FIRST-PRINCIPLES STUDY OF $BaFe_{2-x}Ni_xAs_2$ (x=0, 0.125, 0.25, 1 and 2) SUPERCONDUCTOR USING DENSITY FUNCTIONAL THEORY

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MASTER OF SCIENCE
(PHYSICS)

UNIVERSITI PERTAHANAN NASIONAL MALAYSIA

2022

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Thesis submitted to the Centre for Graduate Studies, Universiti Pertahanan Nasional Malaysia, in fulfillment of the requirement for the Degree of Master (physics).

2022

ABSTRACT

A metal can be known as a superconductive material throughout their transition temperature (T_c) determination. This is done by the macroscopic thermo/electrodynamic experiment. Upon quantum, electronic band theory cannot tell if the material is a superconductor. This is because superconducting band gap (ΔE_{sc}) of the conventional superconductor is too small. However, this might not true for the higher T_c, recently discovered namely Fe-based superconductor (FeBS). This new kind of superconductor is labelled to have an unconventional superconductivity (SC). This is because its SC mechanism could no longer explain the conventional phonon mediated SC. Conventionally, spins (Fe) destroyed phonon SC interaction. Fairly, role of spins played for SC is not yet fully understood. Thereby, it is a chance that the FeBS has other kinds of electronic feature related to its SC mechanism. The aim of this research is to verify electronic features contributed to Fe-SC. This is done by calculating various electronic phase properties of $BaFe_{2-x}Ni_xAs_2$ using Density Functional Theory (DFT). According to their T_c determination experiment, $BaFe_{2-x}Ni_xAs_2$ with x=0, 1 and 2 is the parent FeBS, a non-superconductor (NSC) and the non-Fe; Ni-based superconductor (NiBS), respectively. It is featured on their calculated band structures that the parent FeBS has paired ΔE_{sc} while the NiBS has the inter-band pockets of Charge Density Wave (CDW) which is responsible for the non-Fe SC whereby the NSC has none of those. Referring to the electronic phase diagram data, $BaFe_{2-x}Ni_xAs_2$ with x=0, 0.125 and 0.25 is representing phase before, during and after the Fe-SC. It is concluded from the band structures calculation that the FeBS (x=0.125) is not only depicted an obvious paired ΔE_{sc} but must accompanied by intra-band Spin Density Wave (SDW) nesting pockets to have the spin mediated SC. Also, the SC ended (x=0.25) when it is only intra-band SDW. This proved that spins played role for SC when the atomic Fe distances, its magnetic moment and ordering are precisely favored by the SC interaction. Moreover, direct comparison of the FeBS versus the NiBS is done to understand their mechanism in enhancing SC. Pairing SC mechanism of both superconductors is depicted in their momentum and real space. It is determined from their calculated electronic properties and charge distribution, respectively. This is to demonstrate electrons that responding to SC interaction; super-electrons. It is found that their super-electrons behaved differently. This might be a clue why FeBS (Fe-SC) has higher T_c than the NiBS (non-Fe SC). Overall, the quantum calculation in this first-principles study provided insight for super-electrons behavior. Henceforth, it may improve the understanding of unconventional superconductors.

