists of a square-lattice Fe plane with As atoms above and below the plane alternatively.

The common feature of these main families of iron based superconductors (the 1111, 122, 111, and 11 families of materials) is the presence of an identical Fe plane. It was reported that these families of iron based superconductors attain different value of superconducting temperature Tc

(Table 2.4).

Compounds	family type	maximum Tc
RFeAso	1111	57k
$AFe_{-2}As_2$	122	38k
Life As	111	25k
FeSe	11	15k

Table 2.4.The maximum Tc for the main families of iron based superconductors.

In many publications, much effort has been made theoretically and experimentally to identify the main cause of novel properties of materials. A deeper understanding on the doping effect of the electronic structure of this system can provide in sight in to the interplay between magnetism and superconductivity [40].

2.2 Review on the study of superconducting Lithium Iron Arsenide (LiFeAs)

2.2.1 Introduction to (LiFeAs)

After the original discovery of superconductivity LaOFFeAs with a superconducting transition temperature Tc=26k the

investigation of FeSCs has lead to the discovery of several classes of compounds that all display a high-temperature superconductivity. Despite the fact that the different lattice structures can be lead to significant differences in the electronic structure [41, 42]. A large number of quaternary Iron-oxy pnictides RFeAso(R= Ce, Pr, Wd and Sm), often called „1111“ systems were found to be superconducting with Tc up to 55k for SmFeAs (o.f) series [43].

In a search for the mechanism of super conducting pairing in FeSc, LiFeAs is apparently key compound; This FeSc has attracted recently much attention due to its unusual properties compared to other superconducting iron particles, since it reveals the classical isotopic superconducting gap [44]. It is expected that the pairing glue is provided by phonon [45]. LiFeAs is a very remarkable member in the family of FeSc (mainly 111family) containing FeAs layer with an average Iron valence Fe^{2+} [2, 18, 19] and it is metallic superconductor with itinerant electrons. The magnetic exchange interaction in this compound is anti- ferromagnetic fluctuation [5, 12, and 20]. Because of the spin-density wave (SDW)ordering and the structural transition seen in the parent compounds of the “1111”and the “122”systems are not present in LiFeAs, that

is why un like other stoichiometric Iron-arsenide compounds LiFeAs is an intrinsic superconductor[19,22].

This compound has relatively high transition temperature of 18k without the need for carrier doping or applications of pressure to reduce Superconductivity. More over its electronic structure is quasi-two dimensional (2D) and supports superconductivity in the absence of any notable Fermisurface (FS) nesting or static magnetism. Figure 2.5 shows atypical temperature dependence of the resistivity of LiFeAs as its transition occurs at 18k.

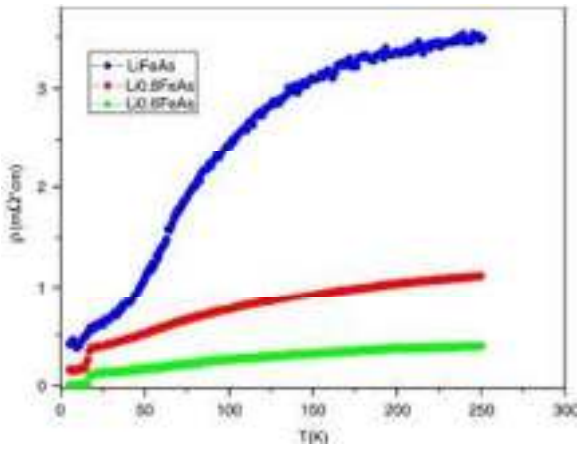

Figure 2.5 Temperature dependence of resistivity for the single crystal $Li_{1.0}FeAs$,

$Li_{0.8}FeAs$ and $Li_{0.6}FeAs$ samples [46]

2.3 Crystal structure of LiFeAs

A crystal is formed by adding atoms in a constant environment [47]. Crystal structure is also a structure consists of identical copies of the same physical unit cell called the Basis: located at all the points of a braviais lattice. The superconducting iron arsenide system LiFeAs (termed"111") family which crystallizes into a Cu_2Sb type tetragonal structure containing FeAs layer with an average iron valence Fe^{2+} like those for "1111"or"122" parent compounds[48]. The dominant magnetic exchange interactions in the LiFeAs are anti-ferromagnetic orders.

No	Parameter	Values
1	Atomic position Li	0.75 0.25 0.2635
2	Atomic position Fe	0 0 0
3	Atomic position As	0.25 0.75 0.8459
4	Fe-As Interlayer distance	2.4142Å
5	Li-As Interlayer distance & also	2.6477Å
6	Li-As Interlayer distance	2.7587Å

Table: 2.5 Crystal structure parameters of LiFeAs

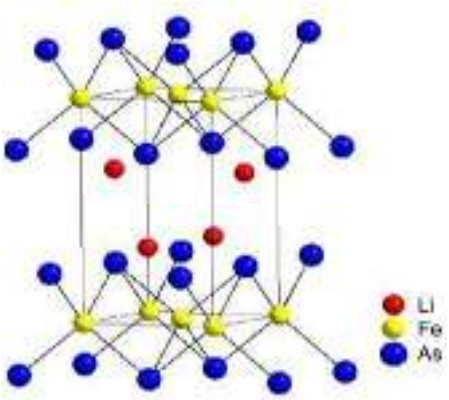

Figure.2.6 Crystal structure of Lithium Iron Arsenide (LiFeAs) characterized by tetragonal layer. In this figure, the red (gray) spheres are Li atoms, the blue (dark gray) spheres are As atoms, and the yellow (light gray) spheres are Fe atoms.

