

The study on superconductivity of Lanthanum hydrides (LaH_X where $X = 1, 3, 4, 6$)



By Tigist Tafa Rikicha

A thesis submitted to the department of applied physics

School of Applied Natural science

Office of graduate studies

Adama Science and Technology University

July 2020

ADAMA, ETHIOPIA

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Approval page

We the undersigned members of the board of Examiners of the final open defense by **TIGIST TAFE** have read and evaluated her thesis entitled **THE STUDY ON SUPERCONDUCTIVITY OF LANTHANUM HYDRIDES (LAH_x WHERE $x=1, 3, 4, 6$)** using density functional theory method and examined the candidate. This is therefore to certify that the thesis has been accepted in partial fulfillment of the requirement of the **Degree of Master of Science in Applied Physics (material physics)**

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List of abbreviation

BCS: Bardeen-Cooper-Schrieffer

CSP: Crystal structure prediction

DAC: Diamond anvil cell

DFT: Density functional theory

DOS: density of state

GGA: generalized gradient approximation

GPA: Giga Pascal

HTS: High-temperature superconductors

IR: infrared

PWScf: The plane-wave self-consistent field

PES: potential energy surface

SC: superconductor

T_C : critical temperature

UV: ultraviolet

VKS: Kohn-Sham potential

ZPE: zero point energy

Abstract

Superconductivity is the phenomenon where the resistivity falls to zero below a certain critical temperature T_C . Currently many report indicated that hydrogen rich compound shows the highest T_C in the history of superconductivity. Most of the experimental and theoretical works has been done under pressure. But the nature of the electronic band structure and DOS was not well explained as far as our knowledge concerns. In this thesis we studied electronic structure of LaH_X ($X=1, 3, 4, 6$) superconductor by using density functional theory (DFT) as implemented in QUANTUM ESPRESSO. The band structure and DOS of LaH_1 and LaH_3 does not show superconductivity and LaH_4 and LaH_6 shows superconductivity in agreement with the experimental reports. With increasing hydrogen atom critical temperature increase from 176.8K (for LaH_4) to 183.6K (for LaH_6).

Key word; Superconductivity, density functional theory, hydrides

CHAPTER ONE

Introduction

1.1 Back ground of study

Superconductors are material where the resistance goes to zero at certain critical which is known as the critical temperature. In 1908 the Dutch physicist Heike Onnes Kamerling began to work in the field of low temperature physics through liquefying helium. Three years later, in 1911, he found that below 4.2K the resistivity of mercury was null [1]. This resistance-less state enables persistent currents to be established in circuits to generate enormous magnetic fields, and to store and transport energy without dissipation.

Kamerlingh Onnes and one of his assistants first studied platinum and found that its resistivity, when extrapolated to depend on purity. They then decided 0 K to study mercury because very pure samples could easily be prepared by distillation. Much to their surprise, the resistance of the mercury sample dropped sharply to an un-measurably small value. It was quite natural that 4.15 K Kamerling Onnes would choose the name superconductivity for this new phenomenon of perfect conductivity. Note that platinum does not exhibit superconducting behavior, as indicated by its finite resistivity as T approaches 0K. In 1913 Kamerling Onnes was awarded the Nobel Prize in physics for the study of matter at low temperatures and the liquefaction of Helium [1].

Superconductivity is a very curious phenomenon characterized by a phase transition at a critical temperature (T_c) in which the conducting phase is in equilibrium with the superconducting phase. The most important properties of the superconducting phase are: zero resistance, ideal diamagnetism (meissner effect), magnetic flux quantization and persistent current in superconducting rings, cylinders or coils.

Superconductors have other unique properties such as the ability to expel and screen magnetic fields, and quantum oscillations controlled by the magnetic field that provide extraordinary measurement sensitivity. The magnetic properties of superconductors are as dramatic and as difficult to understand as their complete lack of resistance. In 1933 W.

Hans Meissner and Robert Ochsenfeld studied the magnetic behavior of superconductors and found that when certain ones are cooled below their critical temperatures in the presence of a magnetic field, the magnetic fluxes expelled from the interior of the superconductor [2].

Superconductor may be an element, inter-metallic alloy and semiconductor, compound of organic or inorganic substance that will conduct electricity without resistance below a certain temperature. All known superconductors are solids, none are gases or liquids, all require extreme cold to enter superconductivity state. [2]

Furthermore, these materials lost their superconducting behavior above a certain temperature-dependent critical magnetic field, B_c (T). In 1935 Fritz and Heinz London developed a phenomenological theory of superconductivity [3], but the actual nature and origin of the superconducting state were first explained by John Bardeen, Leon N. Cooper, and J. Robert Schrieffer [3]. A central feature of this theory, commonly referred to as the BCS theory, is the formation of bound two-electron states called Cooper pairs.

Until 1986, superconductivity was considered to be a low-temperature phenomenon, as all known superconducting materials possessed critical temperatures (T_c) below about 30 K. However, the discovery of the Cuprate superconductors [4] copper-based materials with T_c values as high as 164 K [5], known as the high-temperature superconductors initiated extensive research in an attempt to obtain superconductivity at room temperature. The discovery of superconductivity at 203 K in H_3S at high pressures offered another route in the search for high-temperature superconductivity in conventional superconductors. It provided the first confirmation of the predictions of the Bardeen–Cooper–Schrieffer and Migdal–Eliashberg theories regarding the possibility of high temperature superconductivity in materials with high phonon frequencies [6]. In principle, hydrogen- and carbon-abundant materials can provide the required high frequencies in the phonon spectrum as well as a strong electron–phonon interaction [7].

Lanthanum is one of the rare earth elements (REEs), which are a collective term for the elements from lanthanum to lutetium, atomic numbers 57–71, in the periodic table. The element has an atomic number of 57, an atomic mass of 139, one main oxidation state (+3) and two naturally occurring isotopes (^{138}La and ^{139}La), of which ^{139}La is the most abundant at

99.9%. Lanthanum hydride (LaH_{10}), consists of a hydrogen lattice made of polyhedral with square or hexagonal faces, with a rare earth metal atom lying at the center of each polyhedron. Assuming that this system could be described by BCS theory, the researchers predicted its T_c to lie between 270 and 290 K at ~ 200 GPa [8].

The potential of metallic hydrogen as a high- T_c superconductor [8] was identified few years after the development of the Bardeen-Cooper-Schrieffer (BCS) theory, which explained superconductivity through the electron phonon coupling mechanism. The main argument was that T_c can be maximized for light compounds due to their high vibrational frequencies. In view of the large pressures needed to metalize hydrogen, chemical pre-compression with heavier atoms was suggested as a pathway to decrease the pressure needed to reach metallicity and, thus, superconductivity.

The term hydride is commonly named after binary compounds that hydrogen forms with other elements of the periodic table. Hydrides are classified into three major groups, depending on what elements the hydrogen bonds to. Formally, hydride is known as the negative ion of hydrogen, H^- , also called a hydride ion. Because of this negative charge, hydrides have reducing, or basic properties.

1.2 Statement of the problem

We still have not found a theory, which would bring good explanation for HTS. There are several models, but none of them describes all physical properties. Currently many report indicated that hydrogen rich compound shows the highest T_c in the history of superconductivity. Most of the experimental and theoretical work has been done under pressure. But the nature of the band structure and DOS of were not well explained as far as our knowledge concerns.

The main aim of this thesis is to study the effect of increasing hydrogen on the electronic structure of LaH_X ($X = 1, 3, 4, 6$). Density functional theory (DFT) will be employed to calculate the electronic band structure and density of state (DOS) of this compound computationally. DFT is believed to provide the information about effect of H atom on electronic property of La-H superconductor in brief.

1.3 Objective of the study

The general objective of this work is to study the superconductivity of LaH_X ($X=1, 3, 4, 6$) electronic structure of La-H superconductivity with effect of increasing of Hydrogen atom.

1.3.1 The specific objectives are:

- To obtain the density of state of LaH_X ($X= 1, 3, 4, 6$)

- To obtain band structure of LaH_X ($X = 1, 3, 4, 6$) superconductivity;

- To calculate the superconducting critical temperature

- To study the effect of increase of hydrogen atom on the superconducting properties of the aforementioned compound.

1.4 Significance of the study

The outcome of this work will benefit the scientific community by supplementing the electronic band structure and DOS calculation by applying DFT. It may be used as an input for similar researchers who are engaged in related research areas.

CHAPTER TWO

Literature Review

2.1 History of superconductors

Heike Kamerlingh Onnes discovered superconductivity in 1911. He noticed that the resistance of mercury dropped abruptly at 4.2 K to a value below the resolution of his instruments. Later, in 1913, he won a Nobel Prize in physics for his research in this area. In 1933, W. Meissner and R. Oschenfeld discovered that a metal cooled into the superconducting state in a weak magnetic field expels the magnetic field from its interior. The SC is a perfect diamagnetism. In 1945, the Russian physicist V. Arkadiev first performed the experiment of using this expulsion of a magnetic field to levitate a small bar magnet above the surface of a SC. In the years between 1910 and 1986 superconductivity was only known for some metals and alloys and also ceramic materials, but in all cases critical temperatures were extremely low [1]. In 1973, a niobium alloy was produced with a critical temperature of 23.2 K. The 1980's were a decade of discoveries in field of superconductivity. The first theoretically predicted organic (carbon-based) SCs were successfully synthesized in 1980.