ABSTRAK

Logam diketahui boleh bersifat superkonduktif dari pengesahan suhu kritikal mereka. Inilah yang dijalankan oleh experimen makroskopik termo/elektrodynamik. Dalam kuantum, teori jalur elektronik tidak dapat memberitahu sama ada sesuatu bahan itu superkonduktor atau tidak. Ini kerana jarak jalur tenaga superkonduktor biasa adalah terlalu kecil. Walaubagaimananpun, ini mugkin tidak lagi betul untuk superkonduktor berasas ferum yang baru sahaja ditemui, juga mempunyai suhu kritikal yang lebih tinggi. Jenis superkonduktor yang terbaru ini dilabel mempunyai superkonduktiviti bukan biasa. Ini kerana mekanism superkonduktivitinya tidak lagi menerangkan superkonduktiviti biasa yang dijana oleh fonon. Biasanya, putaran kepunyaan ferum akan memusnahkan interaksi superkonduktiviti fonon itu. Jadi adillah, peranan putaran dalam superkonduktiviti masih tidak difahami sepenuhnya. Oleh itu, berkemungkinan superkonduktor berasas ferum ada ciri elektronik berbeza yang membawa kepada superkonduktiviti. Kajian ini adalah untuk mensahihkan ciri elektronik yang menyumbang kepada superkonduktiviti dengan ferum. Ini dilakukan dengan mengira pelbagai fasa sifat elektronik $BaFe_{2-x}Ni_xAs_2$ menggunakan Teori Fungsi Ketumpatan. Berdasarkan kepada mengesahan suhu kritikal mereka, $BaFe_{2-x}Ni_xAs_2$ dengan x=0, 1 dan 2, masing-masingnya adalah induk superkonduktor berasas ferum, bukan-superkonduktor dan superkonduktor bukan berasas ferum (superkonduktor berasas nikel). Ini telah diketengahkan oleh pengiraan struktur jalur mereka bahawa induk superkonduktor berasas ferum ada jarak jalur tenaga berkembar manakala superkonduktor berasas nikel mempunyai poket jalur rapat dari ketumpatan gelombang cas dan bukan-superkonduktor tiada kedua-duanya. Merujuk kepada data gambar rajah fasa elektronik $BaFe_{2-x}Ni_xAs_2$ dengan x=0, 0.125 dan 0.25 adalah mewakili fasa sebelum, semasa dan selepas superkonduktiviti dengan ferum. Telah disimpulkan dari pengiraan struktur jalur bahawa superkonduktor berasas ferum tidak hanya memaparkan jarak jalur tenaga superkonduktor yang jelas bahkan mesti ditemani oleh ketumpatan gelombang putaran sebagai syarat agar superkonduktivitinya dijana oleh putaran. Juga, fasa superkonduktiviti itu tamat apabila hanya ada jalur antara ketumpatan gelombang putaran. Ini membuktikan bahawa putaran memainkan peranan untuk menjana superkonduktiviti apabila momen, jarak dan susunan atom ferum memihak kepada interaksi superkonduktiviti. Seterusnya, perbandingan terus kepada superkonduktor berasas ferum dari superkonduktor berasas nikel telah dilakukan untuk memahami mekanism mereka dalam mengeluarkan superkonduktiviti. Mekanism berpasangan dalam superkonduktiviti mereka telah ditunjukkan dalam ruangan momentum juga ruangan sebenar. Masing-masingnya yang dikenalpasti dari kiraan sifat elektronik juga pengedaran cas mereka. Ini adalah demonstrasi elektron-elektron yang bertanggungjawab atas interaksi superkonduktiviti; super-elektron. Telah difahamkan bahawa super-elektron mereka berkelakuan berbeza. Jadi mungkin inilah sebabnya suhu kritikal superkonduktor berasas ferum adalah lebih tinggi dari suhu kritikal superkonduktor berasas nikel. Keseluruhannya, kiraan kuantum dalam kajian prinsip-utama ini diharapnya akan menyediakan pandangan bernas tentang super-elektron. Sehingganya, mengemaskini pemahaman tentang superkonduktor bukan biasa.

ACKNOWLEDGEMENTS

First and foremost, I would to express my highest gratitude to Allah S.W.T, for the chance He has given me to futher my study at Universiti Pertahanan Nasional Malaysia (UPNM). It is also a blessing for all the strength and abilities to complete this study. Moreover, I would to express my gratitude to both of supervisors, Prof. Dr Muhd Zu Azhan bin Yahya and Dr Mohamad Fariz bin Mohamad Taib for their helpful guidance and never endless support. I am also grateful for their patience, for their sincere motivations and enthusiasm plus immense knowledge. In addition, the helps that have been given have contribute in accomplishing this research and finishing this thesis.

Then, I would like to thank all the members of computational group-imade UiTM. They are Dr Kamil, Dr Sazwan, Dr Wafi, Dr Hafiz, Dr Hazrie, Syazwan, Mimi, Ani, Sya, Haziq and other beloved colleagues especially, Kak Niza, Puan and Cik Tikah. I am thankful for all their endless supports and motivations. I am also very grateful to them for providing me space to work on plus willing to share and discuss useful ideas within the process of completing this research.

I also want to mention my gratitude to my beloved family members, my parent, Kamaruddin Bin Alang Md Dris and Jamaliah Binti Daud, my brother, Afzul Kamal Sufian, and my other siblings, my son, my beloved husband and also my in-law family for all the love and supports that they have been given. They have been an inspiration and very helpful in finishing my research and study.

APPROVAL

I certify that an Examination Committee has met on **09 December 2021** to conduct the final examination of **Kamaliati Hanum Binti Kamaruddin** on his degree thesis entitled "First-Principles Study of $BaFe_{2-x}Ni_xAs_2$ superconductor using Density Functional Theory". The committee recommends that the student be awarded the Degree of Master (Physics).