From figure 2.6 an edge-sharing $FeAs_4$ tetragonal layer in LiFeAs consists of one layer of iron (Fe) sandwiched between two layers of As [49]. Two layers of Li atoms are interlaced between FeAs and form the neutral cleaving plane without surface reconstruction. This helps to apply scanning tunneling microscope (STM) and angle resolved photoelectric spectroscopy (ARPES) in order to capture the intrinsic of LiFeAs [50].

2.4 Band Structure of LiFeAs

Band structures are representation of the allowed electronic energy of levels of solid materials and are used to better inform their electrical properties. A band structure is a representation of the energies of the crystal orbital in a crystalline material. Sometimes referred to as “spaghetti diagrams”, a band structure plot can quickly reveal whether a material is metallic, semi-metallic, or insulating and for those materials with band gaps whether they are direct or indirect as the magnitude of the gap. Additionally, the curvature of the bands can reflect the carrier mobility through those bands.

The LiFeAs phase belongs to a wide family of compounds with the tetragonal structure and can be considered as the “first representative of the third group (type 111)” of the new FeAs superconductors [51]. Un like other pnictides, such as $BaFe_2As_2$and NaFeAs, LiFeAs is a super conductor in its stoichiometric form and any chemical substitution on the Fe site (with Co or Ni, for instance) causes a reduction in the transition temperature Tc [52]. In contrast with other systems, no ordered magnetic phase or structural transition has yet been observed in LiFeAs [5152]. Thus; the detail of band-structure calculations of this compound resolved by density

functional theory would be discussed (53).

From band structure of LiFeAs one can summarizes that;-

.The valence band for this compound is comprised primarily of the 3d states of Fe and 4p states of As.

.It‟s lower edge includes the over lapping (hybrid) 3d states of Fe and 4p states of As forming the covalent bond Fe-As bonds in the $FeAs_4$.

.The near-Fermi region consists primarily of the 3d states of Fe that make the main contribution to the total density of states at the FL, which are responsible for the conducting properties of the system.

2.5 Application of superconductivity

It was believed on theoretical grounds that there would be no superconductors above 30k [54]. But after the discovery of high temperature superconductivity by Bednorz and Miller in 1986, it was reported that the superconductivity of $(La\ A)_2\ CuO_4$ in doped lanthanum copper oxides occurred at temperatures up to38k [55]. Where, A is Ba or Sr, This is a tremendous excitement, since 38k was above the ceiling of 30k for superconductivity. The investigation of HTSC was not the end, the compound yttrium barium copper oxide (Y

$Ba_2\ Cu_3O_{7)}$ has been found to be superconductor up to 92k [56]. Immediately bismuth strontium calcium copper oxide ($Bi_2Sr_2\ Ca_2\ Cu_3O_{10}$) at Tc of 110k and thallium barium calcium copper oxide($Ti_2Ba_2\ Ca_2Cu_3O_{10}$)at Tc of 125k exhibit superconductivity turn by turn [55,56].

Two decades after the discovery of HTSCs, practical superconducting wires made of these materials are now being manufactured, and trials of electrical and industrial application including a train supported by magnetic levitation, a transmission line, a ship‟s engine, radiation-free magnetic resonance imaging in medical diagnosis and many others are being implemented [57,58]. For instance, in case of transportation, maglev trains have attained top speeds in excess of 500kmph. Some transportation experts believe that maglev trains could modernize transportation in the 21^{st} century in much the same way that airplanes modernized the 20^{th} century transportation system [58, 59]. At present, maglev train lines operating in Japan, Germany, and China make use of low temperature superconductor technology [58, 59]. Of course the applications of HTSCs to maglev trains are under research which will expect in lower costs and stability [58]. In general superconductivity has played a key role

throughout the past century in expanding the frontiers of human knowledge, and today these materials continue to offer important new tools to expand our understanding of the natural world and potentially foster new energy technologies [60].

2.6 Computational Methods

2.6.1 First principle Method-DFT

First principles method called density functional theory (DFT) was introduced by Walter Kohn around 1955. For investing this powerful technique he was awarded the novel prize in chemistry in 1998. DFT is a commonly used method in condensed matter physics, computational physics, material science and quantum chemistry to describe properties of condensed matter systems. DFT is a useful method to understand and predict the properties of many materials. This method allows to study materials even with minimum input parameter like the atomic type and lattice parameters and that is why it is also called first principle method.

A rapid success has been achieved in electronic structure calculation after DFT was introduced in 1960s.here we gave

a short introduction. In DFT, the assumption reduced the problem of studying a system of N electrons interacting with each other to the case of a system of N non–interacting electrons in an external potential. They were done by introducing the electronic density n(r) as the main variable instead of the full electronic wave function.

Density functional theory is a phenomenally successful approach to finding solutions to the fundamental equation for the quantum behavior of atoms and molecules, the Schrödinger equation in settings of practical value.