The search for a ceramic SC began with research conducted by several laboratories around the world. In 1986 the IBM group published results of research showing indications of superconductivity at about 30 K. Building on their work, several other laboratories soon demonstrated bulk superconductivity at 39 K in an oxide of lanthanum, strontium, and copper. Bednorz and Mueller received the 1988 Nobel Prize in Physics for their ground breaking work [9].

The University of Houston and University of Alabama groups came up with the idea of pressurizing the crystal from the inside by substituting similar atoms of a different size rather than using an external mechanical press. In January of 1987 they produced ceramic SC, the oxide $\text{YBa}_2\text{Cu}_3\text{O}_7$ (also known as 123 YBaCuO or YBCO), with a critical temperature 92K. The material has sparked the current technological revolution.

At least ten elements from the lanthanide series have been successfully substituted for yttrium in making the new oxide SCs. The current class of ceramic SCs with the highest transition temperatures are the mercuric-cuprates (cuprate = copper oxide).

The world record from 1993 with T_c of 138 K is now held by a thallium-doped, mercuric-cuprate comprised of the elements mercury, thallium, barium, calcium, copper and oxygen. Under extreme pressure its T_c is 25 to 30 degrees more at 300,000 atmospheres.

In 1997 researchers discovered that at a temperature very near absolute zero an alloy of gold and indium was both a SC and a natural magnet. Conventionally was held that a material with such properties could not exist since then, over a half-dozen such compounds have been found. Recent years have also seen the discovery of the first high temperature SC that does not contain any copper .

2.1.1 Main characteristics of superconductors

The diagram summarizes the phenomena associated with the main characteristics of superconductors (SC): diamagnetism and zero resistivity. Due to the mentioned characteristics, superconducting materials can withstand high currents which are called by super currents. It was also verified that the material loses its superconducting properties when the critical magnetic induction or critical temperature is exceeded.

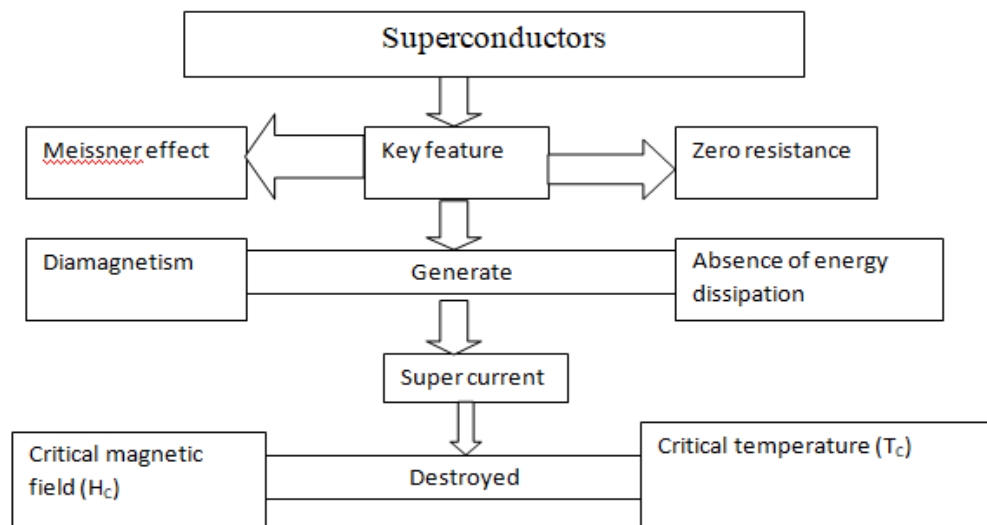


Figure 1: main characteristics of superconductors.

2.1.1.1 Meissner effect:

German physicians Walther Meissner and Robert Oschensfeld verify in 1933 that superconductors present different properties from the ideal conductors. By submitting the tin Sn, and lead Pb, at temperatures below the critical temperature and under the action of a magnetic field, they have found that magnetic field lines do not penetrate the sample of these materials, which corresponds to $\mathbf{B} = 0$ within the sample, being this phenomenon known as the Meissner effect [10]. With this discovery it was demonstrated that a superconductor is a diamagnetic material, while an ideal conductor despite its zero resistivity does not have this property. In this way, it was defined a new state of matter with very particular properties.

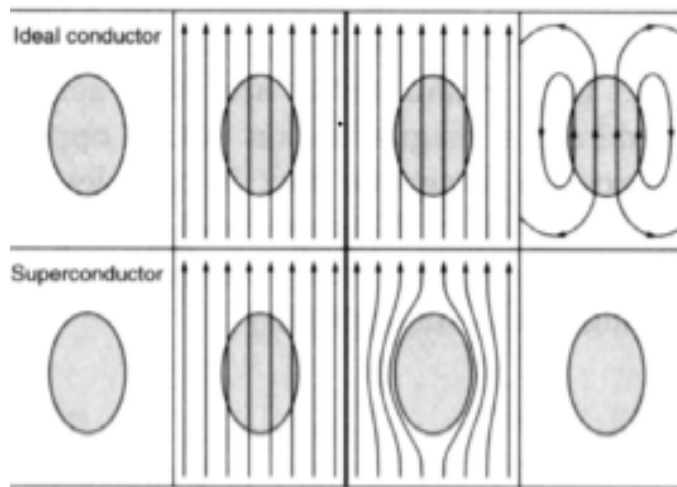


Figure 2: The Meissner effect

It is found that the superconductor expels the magnetic field from inside it, while the ideal conductor maintains its interior field.

2.1.1.2 Zero resistance:

The electrical **resistance** of an electrical conductor is a measure of the difficulty to pass an electric current through that conductor. The inverse quantity is electrical conductance, and is the ease with which an electric current passes. **Zero Resistance** is the condition of Superconductivity; where the Resistance is zero in Electronics [2].

2.1.1.3 Diamagnetism

A superconducting material kept in a magnetic field expels the magnetic flux out its body when cooled below the critical temperature and exhibits perfect diamagnetism. This is called MEISSNER EFFECT [4].

2.1.1.4 BCS theory:

The full microscopic theory of superconductivity presented in 1957 by Bardeen, Cooper, and Schrieffer has had good success in explaining the features of superconductors. The central feature of the BCS theory is that two electrons in the superconductor are able to form a bound pair called a Cooper pair if they somehow experience an attractive interaction. This notion at first seems counterintuitive since electrons normally repel one another because of their like charges. However, a net attraction can be achieved if the electrons interact with each other via the motion of the crystal lattice as the lattice structure is momentarily deformed by a passing electron. The BCS theory has been very successful in explaining the characteristic superconducting properties of zero resistance and flux expulsion [11].

2.1.2 Classification of superconductors

The current flow through the superconductor lowers the transition temperature. The transition temperature also decreases when an external magnetic field is applied. The response of the superconductors to the application of an external magnetic induction led to the classification of the superconductor material into two types: Type I and Type II superconductors.

If the magnetic field exceeds a critical value, different effects are observed depending on the material. Breaks the superconductivity suddenly, it is called a superconductor of the first kind or the Type I. On the other hand, superconductors of the second kind (Type II) have two critical field strengths; from the lower one, the field begins to penetrate; in the higher one, the superconductivity collapses. In the area in between, the magnetic field increasingly penetrates the conductor in the form of microscopically fine tubes. The magnetic flux in these flow tubes is quantized. Type II superconductors are attractive for technical applications due to their high current carrying capacity [12].

The superconductors of Type I are generally metals and some metallic alloys, being generally electrical conductors at ambient temperature, and acquire superconductivity properties at very low temperatures. The first element to be discovered by Heike Onnes in 1911 was the mercury (Hg), which had a virtually zero resistivity when subjected to a temperature of 4.2 K. Type II superconductors are formed essentially by metallic alloys and other compounds. The exceptions are the pure metals Vanadium (V), Technetium (Tc), niobium (Nb) and carbon (C) that are Type II superconductors. In general the critical temperature associated with this type of superconductors is much higher than that of Type I. The first discovered superconducting material of Type II was an alloy of lead and bismuth manufactured in 1930 by W. Haas and Voog which verified that the alloy present different characteristics of the superconductors Type I.

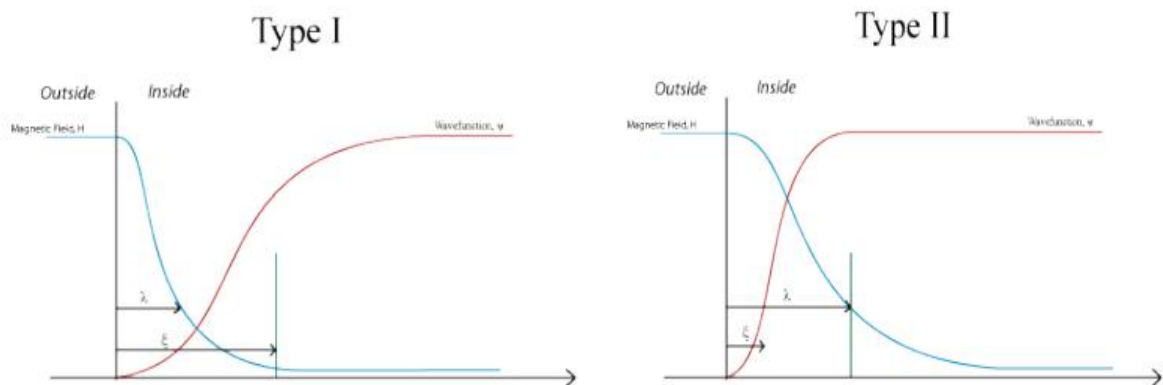


Figure 3: The current flow through the superconductor lowers the transition temperature [12].