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LIST OF SYMBOLS

T_c	-	Critical temperature
T_S	-	Structural phase transition temperature
T_N	-	Neël Temperature
H_c	-	Critical magnetic field
J_c	-	Critical current density
E_f	-	Fermi energy
λ_{eph}	-	Electron-phonon coupling
γ	-	Electronic specific-heat coefficient
ρ	-	Charge density
ρ_T	-	Total charge density
$\Delta\rho_A$	-	Difference density charge between atoms
$\Delta\rho_L$	-	Difference density charge between layers
E_g	-	Energy band gap
ΔE_{sc}	-	Superconducting energy band gap

LIST OF ABBREVIATIONS

SC	-	Superconductivity
NSC	-	Non-Superconductor
NM	-	Non-Magnetic
PM	-	Para-Magnetic
AFM	-	Anti-Ferromagnetic/magnetism
FM	-	Ferromagnetic/magnetism
FrM	-	Ferrimagnetic/magnetism
SDW	-	Spin Density Wave
CDW	-	Charge Density Wave
FeBS	-	Fe-based superconductor
NiBS	-	Ni-based superconductor
BCS	-	Bardeen–Cooper–Schrieffer
BZ	-	Brillouin Zone
FS	-	Fermi Surface
AFQ	-	Antiferro-Quadrupole
Fe	-	Ferrum/Iron
Ni	-	Nickel
As	-	Arsenide
Ba	-	Barium
K	-	Potassium
P	-	Phosphorus
DFT	-	Density Functional Theory
CASTEP	-	Cambridge Serial Total Energy Package
GGA	-	Generalized Gradient Approximation
PBE	-	Perdew-Burke-Ernzerhof
PBEsol	-	PBE for solid
LDA	-	Local Density Approximation
MS	-	Material Studio
EXC	-	Exchange Correlation Functional
DOS	-	Density of States
PDOS	-	Partial Density of States
DPOS	-	Density of phonon of states
VCA	-	Virtual Crystal Approximation
VASP	-	Vienna Ab-initio Simulation Package
QE	-	Quantum Espresso
PWSCF	-	Plane Wave Self Consistent Field
FLPAW	-	Full-potential (Linearized) Augmented Plane Wave
PAW	-	Augmented Plane-Wave
ARPES	-	Angle Resolved Photonemission Spectroscopy

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CHAPTER 1

INTRODUCTION

1.1 Background of Research

Since the accidentally discovery of superconductivity (SC) in cooled solid mercury [1], more and more element and compound materials have been studied at low temperature [2–4]. Until now, the progress on finding new superconductor materials keeps ascending [5–7]. The bizarre behaviour of a superconductor such as supermagnet, pinning vortex, and Johenson jumping has significantly changed the understanding of condensed matter system [3, 8-9]. The advance technology offered by this fascinating material has improved human life wholly. The fusion reactor, hovering vehicle prototype and the most sensitive magnetometer are all thanks to SC [3, 10-11]. Not to mention, the 'super' conducting phenomenon which is conducting electricity by zero resistivity lured many researchers to propose the new superconductor as the best power generator cable [12]. However, every magnificent has pro and cons. SC is a complex state that only happens at certain low temperature which is known as transition or critical temperature, T_c [1]. It is a goal to achieve a high T_c, high enough to be superconducting in power generator cable without any coolant applied. This is motivated by the high cost of stabilizing the SC state [13]. Despite the highest T_c by Cuprate group of superconductors, this type of superconductor is brittle ceramic which is not easily moulded into wire [14]. Moreover, cuprates are unsuitable for application

requiring actual superconducted current because they do not form large, continuous superconducting domains, but only clusters of micro-domains within which SC occurs [15]. On the other hand, Fe-based superconductor (FeBS) is the first choice candidate for superconducting power generator cable due to the physically able to be fabricated into wire [16]. This is because FeBSs are poor metal even when they are not superconducting [17–19]. However, there is no SC theory established for FeBS yet leave alone make it superconducting at the room temperature [20]. Nonetheless, many scientific papers have been established since the discovery of FeBS due to its potential as a superconducting cable [20]. Most of the papers are to recognize the properties of FeBSs especially their parent compound [21–23]. Among the FeBSs, parent compound of 122-type family does not share the Fe atom with the neighbouring unit cell summarize the study on Fe in the FeBS is per unit cell [24]. Plus, direct interaction of Ni on Fe on the electron-doped $BaFe_2As_2$ would tell the role of Fe play in FeAs layer in the FeBS [25]. These both are important in order to understand the differentiation between Matthias rule obeying of most Bardeen-Cooper-Schrieffer (BCS) superconductor and the SC in the magnetic FeBS that is remain unconcluded [20]. Nevertheless, simpler structure by FeBSs as compared to Cuprates, does offered better enabling to be studied in first-principles approaches [26-27]. Therefore, abundance of experimental works has successfully reported and supported by many theoretical works [28–31]. Truly, a decade is fairly too soon to conclude any SC theory of vast FeBS materials but every study regarding it will bring us one step closer to the understanding of the unconventional SC and of course, with lots of study reported, it will help researching become less tedious. For example, there are group researchers proposed possible SC mechanism for FeBS such as spin density wave (SDW), spin-phonon, ±s-wave pairing versus d–wave pairing gap [32–35].