The predominant theoretical picture of solid-state and/or molecular systems involves the in homogeneous electron gas: a set of interacting points electrons moving quantum mechanically in the potential field of a set of atomic nuclei. Which are considered to be static the Born Oppen heimer approximation, Solution of such models generally requires the use of approximation schemes, of which the most basic the independent electron approximation, the Hartree theory and Hartree fock theory are routinely taught to undergraduates in physics and chemistry courses. However, there is another approach-density functional theory [61-62].

DFT, which over the last few years or so has become increasingly the method of choice for the

solution of such problems. The main idea of DFT is to describe a main-body interacting system

Via its particle density and not via its many-body wave function. Its significance is to reduce the

3N degrees of freedom of the N-body system to only three spatial coordinates through its particle density, Density functional theory (DFT) is a quantum mechanical modeling used to study the electronic structure of much body system. The properties of many electrons system can be determined by using functional (function of another function).

In DFT the functional is the spatially dependent electron density. For periodic system, if we can find the electronic states then we can calculate thermal, optical and magnetic properties of solids, equations of state, electron density distributions and cohesive energies. This method has the double advantage of being able to treat many problems to a sufficiently high accuracy, as well as being computationally simpler than even the Hartree schemes. The density functional (DF) formalism shows that ground state (GS) and other properties of a system of electrons in an external field

can be determined from knowledge of the electron density distribution n(r) alone.

Density functional theory (DFT) is the basic theory of electronic structure calculations in condensed matter physics. It was so challenge to approximate functional and computational cost.

In 1990‟s there are widely used functional that give a quite reason able accuracy with the affordable computational cost.

In brief, density functional theory (DFT) attempts to solve the many-body problems by recasting the time-independent Schrödinger equation as a functional of one variable, the charge density n(r). The central role played by the electron density means that it is essential to have a clear picture of its nature in real systems. Electron densities in molecules and solids also show relatively small departures from the overlapped densities of the constituent atoms. The starting point is the stationary Schrödinger equation for a N-electron system in a given external potential [61-62].

$$[\frac{-\hbar}{2m}\sum_{i=1}^{N}\nabla_i^2 + \sum_{i}^{N} V_{ext}(r_i) + \frac{1}{2}\sum\frac{e^2}{|r_i - r_j|}]\,[\Psi(r_1 \cdots r_N)] = E\,\Psi(r_1 \cdots r_N)$$

(2.10)

The first- term in equation gives the electronic kinetic energy, the second gives the effect of the external potential and the third gives the electron-electron interact large number of particles clearly make the direct resolution of this equation impossible. Fortunately, from an experimental point of view we are not interested in the full many-body wave function, but only in contracted quantities such as the electronic density and total energy [63-64].

2.7 Modern density functional formalism

The variation principle on the energy was the basis of the formulation of the exact density functional formalism given by Hohenberge and kohn (1964) HK. A big simplification to the problem of finding the ground-state energy of the system have been provided by Hohenberge and kohn in 1964,via their famous theorem(HK): First they showed that there is a one-to-one relationship between the external potential $V_{ext}(r)$ and the (non-degenerate) GS wave function □ ,and that there is a one-to-one relationship between□ and the ground state density n(r) of an N–electron system, they establish the connection between the density and the many-electron Schrödinger

equation (which is expressed in terms of □$(r_1,r_2, \ldots,rN)$

2.7.1 Hohenberge and Kohn theorem

Density functional Theory (DFT) was proposed by Hohenberge and Kohn (1964) and is nowadays one of the major methods used for electronic structure calculations by physicists as well as chemists. The Hohenberge-kohn theorems set the foundation for DFT.

The first theorem, proved by Hohenberge and kohn, is:

The electron density determines the external potential and the density is the ground state particle

density. Consequence of the first Hohenberge and kohn theorem is that the ground state energy is

Also uniquely determined by the ground-state charge density, in mathematical terms E is a functional E [n(r)]. We can write no(r), so for a given ground state density no(r), it is possible to calculate the ground-state wave function ho(r) and vice versa and contain exactly the same information. This theorem states that there exists a one-to-one mapping between the ground state wave function and the ground-state electron density.

In order to appreciate the use of this result, first, one has to know what a functional. A functional is closely related to the more familiar concept of a function. A function takes a value of a variable or variables and defines a single number from

those variables. It is similar, but it takes a function and defines a single number from the function. So one can restate Hohenberge and kohn result by saying that the ground-state energy E can be expressed as E [n(r)], where n(r) is the electron density.

This theorem can again be restated Hohenberge and kohn result is that the ground-state density uniquely determines all properties, including the energy and wave function of the ground-state. It means that we can think about solving the Schrödinger equation by finding a function of three spatial variables, the electron density, rather than a function of 3N variables, the wave function. Here, by solving the Schrödinger equation we mean, to say it more precisely, finding the groundstate energy. Therefore all the properties of the systems are completely determined given only the ground –state density n(r). A straight forward consequence of the first Hohenberge and kohn theorem is that the ground state energy E is also uniquely determined by the ground –state charge density. In mathematical terms E is a functional, E [n(r)]. We can write

E [n(r)] = □□/T+U+V\□□= □□/T+U/□□+ □□/V/□□= F [n(r)] + $\int n(r)V(r)dr$ (2.11)

Where F [n(r)] is a universal functional of the charge density n(r) (and not of v(r), for this functional a vibration principle holds: the ground-state energy is minimized by the ground-state charge density. In this, DFT exactly reduces the N-body problem to the determination of a 3dimensional function n(r) which minimizes a functional E [n(r)].