The transition temperature also decreases when an external magnetic field is applied. If the magnetic field exceeds a critical value, different effects are observed depending on the material. Breaks the superconductivity suddenly, it is called a superconductor Type I. the field begins to penetrate; in the higher one, the superconductivity collapses. In the area in between, the magnetic field increasingly penetrates the conductor in the form of microscopically fine tubes.

2.2 High temperature superconductivity

High-temperature superconductors (abbreviated high-T_c or HTS) are operatively defined as materials that behave as Superconductors at temperatures above nearly 70 K. This is in fact the lowest temperature reachable by liquid nitrogen, one of the simplest coolant in cryogenics[9]. All superconducting materials known at ordinary pressures currently work far below ambient temperatures and therefore require cooling. The majority of high temperature superconductors are ceramics materials. On the other hand, Metallic superconductors usually work below 70 K: they are then called low temperature superconductors. Metallic superconductors are also ordinary superconductors, since they were discovered and used before the high-temperature ones. Ceramic superconductors are now becoming suitable for some practical use, but they still have many manufacturing issues and there are very few successful practical examples of employment. Most ceramics are brittle which makes the fabrication of wires from them very problematic [9].

The major advantage of high-temperature ceramic superconductors is that they can be cooled by using liquid nitrogen. [10] On the other hand, metallic superconductors require usually more difficult coolants - mostly liquid helium. Unfortunately, none of high-temperature superconductors are coolable using only dry ice, and none of them works at room temperature and pressure (they work well below the lowest temperature recorded on Earth). All high-temperature superconductors require some kind of cooling systems.

2.2.1 under pressure superconductivity

A new era of superconductivity was initiated by the discovery of high-temperature conventional superconductivity in H₂S [13] and LaH₁₀ [14]. This Review is meant to offer an up-to-date perspective on the new exciting field of high-temperature conventional superconductivity in hydrides at high pressure. The observed metallization pressure is consistent with that predicted by the most accurate theoretical calculations, i.e. 400 GPa [15]. Although it is still challenging to reach this pressure in experiments, these conditions are common in the core of celestial bodies, and now it is well established [16] that a large portion of Jupiter's core is formed by hydrogen in a metallic liquid state. At lower pressure, an alternative route to high-temperature hydrogen superconductivity was suggested, through chemical pre compression of the hydrogen sub-lattice in hydride materials [17, 18]. As a

consequence, in 2018, a new record of superconducting transition temperature (T_c) of 250K [14] was reported in a hydrogen-rich solid, LaH_{10} . Superconductivity at room temperature conventionally set at 300, is only away. In contrast to the previous record-holders for superconductivity, such as cuprates and Fe-based superconductors where the high- T_c is most likely due to a complex interplay between charge, spin and orbital fluctuations and lattice vibrations (phonons), superconductivity in hydrides is described by the conventional theory for superconductivity, which describes material such as aluminum, lead or niobium. What are different are the superconducting parameters that determine the critical temperatures that are exceptional compared to all previously studied compounds. This happens because extreme pressures allow stabilizing chemical environments which would not exist spontaneously at ambient pressure.

Pressure (p) is a thermodynamic quantity which plays an important role in modifying the properties of substances; for example, it can turn most semiconductors into metals. In this Review, we will distinguish two regimes: the first, high-pressure, extends from 1 to 100 Giga Pascal (GPa); the second, Mega bar pressure, from 100 GPa to the Tera Pascal range (1,000 GPa or 1 TPa). For comparison, 1 GPa is equivalent to 10,000 bar, or 9869 atmospheres. Thus, a pressure of 100 GPa (1 Mbar) equals roughly one million times the atmospheric pressure. Pressures in the Mega bar range are typically found in the interior of the planets: for example, the pressure in the core of the Earth ranges from 330 to 360 GPa [19], while that in Jupiter core is estimated to be above 1 TPa.

In order to understand how a solid can change when subjected to Mega bar pressures, let us consider a substance compressed at 200 GPa (2 Mbar). In most solids, this would correspond to a volume reduction of factor 1.5. In gases, the volume reduction can be more drastic [20]; for instance, the volume of hydrogen is reduced by a factor 10 from 0 to 200 GPa [21]. One can also estimate the free-energy change of the system induced by such compression. For this range of pressures, the pV term in the Gibbs free-energy, $G = E + pV$ is of the order of 10 eV per two atoms, i.e. it can easily exceed the energy of any chemical bond at zero pressure [22, 23, 24]. In other words, in a system subject to Mega bar pressures, chemical bonds are drastically altered, and new type of bonds may form. These arguments can provide a first hint on how high pressure may be used to form materials with physical and chemical properties different from

ambient pressure and hence shed light on problems such as room-temperature superconductivity.

2.3 Super hydrides

2.3.1 Clathrate based hydrogenic lattices

A number of CSP-based studies have computed very high T_c for binary alkaline earth or rare earth metal hydrides whose hydrogenic lattices are reminiscent of clathrates. The first system of this type to be predicted was a CaH_6 phase, which was thermodynamically and dynamically stable above 150 GPa [64]. The building block of this phase is the H_{24} sodalite-like cage illustrated in the top panel of Fig. 2 (a), which consists of six square and eight hexagonal faces. The metal atom lies in the center of this cage, and because the shortest H–H distance measures 1.24 Å, these hydrogen atoms are only weakly bonded to each other. The crystalline lattice that is formed from joining the $[4^6 6^8]$ polyhedral at the faces, shown in the bottom panel of Fig. 2(a), has Im_3m symmetry. The band structure of Im_3m CaH_6 contains degenerate bands at the Γ point that are partially occupied. Therefore, Wang et al. suggested that a John-Teller distortion, which removes this degeneracy, could yield a substantial electron-phonon coupling parameter. Indeed, this phase was calculated to have a remarkably large λ (electron-phonon coupling parameter) of 2.69, with the most significant contribution arising from modes associated with the vibrations of the atoms comprising the H_2 faces. Because of the large, λ T_c was estimated by solving the Eliashberg equations. It was calculated to be between 220 and 235 K for typical values of μ^* (coulomb potential), as shown in Table I, and it decreased at higher pressures.

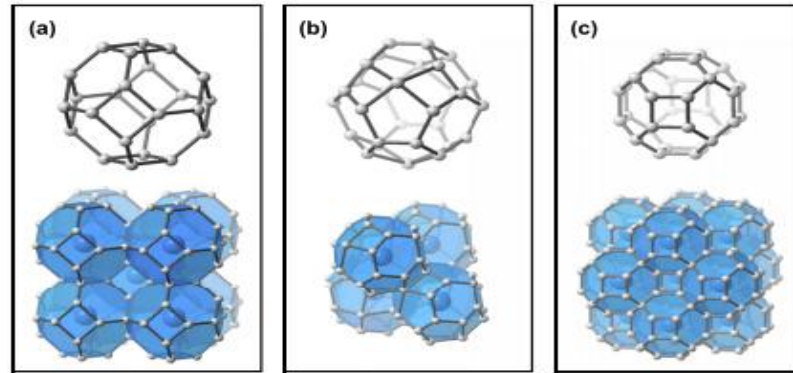


Figure 4: (Top panel) The hydrogenise clathrate cage structures

FIG.2. (Top panel) The hydrogenise clathrate cage structures and (bottom panel) extended (a) Im3m MH₆, (b) P6₃ /mmc MH₉, and (c) Fm3m MH₁₀ systems they form with a subset of the alkaline earth and rare earth metals.

The prediction of high T_c in CaH₆ inspired a computational study of an isotopic MgH₆ phase, which was found to become stable with respect to decomposition into MgH₂ and H₂ above 263 GPA when the ZPE was included [65]. But, because a convex hull plotting the ΔH_F of Im3m MgH₆ along with the ΔH_F of other stoichiometries that were previously found to be stable at lower pressures was not constructed, it is not clear if MgH₆ is thermodynamically stable or if it is only meta stable. The estimated T_c of MgH₆ at 300 GPA (see Table I) was somewhat higher than the largest T_c calculated for CaH₆. An isotopic strontium hex hydride was not a local minimum on the PES. However, R3m SrH₆, which can be derived from the Im3m structure by elongating four out of six of the closest metal-metal contacts and distorting the face that bisects them so it is no longer hexagonal, was stable at 250GPA [66]. This symmetry breaking distortion transformed the sodalities hydrogenic lattice into one-dimensional helical chains, and the resulting structure had a smaller λ and concomitantly a lower T_c 63 than its lighter cousins. A structurally analogous BaH₆ phase with a high T_c could not be located via CSP.