In this thesis, first-principles study is done on the SC related properties such as phonon and electronic for SC mechanism in $BaFe_{2-x}Ni_xAs_2$ superconductors. superconducting $BaFe_{2-x}Ni_xAs_2$ is one of the FeBS. Without Fe (x=2), $BaFe_{2-x}Ni_xAs_2$ is a Ni-based superconductor (NiBS). Their SC related properties were calculated using density functional theory (DFT) with Local Density Approximation (LDA) and Generalized Gradient Approximation (GGA) exchange correlation within the Cambridge Serial Total Energy Package (CASTEP) computer code. This work is an aid to theoretically understand the unconventional SC mechanism in a way to provide more insight of establishing a SC theory that involving magnetic element. May the theory potentially develop an equation to formulate the higher T_c superconductor if not, the room temperature superconductor. Next, make it possible to manufacture the electric power generator cable with 100% efficiency.

1.2 Challenge and Motivation

In near future, superconductors have been seen as very advantageous on performing a better qubit [36]. Generally, superconducting wire is the best hope to end deficiency of the current power grid supply cable. Half of the electrical power lost to be heat in the transmission distance of the current commercial power grid cable wire [37]. This caveat can be removed by replacing those transmission cable wires with the superconducting wires. Therefore, they can operate without any internal resistance. The problem is; superconductors only work at the very cold temperature [1]. Nowadays, most of superconductor devices are included cooling application [38]. Though the price of coolants is getting cheaper [39], it is a finicky process to maintain the superconducting state. This is now happened to the Tokamak's fusion reactor [10]. In

order to skip refrigerating the superconductors, scientists came out with an idea so thus they can achieve higher T_c, high enough to be in the warm ambient temperature. The idea is; to alter/modify the properties of superconductors to such an extent that their T_c suit application without requirement of cooling. Hence, it is what happened to the metal hydrogen superconductor [40]. This is scientist done improvement they learned from BCS theory of conventional superconductors [41]. Such theory propositions electron-phonon interaction mediated SC in the low T_c element superconductors [1]. In this context, experimentalists applied a forceful pressure onto the hydrogen therefore its lattice –ion interaction is improved to pursuit SC. Recently, the metal gas compound is reported to have superconducting state at 15ºC under 272 GPa pressure [7]. This is in oppose to Cuprates, the unconventional superconductors that capable to be superconducting without being under pressure instead, their T_c are chemically enhanced by doping [42]. They also leave us at surprise when their T_c are able to get as high as 155K [43]. This is a bizarre phenomenon according to the BSC electron-phonon mediated SC because its SC interaction that sustain Copper pairs is supposed to thermally limit at 30K ~ 40 K [44]. Despite their high T_c, Cuprates are not suitable to be candidates of the commercial superconducting wire since they are physically ceramic [45]. On the other hand, FeBSs naturally are metal even when they are in parent state [46]. Additionally, they are stable in large growth crystal [47], robust to impurities [20] and most of all, they are great enough to undergo SC by chemical doping [23]. Due to these qualities, there are rich variety of dopants reported as the catapults of SC in these group of superconductors [27, 47–49] including the dopants that lead to their non-superconducting state [31, 50]. Originally, FeBSs have perplexed every scientist because they are superconducting within Fe, a magnetic element compound. Which is made them the unconventional disobeyed Matthias rules superconductors [53]. Matthias guides of synthesizing conventional superconductor has been avoided such

element because the long range of Fe moment attraction will collapse the dynamic of Cooper pair formation [20]. Guided by the fundamental level understanding, Fe roles in these unconventional superconductors have become more and more defined [16].

Additionally, credibility of first-principles study complementing the experiments results undeniably meet a comprehensive understanding of certain material [52–54]. Based on intensive research done by both experimentalists and theorists, soon or later the SC mechanism of FeBSs will no longer a mystery. It will be transparent enough to reveal clues for deriving the equation of formulating warm T_c temperature FeBS. Undoubtedly, FeBS have the best potential to be mass manufacture as resistance-less electrical power transmission wire of the future [16].

1.3 Problem Statements

No superconducting energy band gap (ΔE_{sc}) has been identified upon FeBS electronic band structures. Available plotted band structures only identified the parent FeBS as poor metallic compound [24, 57–59]. Parent FeBS is not FeBS, it must be doped or applied pressure in order to be FeBS [51, 60–65]. Probably, the missed identification of Fe super-electrons upon quantum energy behavior is what bring contradiction onto explaining Fe-SC mechanism though Fe is agreed as the SC contributor [32–35, 66–70].

Moreover, role of Fe in SC is yet to be understood. If Fe is the SC contributor, why antiferromagnetic (AFM) order of Fe is to be suppressed for the FeBS to be superconducting? [51, 60–65, 71]