The second Hohenberge- kohn theorem defines an important property of the functional:

Hohenberge and kohn expressed the minimum energy using density. The electron density that minimizes the energy of the overall functional is the true electron density corresponding to the full solution of the Schrödinger equation. Or a universal function for the energy E (n) in terms of density n(r) can be defined, valid for any external potential Vext(r).

For any particular Vext(r), exact ground state energy of the system is the global minimum value of this functional, and the density n(r) that minimizes the functional is the exact ground state density no(r). Or the second Hohenberge–Kohn theorem asserts that there exists a functional for the energy, E [n(r)], that is a unique functional of the density, and a universal functional that is in dependent of the external

potential: and the true ground state density is one which minimizes the energy functional [64].

2.7.2 The Self-Consistent Kohn-Sham Equations

In 1965, Kohn and Sham showed that it is possible to reduce the many-body quantum mechanical problem to an exact equivalent set of one –electron equations solved self consistently. Inspired by the idea of the Hohenberge-kohn theorem, the Kohn-Sham total energy functional of an electron gas subject to an external potential (including kinetic, Hartree, exchange-correlation energy) for a set of doubly occupied orbital‟s □I (a single slate determinant) is rewritten as:

$$E[\Psi] = -2\left[\frac{\hbar^2}{2m}\right]\sum_i \int \psi_i^* \nabla^2 \psi_i dr + E_H[n] + \int V_{ext} n(r) dr \qquad (2.12)$$

Where the kinetic energy functional has been replaced by its exact analytical expression on the set of orbital‟s□, the ground state electron density is given by, n(r)

$$n(r) = 2\sum|\square(r)|^2$$

As the DFT, only the minimum value of the Kohn-Sham energy functional has a physical meaning and in order to determine the ground state total energy of the electronic system, one then needs to determine the set of orbital‟s □(r)

that minimizes it. This is done by self-consistently solving the Kohn-Sham equations:

$$\left[\frac{-\hbar^2}{2m}\Delta^2 + V_{ion}(r) + V_H(r) + V_{xc}(r)\right]\Psi_i(r) = \varepsilon_i\Psi_i$$

(2.13)

Where ε_i is the Kohn-Sham Eigen value associated with electronic state i. VH is the Hartree potential given by:

$$V_H(r) = e^2\int \frac{n(r')}{|r-r'|}d^3r' \qquad (2.14)$$

V_{ion} is the ionic potential describing the attractive interaction between electrons and nuclei, and V_{xc} is the exchange-correlation potential given by the function derivative

$$V_{xc}(r) = \delta E_{xc}\frac{[n(r)]}{\delta n(r)} \qquad (2.15)$$

The Kohn-Sham equation is in fact a reformulation of the Hohenberge-Kohn problem, where one maps the many-electron system on to a system of non-interacting particles under an effective potential due to the other electrons and their interaction with the nuclei [65].

2.8 Exchange-correlation Functional

Although DFT is formally an exact theory, unfortunately one does not know the exact for the kinetic energy functional nor for the exchange-correlation functional in terms of the

density. How to describe exchange and correlation exactly is unfortunately not known. There is, however, a number of approximation of increasing accuracy as well as computational cost. Some of the most common will be presented below.

A great deal of work has been and is still being done in order to derive reliable expressions for those functional. Particularly, one distinguishes two different formulations for the exchangecorrelation functional: the local density approximation, or LDA, and the Generalized Gradient Approximation, or GGA.

2.8.1 Local density Approximation (LDA)

The simplest and the most widely used and most simple approximation for E_{xc} is the local density approximation (LDA) in which we only consider the exchange and correction energy to depend on the local density n(r). In the LDA formulation, the exchange-correlation energy per electron at appoint r in space is assumed to be the exchange-correlation energy per electron in a homogeneous electron gas which has the same density as the electron gas considered at the same point in space.

Its analytic expression is given by:

$$E_{xc}^{LDA} = \int n(r) \varepsilon_{xc}[n(r), r] dr$$

(2.16)

Where E_{xc} is the exchange-correlation energy density of the homogeneous electron gas .The local density approximation, originally proposed by Kohn and sham because of its final simplicity, is clearly wrong, due to the simple fact that the electron density around an atom cannot be assumed to be homogeneous. Nevertheless, it is amazing how much success the method has in describing condensed phase systems.

The method not only has proven to be simple in formalism, but also useful and very powerful in describing many properties of many systems. Of course, the approximation shows serious break down when a system exhibits substantial electronic density spatial fluctuations. It is therefore necessary to take in to the functional F_{xc} [n], which generally comes at a non-negligible cost in terms of formalism complexity, and numerical difficulties. Also for spin polarized systems local

Spin density approximation given more satisfactory result for DFT calculation. In such a case Exec is given by taking spin in to account we get the local spin density (LSD) approximation, i.e.

$$E_{xec}[n(r)] \rightarrow E_{xc}[n\uparrow(r), n\downarrow(r)]$$

(2.17)

Where $E_{xec}[n\uparrow(r), n\downarrow(r)]$ is the exchange –correlation energy per particle in a homogeneous

,spin-polarized electron gas with spin-up and spin-down densities[63-64,65,65-66].