Moving to the d-block elements, computations have shown that ScH₆ and YH₆ phases with Im3m symmetry are also stable at pressures attainable in DACs. A related I4/mmm symmetry ZrH₆ phase, which can be obtained via a distortion of the Im3m lattice, has also recently been found via CSP calculations. In one study Im3m LaH₆ was computed to be thermodynamically stable at 100 GPA and 150 GPA, where as in another investigation, the LaH₆ stoichiometry was predicted to lie slightly above the convex hull and assumed the same R3m symmetry structure previously found for SrH₆. As shown in Table I, the electron_ phonon coupling of YH₆ was computed to be particularly high, $\lambda = 2.93$ at 120 GPA, and therefore its T_c was estimated to be at least 100 K higher than any of the other stable superconducting d-block hex hydrides.

The [4⁶5⁶6⁶] H₂₉ polyhedron shown in the top panel of Fig. 2(b) is composed of six irregular squares, six pentagons, and six hexagons. It is the building block of a hydrogenic clathrate-like lattice with P6₃ /mmc symmetry that has been predicted for a number of MH₉ stoichiometry rare-earth hydrides [68]. Phases with the MH₁₀ stoichiometry, on the other hand, were often

found to assume an Fm3m symmetry structure comprised of the $H_{32} [4^6 6^{12}]$ polyhedron, which is shown in Fig. 2(c) [68]. The stability of the clathrate cages under pressure was attributed to their dense packing, which yields a substantially lower PV term to the enthalpy. For example, at 300 GPA, a $P6_3/mmc$ symmetry YH_9 clathrate phase had the smallest volume out of any of the 500 lowest enthalpy structures found via CSP searches. The enthalpy of a phase that did not possess a clathrate-like structure was slightly lower, but the ZPE-corrected enthalpies of the two dynamically stable phases were within a few MeV /atom of each other [68]. However, because the estimated T_c s of the clathrate-like structures were significantly higher, they are provided in Table I. Below 210 GPA, Fm3m LaH_{10} was not a minimum on the PES, but a C2/m symmetry lattice that could be derived from the ideal structure via a slight distortion was dynamically stable. . of phases assuming the Im3m (MH_6), $P6_3/mmc$ (MH_9), and Fm3m (MH_{10}) sodalite structures illustrated in Fig. 2 computed at the pressures, P, and using the values of the Coulomb pseudo potential, μ^* , listed. Data are also provided for four structurally related phases that can be derived via a symmetry breaking distortion of the clathrate cages.

Table 1: Electron phonon coupling parameter, and superconducting critical temperature, T_c

Compound	P(GPa)	λ	μ^*	T_c (K)	Ref
MgH ₆	300	3.29	0.12	263	65
CaH ₆	150	2.69 – 2.71	0.13- .10	220- 235	64 ,69
SrH ₆	250	1.10	0.10	156	72
ScH ₆	350	1.25	0.10	135 ,169	70
ScH ₆	285	1.33	0.13- 0.10	130- 147	71
ScH ₆	300	1.20	0.13- 0.10	90- 100	68
YH ₆	120	2.93	0.13- 0.10	251- 264	68,73
YH ₆	120	3.19	0.10	247	69
ZrH ₆	295	1.20	0.13	114	71
LaH ₆	100	2.00	0.13- 0.10	150- 160	68
ScH ₉	400	1.50	0.13-0.10	150-190	68
YH ₉	150	4.42	0.13- 0.10	253- 276	68
CeH ₉	200	2.30	0.10	117	74
YH ₁₀	400	2.41	0.13- 0.10	287-303	68
YH ₁₀	250	2.58	0.13- 0.10	244- 265,305- 326	75
YH ₁₀	250	2.67	0.1	291	69
LaH ₁₀	200	2.28	0.1	288	68
LaH ₁₀	210	3.41	0.13- 0.10	219- 238, 274- 286	75
LaH ₁₀	300	1.74	0.10	231	69
LaH ₁₀	200	3.57	0.13- 0.10	218-200, 245- 229	67
AcH ₁₀	200	3.46	0.15- 0.10	177-204, 226-251	74

As shown in Table I, enticingly high T_c values, some which even surpass room temperature, have been computed for the YH₉, YH₁₀, and LaH_{10n} stoichiometries. Although stable clathritic LaH₉, CeH₉, CeH₁₀, and PrH₉ phases were also found via CSP, their computed T_c values were much lower, < 56 K [68] because the lower frequency vibrations, which are result of the heavier element, reduce T_c in a BCS superconductor. On the other hand, a Meta stable R3m symmetry AcH₁₀ phase was computed to have a quite high T_c [74]. Its hydrogenic lattice resembled the

clathrate structure illustrated in Fig. 2(c), except the square faces were replaced by trapezoids. A combined experimental-theoretical study recently reported the synthesis of $P6_3/mmc$ CeH_9 at 80 GPa. In contrast to the findings of Ref. [68], the authors concluded that the computed T_c of $P6_3/mmc$ CeH_9 was quite appreciable [64].

Out of any of the binary hydrides studied computationally, YH_{10} and LaH_{10} hold the record T_c values to date. A detailed analysis of the functional derivative of T_c with respect to $\alpha^2 F(\omega)$ for the MH_6 and MH_{10} stoichiometry clathrate cages revealed that because of the long H–H distances in their hydrogenic lattices, a clear distinction could not be made between the bending and stretching modes of the hydrogenic motifs. All of these phonon modes contributed to the electron-phonon interaction, and it was proposed that this is the origin of the very high T_c computed for these phases [69].

The aforementioned theoretical predictions inspired experimental studies. In 2016 a superhydride of lanthanum consistent with the theoretically predicted structure for LaH_{10} was synthesized at [69] GPa and decompression led to $aFm3m \rightarrow R3m \rightarrow C2/m$ phase transformation. Two very recent studies observed dramatic drops in resistivity in the lanthanum/hydrogen system under pressure, tantalizing with the allure of high temperature superconductivity. If confirmed, both of these findings would break the current record for the highest measured T_c values previously observed in the hydrogen/sulfur system. Measure T_c up to 260 K at 185 GPa, and preliminary studies suggested T_c may be as high as 280 K at 200 GPa, in a sample whose diffraction peaks were consistent with the previously synthesized $LaH_{10} \pm x$. Because the samples were synthesized using different methods, and the measurements were obtained at different pressures, it is likely that the phase, or mixture of phases, made in the two studies are not the same.

2.3.2 Superconductivity in P-H and La-H Hydrides

Sulfur-hydride is not an isolated example of conventional high- T_c superconductivity at high pressures [31]. Less than a year after the discovery of superconductivity in sulfur hydride [13], Drozdov and coworkers have reported high- T_c superconductivity in a second hydrogen rich compound at extreme pressures: resistivity measurements on phosphane (PH_3) show that the samples, which are semiconductor at ambient pressure, metalized above 40 GPa and become

superconducting at around 80 GPa, exhibiting a Maximum T_c of 100 K at about 200 GPa [32]. In the original publication, the composition responsible for the superconducting phase and its crystal structure, nor the mechanism responsible for T_c was addressed.

Analogies with the superconducting sulfur-hydride, obtained from a H_2S precursor, suggest that the superconductivity in the P-H system is conventional, but that the composition of the superconducting phase might be different from the original PH_3 stoichiometry. In order to shed light on this matter, some of us used ab initio techniques to map out the high-pressure phase diagram of the P-H binary system by exploring the compositional and configurationally space of PH_n with structure prediction methods, and estimated the superconducting properties of the most promising phases [33]). Interestingly, our results, as well as similar theoretical studies, reported that all the high-pressure binary phases of P and H are metastable to elemental decomposition in the pressure range 100–300 GPa. However, the critical temperatures of the three phases closest to the convex hull (PH , PH_2 , and PH_3) reproduce to a good approximation the experimental values.

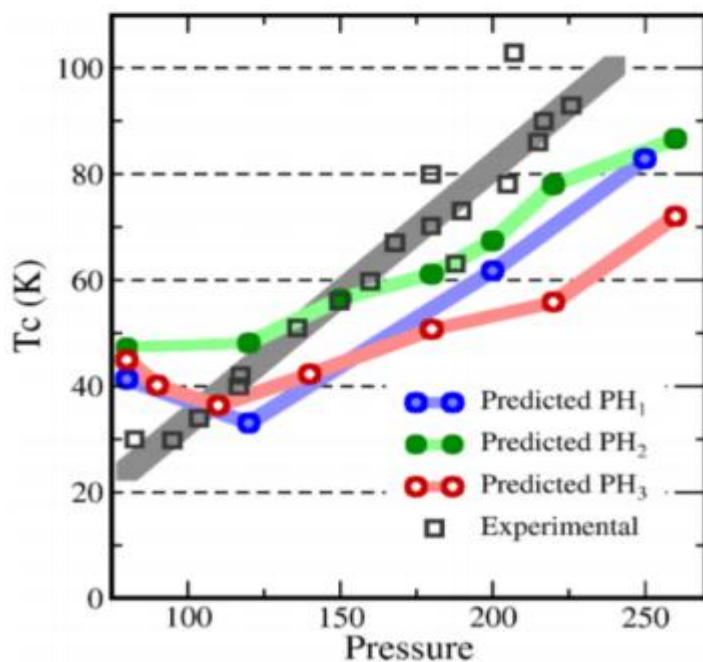


Figure 5 SCDFT calculated critical temperatures T_c for P-H composition as function of pressure as presented in Ref. [33].

Experimental values of T_c extracted from Drozdov et al. [32] are shown in black squares.