2.8.2 Generalized Gradient Approximation (GGA)

In LDA one uses the knowledge of the density in appoint r. In real systems the density varies in space. For the rapidly varying electron densities of many materials a reasonable approximation has to be considered and the gradient of the density (n(r)) needs to be included. 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 [61-62, 63, 63-64, 65].

$$E_{xec}^{GGA} = \int f^{GGA}[n(r), \nabla n(r)]dr \qquad 2.18$$

2.9 Pseudo potential (pp)

A pseudo potential or effective potential is used as an approximation for the simplified description of complex systems. Applications include atomic physics and neutron scattering. The pseudo potential approximation was first introduced by Hans Hellmann in 1934[66]

The pseudo potential is an attempt to replace the complicated effects of the motion of the core (i. e non-valence) electrons of an atom and its nucleus with an effective potential, pseudo potential, so that the Schrödinger equation contains a modified effective potential term instead of the columbic potential term for core electrons normally found in the Schrödinger equation.

The pseudo potential is an effective potential constructed to replace the atomic all-electron potential (full-potential) such as core states are eliminated and valence electrons are described by pseudo-wave functions with significantly fewer nodes. This allows the pseudo wave functions to be described with far fewer Fourier modes, thus making plane-wave basis sets practical to use. In this approach usually only the chemically active valence electrons are dealt with explicit, while the core electrons are „frozen“, being considered together with the nuclei as rigid non- Polarize able ion cores. It is possible to self-consistently update the pseudo potential with the chemical environment that it is embedded in, having the effect of relaxing the frozen core approximation, though this is rarely done .In codes using local basis functions, like Gaussian, often effective core electrons.

First- principles pseudo potentials are derived from an atomic reference state, requiring that the pseudo-and all electron valences Eigen states have the same energies and amplitude. Different
elements have different values of pseudo potentials; i.e Li. Pbe-spn-van.upf, Fe Pbe-spn-kjpaw-psl.0.2.1.upf and As. Pbe-n-kjpaw-psl.0.2. upf respectively

Steps for pseudo potential construction

Step 1 Choose a reference configuration;

Li. $1s^2$ $2s^1$

Fe. $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$

$4s^2$ $3d^6$ …….3d As.

$1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $4s^2$

$3d^{10}$ $4p^3$ ……..4p

Step 2. Solve the all-electron problem.

Step 3. Construct the pseudo-wave function that satisfies rules.

OPTIMIZATION OF APSEUDO-POTENTIAL

Pseudo-potentials are optimized with regard to;

.Accuracy and transfer ability-leads to choose small cutoff radius r and harder Pseudo-potentials

.Smoothness-leads to choose a larger cutoff radius r and softer pseudo potentials

2.10 Quantum-ESPRESSO (QE)

Quantum-ESPRESSO is an integral suite of computer codes for electronic structure calculations and materials modeling based on density-functional theory, plane waves basis sets and pseudopotentials to represent electron-ion interactions. It implements a varies of methods based on the solution of the density-functional theory (DFT)problem, using a plane waves (PWs) basis set and pseudo-potentials(PPs) to represent electron ion interactions[67]. The codes are constructed around the use of periodic boundary conditions, which allows for a straight forward treatment of infinite crystalline systems, and an efficient convergence to the thermodynamic limit for a periodic but extended system, such as liquids or amorphous materials. Quantum-Espresso is a full A b-initio package implementing electronic and energy calculations,

linear response methods and third-order a harmonic perturbation theory. Quantum-Espresso also contains two molecular-dynamics codes,
CPMD (Car-parrinello Molecular Dynamics) and FPMD (first-principles Molecular Dynamics).

In side this package, PWSCF is the code we would use to perform total energy calculations which uses both norm-conserving pseudo-potentials (NC-PP) and ultra-soft pseudo-potentials (USPP), with in density functional theory (DFT) [67]. The PWSCF code computes the electronic band structure, the electronic charge density and the total energy of a periodic crystal, with a given braviais lattice and a given space group symmetry. The program exploits the point group symmetry of the solid to reduce the number of operations necessary to compute the charge density and the total energy. The computation of these quantities allows the study of structural lattice constants, bulk modulus and elastic (constants) and dynamical (zone-centre phonon frequencies) properties the study of structural phase transitions and of the effect of pressure on the solid. Furthermore, by using the super cell approach, defects, interfaces and surfaces can be studied. Some of the most important points on the input file of PWSCF are:-

CONTROL;-is the control block, describing how the calculation starts, which will be done in the calculation, and where output will go;

i calculation= scf specifies a self-consistent field calculation (DFT). Re- member: in DFT, the potential that the electrons see is determined by the charge density, which is determined by their wave functions. This needs to be self-consistent.

ii. restart-mode= from-scratch, declares that we will be generating a new structure and not Reading in charge densities or wave functions from a file (unlike a Continuation run) iii. Prefix= LiFeAs specifies the name prefix to be used for temporary files iv. Tstress=.true. Turns on the calculation of the stress tensor

v. tprnfor=.true . Turns on the calculation of forces

Vi. pseudo-dir=specifies the location the directory where we store the pseudo potentials

vii. Out dir= defines the location of the temporary

SYSTEM; - is the block that describes the geometry of the calculation and input variables that Specify the system under study.

i.ibrav= specifies the crystal system. Ibrav=1 is a simple cubic structure.

ii.celldm= specifies the dimensions

of the cell iii.nat = specifies

the number of atoms (each individual

unique atom)

iv.ntyp= specifies the number of types of

atoms (distinct chemistry)

v.ecutwfc= is the cut off for in Rydbergs. The one is important: you will be changing this parameter to do a convergence study

ELECTRONs; - is the electrons block that control how the calculation is performed. We use iterative diagonalization, and both the charge density a wave functions are improved towards the true solution

I.conv-thr = is the convergence threshold. This means that self-consistency is achieved when the energy changes by less than 10^{-8} Ryd in each cycle

ii.diagonalization=is the method for diagonal zing the Kohn-Sham Hamiltonian, David-son is

Fine for now

Iii.mixing-mode = is the mixing method. This dictates how the charge density is

Charged (mixed) from step to step towards self-consistency [54-56]

Chapter 3

Methodology

In this work we were going to apply density functional theory (DFT) as implemented in quantum Espresso (QE). We would prepare input file for the simulation using experimental values and also we would made use of pseudo potential from the quantum Espresso (QE) home page.

For these reasons density functional theory(DFT) has became a common tool in first–principles calculations aimed at describing or even predicting properties of molecular and condensed matter systems. Density functional theory (DFT) was implemented by using different first principle codes for electronic structure calculations, such as quantum-ESPRESSO, ABINIT, CPMD.. etc. We calculated the electronic structure of superconducting Lithium Iron Arsenide (LiFeAs) by using one of the quantum-Espresso package PWSCF code. This code uses pseudo-potentials that consist of important in put parameters for the electronic structure calculation. In superconducting Lithium Iron Arsenide, there are a number of pseudo-potentials presented in the quantum-Espresso website.

We also tried different calculations of the electronic structure of Lithium Iron Arsenide (LiFeAS) using varies pseudo-potentials we used the one which gave a band structure similar to (4.2).The pseudo-potential that given for the compounds are; - Li. pbe-spn-van.upf, Fe.pbe-s-spn-kjpawpsl.0.2.1.upf, As.pbe-n-kjpaw-psl.0.2.upf respectively.

The PWSCF code used different in put parameters for the electronic structure calculation. In this thesis we used the following unique in put parameters for the electronic structure calculation of Lithium Iron Arsenide.

No	Parameter	Values
1	Number of atoms	3
2	Number of types of atoms	3
3	Energy cut off	30Ry
4	Charge density cut off	120Ry
5	Atomic mass of the	Li=6.941,Fe=55.845,

	elements	As=74.92160
6	Pseudo potential of Lithium	Li. pbe-spn-van.upf
7	Pseudo potential of Iron	Fe.pbe-spn-kjpaw-psl.0.2.1.upf
8	Pseudo potential of Arsenide	As.pbe-n-kjpaw-psl.0.2.upf
9	Atomic position of Lithium	0.75 0.25 0.2635
10	Atomic position of Iron	0 0 0
11	Atomic position of Arsenide	0.25 0.75 0.8459
12	Lattice parameters	a =3.7914 and c =6.3639

Table 3.1 Input parameters for the Electronic structure of LiFeAs.

Table 3.1 summarizes some unique input parameters that were used by the PWSCF code to calculate the electronic band structure of superconducting lithium iron arsenide (LiFeAs).

In addition to the above input parameters, we had made a lot of changes in the quantum ESPRESSO code, for example in density of state we used tetrahedral calculation. We used latex to write thesis, grace soft ware to plot the band structure, Dos and different graphs of LiFeAs compound and XcrySden software used for draw crystal structure of LiFeAs. At the end of our work we had also know the methods to

calculate the transition temperature of lithium Iron Arsenide (LiFeAs).

Chapter 4

Result and Discussion of the electronic Band Structure of LiFeAs

Applying density functional theory (DFT) as implemented in quantum-ESPRESSO code and using proper inputs we calculated the total energy on the Fermi level. By using those particular input parameters from table 3.1 and some additional common parameters we have also plotted the crystal structure, electronic band structure and density of state structure of Lithium Iron and Arsenide as shown in fig 4.1, 4.2 and 4.3 respectively by the same code. We plotted the data using grace soft ware.

The Lithium Iron Arsenide (LiFeAs) phase belongs to a wide family of compounds with Tetragonal structures (the crystallographic type of Cu_2Sb, space p_4/nmm) [68] and can be considered as the "first representative of the third group (type 111)" of the new FeAs superconductor. In the unit cells of the tetragonal (space group p_4/nmm) phase LiFeAs, the atoms are in the following position:-

Fe (0, 0, 0), Li (0.75, 0.25, 0.2635) and As (0.25, 0.75, 0.8459) and the structure is body centered Tetragonal. The

figure of crystal structure of Lithium Iron Arsenide could be drawn from XcrySden soft ware like figure 4.1below.