In 2018, the work on H-rich compositions in the La-H system set a new superconducting record, representing the first measurement of T_c near room temperature. Ab initio techniques have been vital to predict the initial phase diagram [34, 35]. Fig. 4 shows the calculated convex hull of formation enthalpy without zero-point energy at 200 GPa. In this figure, one can see that there are many stable compositions in the convex hull. An exciting composition, predicted to be responsible for the nearly room-temperature superconductivity, is LaH_{10} [34, 35], which becomes enthalpically stable for pressure above 175 GPa and remains on the convex hull well above 300 GPa [36].

This first lanthanum super hydride was synthesized under pressure above 160 GPa and upon heating to 1000 K. The X-ray data indicated that the stoichiometry corresponds to LaH_{10+x} ($-1 < x < 2$) which is close to the predicted high- T_c LaH_{10} [34, 35]. Measured the temperature dependence of the resistivity of La heated with NH_3BH_3 as hydrogen source under similar pressure and observed a drop in the resistance at 260 K upon cooling and 248 K upon warming the sample, which was assigned to the superconducting transition of LaH_{10+x} ($1 < x < 2$). In their original claim, they also observed a series of resistance anomalies at temperatures as high as 280 K. However, neither a zero resistance state nor additional confirmations (such as the Meissner effect or isotope effects or the effect of an external magnetic field on the transition temperature) were provided. Simultaneously, an independent research measured a superconducting transition T_c 215 K in LaH_x [37] and subsequently a T_c of 250 K [38].

Apart from setting a new T_c record, high-pressure experiments in the La-H system played a significant role also in establishing methods to control the high-pressure synthesis of materials. This is a crucial point since many –if not all– of the structures observed in high-pressure experiments are Meta stable phases [39] (or near thermodynamic equilibrium), and it represents one of the most significant challenges when using high pressures in practical applications [40].

Different strategies to help the stabilization of HP-materials have been proposed. A major role is played by the precise control of thermodynamic conditions [36] and the case of La-H represents a step towards mastering it.

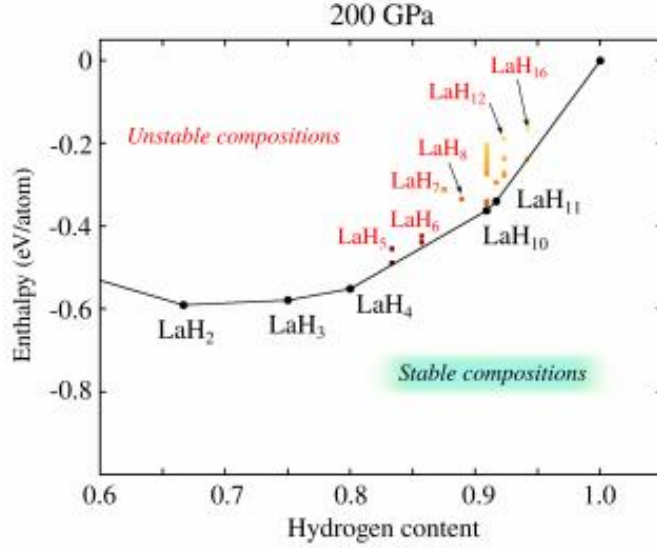


Figure 6: Computed phase diagram of La-H compositions under pressure at 200 GPa (see Ref. [36]).

For low pressures, the LaH_{10} composition is not stable and only develops as a stable point in the classical convex hull of enthalpy formation above 175 GPa. Interestingly many other phases are stable points and could be accessible by controlling thermodynamic conditions.

2.3.2.1 Superconductivity of LaHm

It was shown before that different lanthanum hydrides can undergo a series of superconducting transitions at different pressures with different T_C [25], LaHm phases ($m = 4, \dots, 9, 11$) at different pressures, and calculating their T_C using the SCDF method or the numerical solution of the Eliashberg equation would have been very computationally expensive. The calculated T_C of LaHm phases ($m = 4, \dots, 9, 11$) using the Allen–Dynes (A-D) formula [27,28] in the pressure range of 150–180 GPa, which is the experimentally studied pressure region [25], with the commonly accepted μ^* values (0.1–0.15). We consider this interval of μ^* reasonable because for LaH_{10} and LaH_{16} the A-D formula yielded μ^* equal to 0.11 and 0.2, respectively. The results point to LaH_4 , LaH_6 , and LaH_7 as the compounds that could undergo the experimentally observed transition at ~ 215 K with the critical magnetic field $\mu_0 H_C(0) = 60\text{--}70$ T; the other transition at ~ 112 K with the critical magnetic field $\mu_0 H_C(0) = 20\text{--}25$ T could occur in LaH_5 , LaH_8 , and LaH_{11} .

2.3.2.2 Superconductivity of LaH_{10} phases

Superconductivity of LaH_{10} has been confirmed in experiments [25, 26]. The experimental observations found the maximum $T_C \sim 251$ K at 168 GPa [26] or $T_C \sim 260$ K at 180 GPa [25], which is close to the $R3\bar{m}$ - $Fm3\bar{m}$ phase transition (but in the cubic phase). The value of the Coulomb pseudo potential μ^* for the LaH_{10} phases determined using the SCDFPT equals 0.2 at 200 GPa. For $Fm3\bar{m}$ - LaH_{10} , the calculations within the DFPT give a very high EPC coefficient $\lambda = 3.75$, which leads to $T_C = 271$ K at 200 GPa. The crystal structures were generated using VESTA software [28]; the atoms of La and hydrogen are shown as large orange and small black balls, respectively; blue arrows show displacements of the hydrogen atoms in comparison with the cubic H_8 cluster.

For $Fm3\bar{m}$ - LaH_{10} , the calculations within the DFPT give a very high EPC coefficient $\lambda = 3.75$, which leads to $T_C = 271$ K at 200 GPa.

The Eliashberg function for the cubic $Fm3\bar{m}$ LaH_{10} at 200 GPa. The numerical solution of the Eliashberg equation for the cubic LaH_{10} at the experimental pressure of 170 GPa results in $T_C = 259$ K which is in close agreement with the theoretical results [30] and experiments [25, 26].

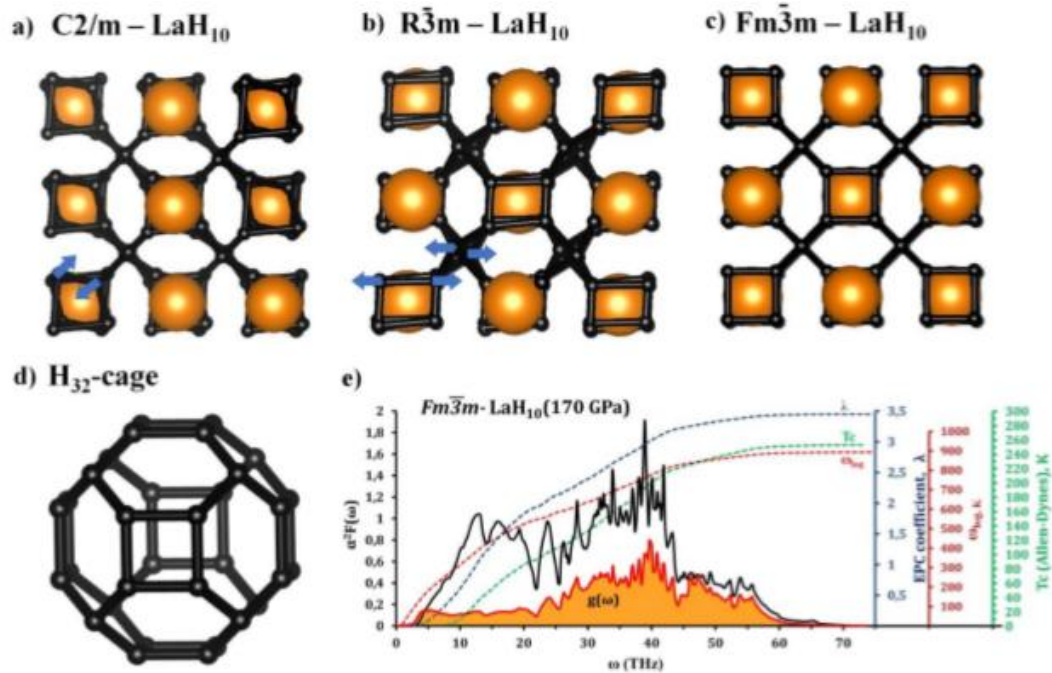


Figure 7: Crystal structures of LaH_{10}

Crystal structures of a) $C2m/-LaH_{10}$, b) $R3 m-LaH_{10}$, c) $Fm3 m-LaH_{10}$, and d) hydrogen H 32 cage common for these phases; e) the Eliashberg $\alpha^2F(\omega)$ function (black curve), phonon density of states (orange), cumulative ω_{log} (red), EPC coefficient λ (blue), and critical transition temperature TC (green) of $Fm3 m-LaH_{10}$ at 170 GPa [28].

2.3.2.3 Superconductivity of LaH16

The lanthanum atoms form an hcp sub lattice and are coordinated by 12 hydrogen atoms (Fig. 6a). These H-units consist of three parallel layers of hydrogen atoms. The distances between the hydrogen atoms in the first, second, and third layers at 150 GPa are 1.07, 1.02, and 1.07 Å, respectively. The distance between the closest hydrogen atoms from different layers is 1.25 Å, so these layers form infinite 2D networks [29].

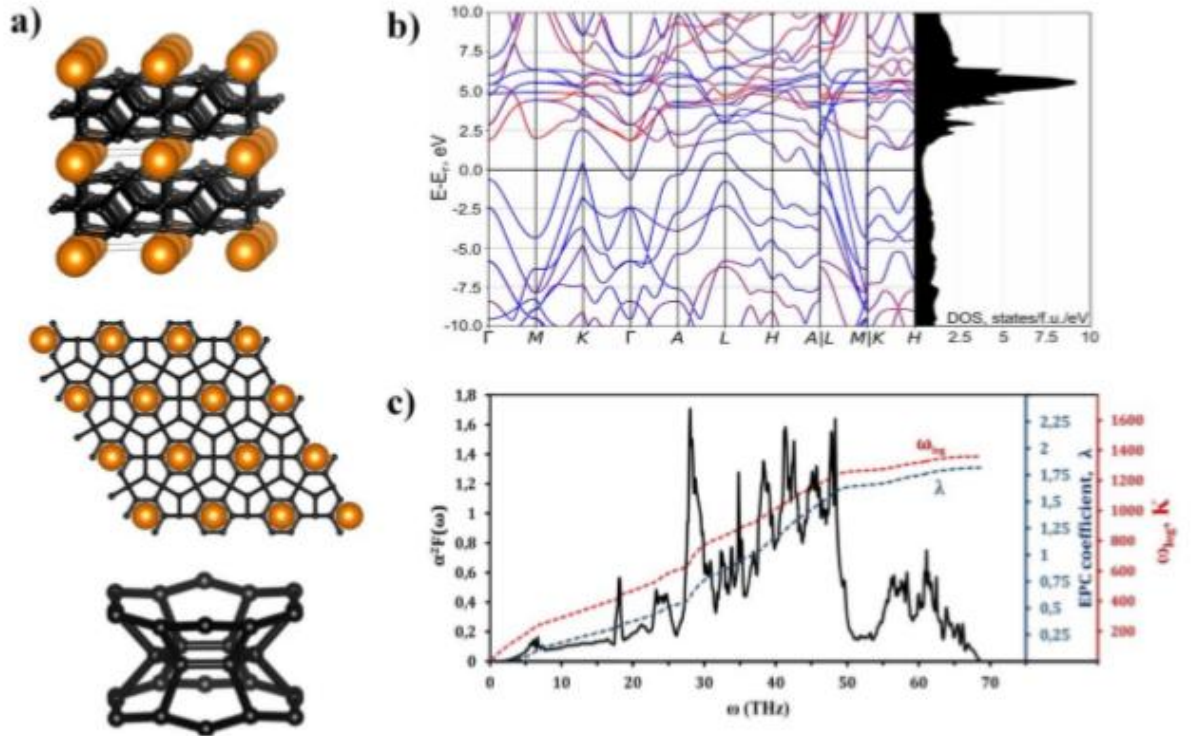


Figure 8: Crystal structure of $P6mmm/-LaH_{16}$

a) Crystal structure of $P6mmm$ / - LaH_{16} at 150 GPa; b) band structure and DOS of LaH_{16} (red lines are for La, blue — for H) at 250 GPa; c) the Eliashberg function $\alpha^2F(\omega)$ (black), cumulative $\omega_{\log}$ (red), and the EPC coefficient λ (blue) of $P6/mmm\text{-LaH}_{16}$ at 200 GPa [29].

2.5 Estimating the superconducting critical temperature

The equations that are typically employed to estimate T_c for compressed hydrides from first principles calculations are introduced. If the superconducting properties of a material can be described using BCS theory, or its extensions, the material is referred to as a conventional superconductor. The electron-phonon coupling mechanism that leads to superconductivity within BCS theory can be pictured as follows. When an electron passes through a crystalline lattice of positively charged ions, the Coulomb attraction between the electron and the ion causes the lattice to distort. The ionic displacement, in turn, attracts another electron with opposite spin and momentum. The two electrons become correlated and form a boson-like quasi particle called a Cooper pair. All of the Cooper pairs in a superconductor break up at a temperature higher than T_c , thereby destroying the superconducting state.

Within BCS theory, T_c can be estimated via

$$T_c = 1.14 \langle \omega \rangle \exp \left[\frac{-1}{g(E_f)V} \right] \dots \dots \dots 1$$

Where $\langle \omega \rangle$ is the average phonon energy, $g(E_f)$ is the single spin electronic DOS at E_f , and V is the pairing potential between two electrons that occurs via the electron-phonon interaction (which is assumed to be constant within $2\hbar\omega_{\text{cut}}$ of the Fermi surface, and zero otherwise). The cutoff frequency, ω_{cut} , is often taken to be the Debye frequency or the average frequency, and it defines the size of the superconducting band gap.

Despite the tremendous successes of BCS theory in describing the properties of conventional superconductors, substantial differences between theory and experiment became apparent, for example, for the metals Pb and Hg. The reason for this turned out to be that the assumption of constant V is too simple: the electron-phonon interaction is not instantaneous, but rather it is retarded in time, and the quasi particle states have a finite lifetime. Eliashberg theory is an extension of BCS theory that explicitly includes the retardation effects. It is beyond the scope of this Perspective to discuss the Eliashberg equations, which can be solved numerically.

However, we introduce the key quantity of Eliashberg theory, the Eliashberg spectral function, which can be calculated (from first principles) or measured (by inverting tunneling spectra).

The Eliashberg spectral function, $\alpha^2F(\omega)$, is defined as

$$\alpha^2F(\omega) = \frac{1}{2\pi g(E_F)} \sum_{\mathbf{q}, \mathbf{j}} \frac{\gamma_{\mathbf{q}, \mathbf{j}}}{\omega_{\mathbf{q}, \mathbf{j}}} \delta(\hbar\omega - \hbar\omega_{\mathbf{q}, \mathbf{j}}) \quad \dots\dots\dots 2$$

Where the line width, $\gamma_{\mathbf{q}, \mathbf{j}}$, of a phonon mode $\mathbf{j}$ with a wave vector $\mathbf{q}$, $\omega_{\mathbf{q}, \mathbf{j}}$, is given by

$$\gamma_{\mathbf{q}, \mathbf{j}} = 2\pi\omega_{\mathbf{q}, \mathbf{j}} \sum_{\mathbf{k}, \mathbf{n}} |g_{\mathbf{k}, \mathbf{n}, \mathbf{k}+\mathbf{q}, \mathbf{j}}^j|^2 \frac{\epsilon_{\mathbf{k}, \mathbf{n}}}{\omega_{\mathbf{q}, \mathbf{j}}} \delta(\epsilon_{\mathbf{k}, \mathbf{n}} - E_F) \delta(\epsilon_{\mathbf{k}+\mathbf{q}, \mathbf{n}} - E_F) \quad \dots\dots\dots 3$$

These equations describe the scattering of an electron on the Fermi surface with a resulting transfer of momentum to a phonon, where $g_{\mathbf{k}, \mathbf{n}, \mathbf{k}+\mathbf{q}, \mathbf{j}}^j$ is the electron-phonon matrix element, or the probability, associated with this process. Given the Eliashberg function, the electron-phonon coupling, λ , can be calculated via

$$\lambda = 2 \int_0^\infty \frac{\alpha^2F(\omega)}{\omega} d\omega$$

The Eliashberg formalism requires as input a parameter that describes the screened Coulomb repulsion between the electrons within a Cooper pair. This renormalized Coulomb repulsion parameter, μ^* , is often called the Coulomb pseudo potential. Analytical expressions that can be used to approximate, μ^* have been proposed, but typically it is used as a free parameter with reasonable values lying in the range of 0.1–0.2. We note that there is one theoretical approach, density functional theory for superconductors (SCDFT), which takes into account the retardation effects and does not require any empirical parameters for the calculation of T_c . However, only a few studies have used SCDFT for hydrides under high pressure [62].

One of the first simple expressions that could be used to estimate T_c was developed by McMillan. Based on twenty two numerical solutions of the Eliashberg equations for $0 \leq \mu^* < 0.25$, $0 < \lambda < 1.5$, and a single shape for the $\alpha^2F(\omega)$, function modeled after the phonon DOS in Nb, McMillan showed that the following expression, where ω_D is the Debye temperature, could be used to provide a reasonable estimate for T_c [63] :

$$T_C = \frac{\omega_D}{1.45} \exp \left[-\frac{1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)} \right] \dots\dots\dots 5$$

Subsequently, Allen and Dynes carried out 200 numerical solutions for various shapes of the Eli ash berg function, using a wide range of λ values [63]. They proposed the following modification of the McMillan equation:

$$T_C = \frac{\omega}{1.2} \ln \exp \left[-\frac{1.04(1+\lambda)}{\eta - \mu^*(1+0.62\lambda)} \right] \dots\dots\dots 6$$

Where $\omega_{\ln}$ is the logarithmic average frequency of the phonon modes obtained via

$$\omega_{\ln} = \exp \left[\frac{2}{\lambda} \int_0^{\infty} \frac{d\omega}{\omega} \alpha^2 F(\omega) \ln \omega \right] \dots\dots\dots 7$$

Usually, once DFT calculations have been carried out to determine the Eli ash berg spectral function, and from it, λT_C is estimated via Eq. (6) for a range of μ^* values. However, whereas the Allen-Dynes modified McMillan equation implies that T_C reaches a maximum limit when $\lambda \rightarrow \infty$ a maximum does not exist for the exact solution of the Eli ash berg equations. In cases where the electron-phonon coupling is strong, i.e., $\lambda \geq 1.5$, Eq. (6) often yields a lower limit to T_C . To remedy this, Allen and Dynes proposed multiplying Eq. (6) by scaling factors that correct for the strong coupling and shape dependence of T_C . However, the studies discussed herein typically solved the Eli ash berg equations numerically when λ was calculated to be large.