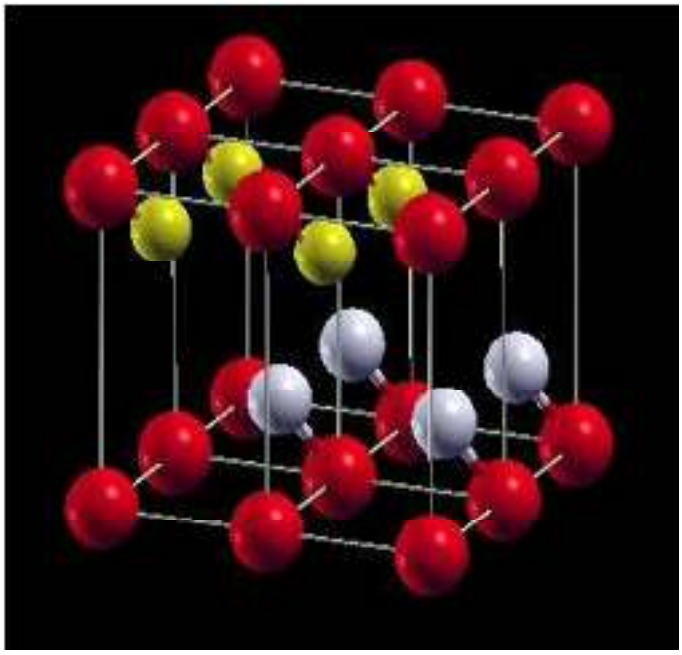

Figure 4.1 crystal structure of Lithium Iron Arsenide (LiFeAs)

In the above Fig 4.1, the red (gray) spheres are Li atoms, the blue (dark gray) spheres are As atoms and the yellow (light gray) spheres are Fe atoms**.**

Figure 4.1is drown based on the input parameter and is agreement with the already published structure of Lithium Iron Arsenide (LiFeAs).

Our calculated electronic band structure of Lithium Iron Arsenide revealed us with some fundamental points that should be considered. In fact we plotted the electronic band structure of superconducting Lithium Iron Arsenide along the high symmetry of Γ-X-M- -Z-R-A-Z direction of the Brillouin zone as suggested in [69]. As it has been known in most Iron based superconductor (FeSC), the band structure shows a multi band nature. It is also possible to find the inter layer distance between the high symmetry of LiFeAs, the maximum distance between M-Γ is 0.1908Å and the minimum distance between Γ-Z is 0.0816Å. The valence band (in range from -3.6 e v to the Fermi level Ef) for LiFeAs is comprised primarily of the 3d states of Fe and 4p states of As. Its lower edge (in the range from -3.6ev to -2.3ev below Ef) includes the over lapping hybrid 3d states of Fe and 4p states of As forming the covalent Fe-As bonds in the $FeAs_4$ tetrahedral. The tetrahedral angle of LiFeAs is 103.1^0 in the form ofAs-Fe-As. The near Fermi region (from -2.3 ev to Ef) consists primarily of the 3d states of Fe, which make the main contribution to the total Dos at the Fermi level as shown in figure 4.2 below.

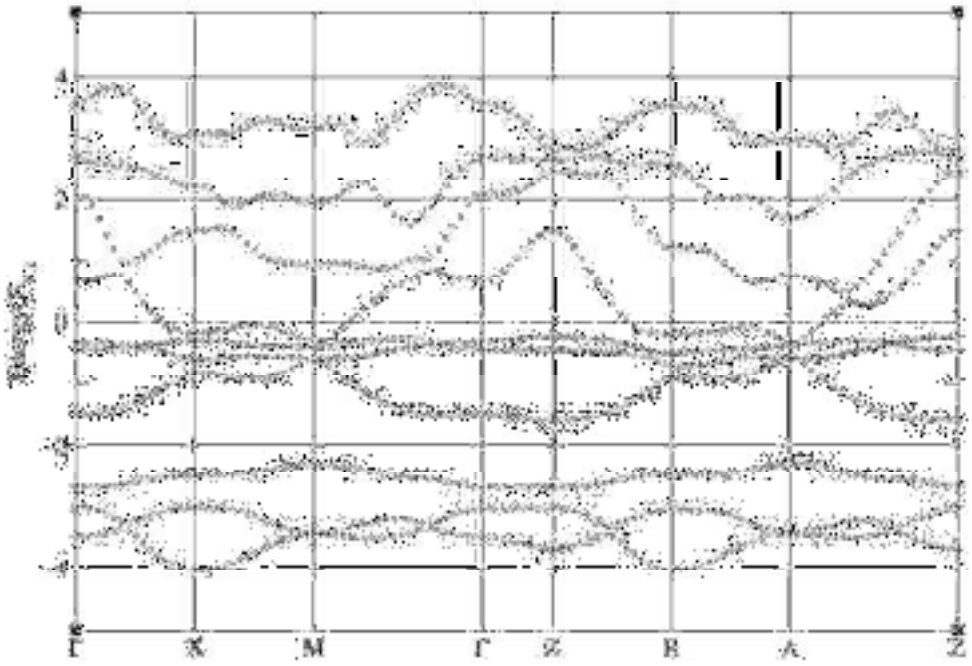

Figure 4.2Electronic band structure of superconducting Lithium Iron Arsenide (LiFeAs)

Density of state (DOS) in superconductivity is an important parameter to understand several properties. If the number of DOS near the Fermi level is changing, for instance by doping, then the properties of the material may change dramatically. Applying density functional theory as implemented in Quantum Espresso(QE)code one can calculate the DOS of a compounds, as shown in (Fig.4.3) for LiFeAs. The density of states (DOSs) near the Fermi level is dominated by the Fe3dstates. Thus, electronic structure of

stoichiometric LiFeAs is similar to that of the parent compounds of the first class, with a hole cylinder at the Brillouin zone (BZ) center, electron cylinders at the BZ corners and an electronic DOS that decreases strongly with increasing energy in the vicinity of the Fermi energy. When we go from left to the Fermi level the hole band increase to that near the Fermi level it became very sharp, after crossing the Fermi level as hole band decreases the electron band increases, like Figure 4.3 below.