2.6 Computational and theoretical considerations

Pressure can have a profound effect on the compositions, structures, properties, and stability of solid phases [53]. Who would have guessed that the “simple metal” sodium becomes an insulator by 200 GPa, the “noble” gas helium reacts with sodium to form a stable Na_2He [54] phase at GPa, and hydrides with unusual stoichiometries such as NaH_3 , $118 \text{ Xe}(\text{H}_2)_8$, [55] and FeH_5 [56] can be synthesized in a DAC Such chemistry could not have been predicted using rules and bonding schemes that are based upon our experience at 1 atm. At the same time, experiments that approach the pressures in the Earth’s core (~350 GPa) are challenging, and the results can be difficult to analyze. This has led to the development of a symbiotic relationship between theoreticians and experimentalists, where a feedback loop between experiment and theory has often led to important discoveries.

Because of the difficulty inherent in performing high pressure syntheses and fully characterizing the phases made, many theoretical groups have employed a priori methods for CSP to propose stable structures to experimental groups. Structure prediction is a global optimization problem, where the goal is to determine the unit cell parameters and atomic coordinates that correspond to the global minimum, as well as low lying local minima, in the potential energy surface (PES). However, as with all optimization problems, it is not possible to guarantee that the global minimum has been found within a CSP search. Thus, many of the algorithms that have been adapted towards CSP employ well known Meta heuristics that can find sufficiently good solutions for the minima. This includes (quasi) random searches, techniques based on swarm behavior, evolutionary (genetic) algorithms, and basin or minima hopping, as well as simulated annealing and Meta dynamics. A number of excellent reviews describing these methods, [57] and the synergy between CSP and experiment in high pressure research [53] are available.

Typically hundreds, if not thousands, of structures are optimized to the nearest local minimum within a single CSP search. Moreover, often multiple searches need to be carried out for different stoichiometries and for a range of pressures. Because computations of the vibrational contributions to the free energy are significantly more time consuming than geometry optimizations, most CSP searches explore the 0 K PES. Reliable force fields are often not available for matter at extreme conditions, so the local optimizations are usually performed using DFT with a functional based on the generalized gradient approximation (GGA); often the Perdew, Burke and Ernzerhof (PBE) [58] GGA is employed. However, the inclusion of HartreeFock exchange can significantly affect the calculated transition pressures between different phases, [59] stabilization pressures, [60] computed T_c values, and it can lead to symmetry breaking structural distortions. Even though still rare, it is becoming more common to re-optimize the most stable structures found in a GGA-CSP search using hybrid functional. [60] In situations where metallization occurs because of pressure induced band broadening of the valence and conduction bands, and their eventual overlap, GGA functional predict a too low metallization pressure. Hybrid functional provides better estimates of the pressure at which band gap closure occurs. The inclusion of dispersion can also affect transition pressures for molecular solids, and DFT+U has been employed for strongly correlated systems. An adaptive genetic algorithm, which uses DFT calculations performed on a small set of candidate

structures to parameterize, on-the-fly, classical potentials that are then employed for the local minimizations, has successfully been applied to predict the structures of binary and ternary phases under pressure.

For systems containing light elements, the inclusion of the zero point energy (ZPE) can influence the relative enthalpies of different phases, as well as the identity of the thermodynamically stable species and their stability ranges. This is especially true if the hydrogen sub lattices of the structures whose enthalpies are compared have different motifs. Cold melting, which can occur if the difference in enthalpy between different phases is smaller than the ZPE, has been proposed for metal hydrides that contain a heavy element. It is currently standard practice to consider how the ZPE affects the stability of the phases found in a CSP search carried out at 0 K, but finite temperature contributions to the free energy are rarely considered, even though they may also be important. Because the experimental conditions employed can affect which phases (i.e., stable or Meta stable) are made, [61] it is important for theory to identify not only the global minimum but also low lying local minima.

Figure 9 illustrates the typical work flow employed by theoreticians searching for novel pressure stabilized superconducting phases, including those discussed in this Perspective. First, CSP searches are carried out on the 0 K GGA, PES as a function of composition and pressure. Promising candidate structures are optimized using more accurate settings, and their enthalpies of formation, ΔH_F , are plotted vs. the mole fraction of H_2 they contain. The ΔH_F is employed to generate the convex hull, which is the set of line segments below which no other points lie. The phases whose ΔH_F comprise the hull are thermodynamically stable. Phonon calculations are carried out to confirm the dynamic stability of phases that are on the hull or close to it, and the results are used to construct a new convex hull that includes the ZPE contributions to the enthalpy at 0 K. The structure and electronic structure of select systems are computed and analyzed.

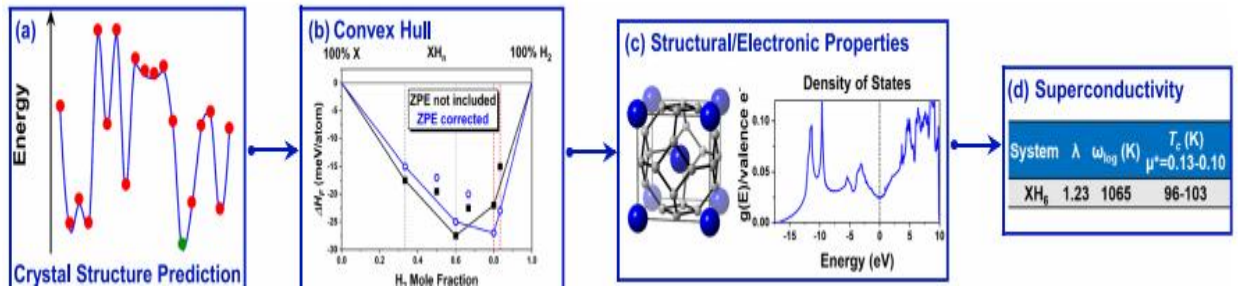


Figure 9: Typical work flow used to predict pressure stabilized hydride based superconductors [61].

- (a) Candidate structures are found using ab initio crystal structure prediction techniques.
- (b) The ΔH_F of the most promising phases is plotted vs. the mole fraction of H_2 they contain. The convex hulls without and with ZPE contributions are determined.
- (c) The electronic structure of thermodynamically stable and select Meta stable species is computed to identify systems that have a high DOS at EF.
- (d) Electron-phonon coupling calculations are carried out,

2.6.1 BCS theory

The theory of Bardeen, Cooper and Schrieffer (BCS) [11] has been the first theory of superconductivity able to explain the microscopic nature of the superconducting state. BCS is perhaps one of the most successful theories in condensed matter physics. Although its predictive power is limited, compared to modern ab initio methods, it is still today an essential theoretical and computational framework for the characterization and the understanding of superconducting materials.

BCS theory assumes the following electronic Hamiltonian:

$$H = H_0 + H_{\text{int}} \dots\dots\dots(8)$$

$$H_0 = \sum_{k\sigma} c k \sigma + c k \sigma \dots\dots\dots(9)$$

$$H_{\text{int}} = \sum V k k' (c \pm k \downarrow c + k \uparrow) (C k \uparrow C - k \downarrow) \dots\dots\dots (10)$$

Where $C_{\mathbf{k}\sigma}$ and $C_{\mathbf{k}\sigma}^+$ are annihilation and creation operators for the Bloch-wave with a wave vector $\mathbf{k}$ and spin σ respectively. $V_{\mathbf{k}\mathbf{k}'} = 0$ are matrix elements of the leading superconducting interaction. Under the assumption of a momentum independent phononic coupling, it can be written as:

$$V_{\mathbf{k}\mathbf{k}'} = -V\theta(\hbar\omega_D - \epsilon_{\mathbf{k}'})\theta(\hbar\omega_D - \epsilon_{\mathbf{k}}) \dots \dots \dots (11)$$

Where ω_D is the Debye frequency BCS solved this model by an ansatz for the many-body wave function and found an exact solution. The same can be achieved following Gor'kov [51] and solving for the Green's function:

$$G(\mathbf{k}, \tau) = C_{\mathbf{k}\sigma}(\tau)C_{\mathbf{k}\sigma}(0) - T\tau \dots \dots \dots (12)$$

Where the imaginary-time dependence of the operators are defined as $X(\tau) = \exp(H\tau)X \exp(-H\tau)$ and $T\tau$ denotes time ordered product, and the expectation value of physical quantity A is calculated as:

$$\langle A \rangle = Tr(\exp(-\beta H) A) / Tr \exp(-\beta H) \dots \dots \dots (13)$$