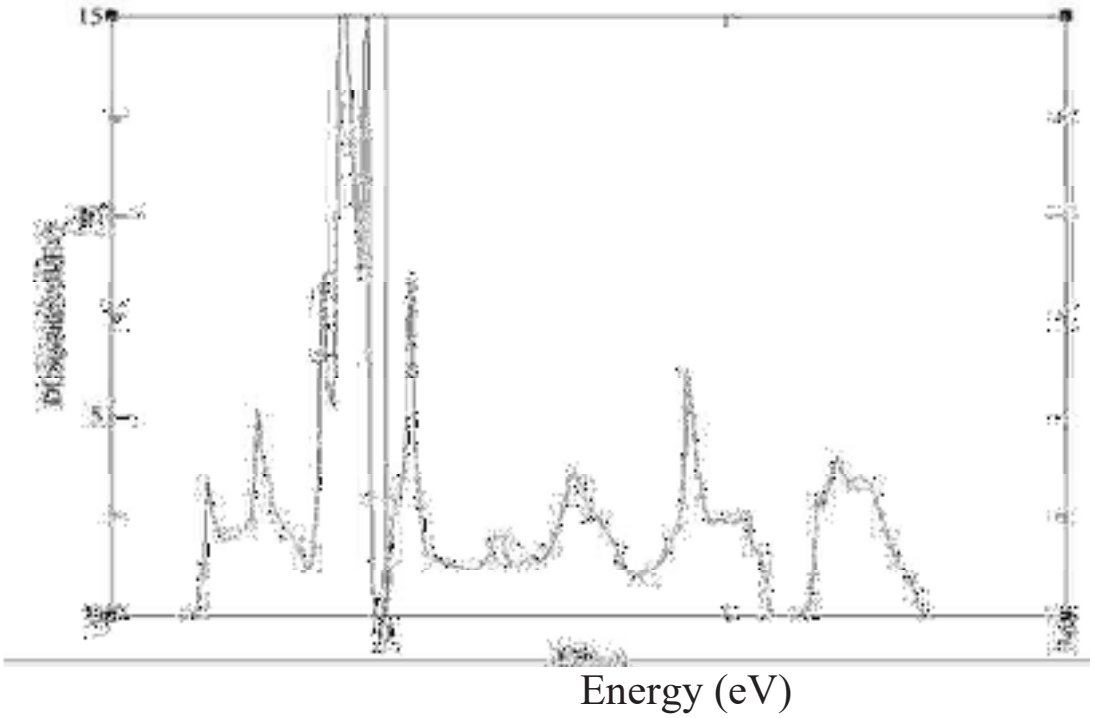

Figure 4.3 Density of state of Lithium Iron Arsenide (LiFeAs).

Finally, using our calculated density of state and applying Equation (2.7) we calculated the Superconducting critical temperature of Lithium Iron Arsenide (LiFeAs) as follows:

$$T_c = \theta_D \exp\left(\frac{1}{\lambda N(0)V}\right) \quad (4.3)$$

Since Lithium Iron Arsenide (LiFeAs) should a BCS type, we have used equation 4.3 and a typical value for Debye temperature, 386k.

For weak coupling $\lambda < 0.5$ and in this case we used 0.29. With all these substitution

$$T_c = 17.37k.$$

This theoretical result was approximately in agreement with the experimental value.

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Conclusion

In this work we had calculated the electronic band structure of superconducting Lithium Iron Arsenide (LiFeAs) by using density functional theory. In fact we employed by using the known quantum espresso package called PWSCF. From calculation, we observed that using different pseudo-potentials an input has brought about a great difference on the electronic band structure of superconducting Lithium Iron Arsenide (LiFeAs).

From the simulation we found that the crystal structure, band structure and Density of states of Lithium Iron Arsenide by using our proposed inputs. The compound has a tetragonal structure as seen from XcrySden and similar to already published structure. The band structure of LiFeAs is calculated along the high symmetry point Γ-X-M-Γ-Z-R-A-Z direction of the Bz[69]. Its band structure shows a multi band nature. We noticed that electron bands are far from the Fermi level compare to the hole bands. This suggested that increasing transition temperature can be achieved by understanding the effect on the hole bands.

The density of states (DOSs) near the Fermi level is dominated by the Fe3d states and an electronic DOS that decreases strongly with increasing energy in the vicinity of the Fermi energy. In addition to this the theoretical calculated values of the superconducting critical temperature (17.37k) is compared to the experimental values.

We recommend that understanding the role of electronic structure can led for improving transition temperature of certain Iron based superconductors.

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