G satisfies the equation of motion

$$\left(-\frac{d}{d\tau} - \epsilon_{\mathbf{k}}\right) G(\mathbf{k}, \tau) = \sigma(\tau) - \sum_{\mathbf{k}'} V_{\mathbf{k}\mathbf{k}'} \langle T\tau C_{\pm\mathbf{k}\downarrow}(\tau) C_{-\mathbf{k}'}(\tau) C_{\mathbf{k}\uparrow}(0) \rangle \dots \dots \dots (14)$$

That can be solved by introducing the mean-field approximation:

$$\langle T\tau C_{\pm\mathbf{k}\downarrow}(\tau) C_{\mathbf{k}\uparrow}(\tau) C_{-\mathbf{k}\downarrow}(0) \rangle \rightarrow F(\mathbf{k}, 0) F^*(\mathbf{k}, \tau) \dots \dots \dots (15)$$

With the definition of the anomalous Green's function

$$\tilde{G}(\mathbf{k}, i\omega_n) = \frac{-i\omega_n - \epsilon_{\mathbf{k}}}{\omega_{2n} + E_{\mathbf{k}}} \dots \dots \dots (16)$$

$$F(\mathbf{k}, i\omega_n) = \frac{\Delta_{\mathbf{k}}}{\omega_{2n} + E_{\mathbf{k}}} \dots \dots \dots (17)$$

Where $\omega_n = (2n + 1)\pi k_B T$ are the Matsubara frequencies, $E_{\mathbf{k}}^2 = \epsilon_{\mathbf{k}}^2 + |\Delta_{\mathbf{k}}|^2$ and the function $\Delta_{\mathbf{k}}$ is define as:

$$\Delta_k = \sum_{k'} V_{kk'} F(k', 0) \dots \dots \dots (18)$$

This quantity carries the meaning of a (superconducting) gap and satisfies the self-consistent BCS equation:

$$\Delta_k = \frac{1}{\beta} \sum_{k'} \frac{V_{kk'} \Delta_{k'}}{\omega_{k'}^2 + E_k^2} = \sum_{k'} \frac{V_{kk'} \Delta_{k'}}{2E_k} \tanh \left(\frac{E_{k'}}{2K_B T} \right) \dots \dots \dots (19)$$

1. For $T \rightarrow 0$ and $V_N(E_F) \ll 1$

$$\Delta \approx 2\omega_D \exp(-1/V_N(E_F)) \dots \dots \dots (20)$$

Where $N(E_F)$ is the density of states at the Fermi level

2. For $T \rightarrow T_c$ then $\Delta \rightarrow 0$, one obtains

$$T_c = 1.13 \omega_D \exp \left(\frac{-1}{V_N(E_F)} \right) \dots \dots \dots (21)$$

By comparing (19) and (20), we find the universal BCS ratio:

$$2\Delta/T_c = 4/1.13 \approx 3.54$$

The main drawback of BCS theory is that the pairing interaction between electrons assumed in Eq. 10 is an instantaneous effective field, while, as we will see from the ab initio density functional framework, is dynamical. The intrinsic timescale should be taken into account to achieve a quantitative accuracy using many-body perturbation theory including explicitly the lattice degrees of freedom.

2.6.2 Density Functional Theory

Due to its excellent cost/accuracy ratio, density functional theory (DFT) is the method of choice for the calculations of electronic and lattice properties of materials [34]. In particular, it is the universally used approach to compute, from first principles, DFT is most conveniently employed in practice using the Kohn and Sham (KS) construct i.e. introducing an auxiliary system of non interacting electrons which reproduces exactly the ground-state density of the

fully interacting system. Although density functional theory has its roots in the Thomas–Fermi model for the electronic structure of materials, DFT was first put on a firm theoretical footing by Walter Kohn and Pierre Hohenberg in the framework of the two Hohenberg–Kohn theorems (H–K) [78]. The original H–K theorems held only for non-degenerate ground states in the absence of a magnetic field, although they have since been generalized to encompass these.

The Hohenberg–Kohn theorems relate to any system consisting of electrons moving under the influence of an external potential.

Theorem1. The external potential (and hence the total energy), is a unique functional of the electron density.

If two systems of electrons, one trapped in a potential $v_1(r)$ and the other in $v_2(r)$ have the same ground-state density $n(r)$ then is necessarily a constant.

Corollary 1: the ground-state density uniquely determines the potential and thus all properties of the system, including the many-body wave function. In particular, the H–K functional, defined as $F[n] = T[n] + U[n]$ is a universal functional of the density (not depending explicitly on the external potential).

Corollary 2: In light of the fact that the sum of the occupied energies provides the energy content of the Hamiltonian, a unique functional of the ground state charge density, the spectrum of the Hamiltonian is also a unique functional of the ground state charge density.[76]

Theorem2. The functional that delivers the ground-state energy of the system gives the lowest energy if and only if the input density is the true ground-state density.

In other words, the energy content of the Hamiltonian reaches its absolute minimum, i.e., the ground state, when the charge density is that of the ground state.

For any positive integer N and potential $V(r)$, a density functional $F(n)$ exists such that

$$E(V,N)[n] = F(n) + \int V(r)n(r)d^3r \dots\dots\dots (22)$$

Reaches its minimal value at the ground-state density of N electrons in the potential $v(r)$ The minimal then the ground-state energy of this system. From the content of the current literature,

an apparent miss understanding have arisen concerning this second theorem. It has persisted for more than 50 years. Indeed, the above correct statement of the second theorem can also be written as

$$E(V,N)[n'] = F(n') + \int V(r)n'(r)d^3r \geq E(V,N)[n] \\ = F(n) + \int V(r)n(r)d^3r \dots \dots \dots (23)$$

Where n is the true ground state density and n' is any other density different from that for the ground state. It is important to note that the external potential, a unique functional of n , is the same on both sides of the inequality.

The total number of particle, N , kept constant. The charge density is obtained by summing over basis functions for the occupied states only. For every set of trial basis functions, the iterations for self-consistency lead to a stationary solution. The Rayleigh theorem for Eigen values states that as one increases the size of the basis set, by augmenting an initial basis set, the Eigen values obtained with the larger basis set are lower than or equal to their corresponding values obtained with the initial basis set. This fact leads to the conundrum of self-consistent calculations. A DFT calculation with a single basis set, upon reaching self-consistency, produces a stationary solution that can vary with the size of the basis set. There exist an infinite number of such solutions. The referenced misunderstanding of the second theorem of DFT has consisted of assuming that a given stationary solution, obtained with a judiciously selected single basis set, is the actual ground state solution. The reader should consult the Rayleigh theorem for Eigen values for the generalized minimization of the energy to reach, in a verifiable manner, the actual ground state of the system under study.

In the context of computational materials science, ab initio (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. Thus, a problem for a representative super cell of a material with n electrons can

be studied as a set of n one-electron Schrödinger-like equations, which are also known as Kohn–Sham equations[77].

The Kohn-Sham system is obtained from the solution of the Schrödinger equation:

$$H_S \Psi_n(r) = (-\frac{1}{2} + v_s(r)) \Psi_n(r) = E_n \Psi_n(r) \dots\dots\dots (24)$$

Where the effective potential v_s is to be computed self consistently and reads:

$$v_s(r) = V_{ext}(r) + e^2 \frac{\rho(r')}{|r-r'|} + V_{xc}(r) \dots\dots\dots (25)$$

Where $V_{ext}(r)$ is the potential due to the bare nuclei, the second term on the right-hand side is the Hartree potential, and V_{xc} is the functional derivative of $E_{xc}[\rho]$ with respect to the electronic density. $E_{xc}[\rho]$ is a universal (not material-dependent) functional of the density; it is a central object in DFT, for which many good approximations exist [49]. The electronic density is obtained by occupying the orbital's that are solutions of Eq. 1, $\Psi_n(r)$ with the lowest Eigen values (E_n) according to the Pauli principle:

$$\rho(r) = 2 \sum_{n=0}^{N/2-1} |\Psi_n(r)|^2 \dots\dots\dots (26)$$

For a metallic system the occupation of the states can be smeared around the Fermi level, with a distribution function $S(\epsilon)$:

$$\rho(r, \epsilon) = 2 \sum_n |\Psi_n(r)|^2 S(\epsilon - E_n) \dots\dots\dots (27)$$

Among other functions, S can be chosen as the Fermi-Dirac distribution with a fictitious electronic temperature that helps to stabilize numerical calculations. Using DFT in this scheme, the total energy of a given system is expressed a sum of terms:

$$E(\rho) = 2 \sum_n S(\epsilon_n) \epsilon_n - e^2/2 \iint \rho(r) \rho(r') / |r-r'| dr dr' + E_{xc}(\rho) - \int \rho(r) V_{xc}(r) dr \dots\dots\dots (28)$$

This equation allows us to directly compute the dynamical matrix and the phonon spectrum by performing numerical derivatives through small finite displacements of the atoms. Alternatively, assuming small amplitudes, phonon's can be studied as infinitesimal perturbations, using density functional perturbation theory (DFPT) applied to the phonon

perturbation [50]. A great advantage of this method consists in its capability to treat perturbation of whatever wavelength without the need to simulate the lattice distortion on a unit cell commensurate with the q -vector of the phonon.

2.6.3 A Computational Procedure of the Quantum-ESPRESSO Code

Quantum-ESPRESSO (QE), an open-source code, is used to perform all the first-principles calculations presented in this thesis. QE is an integrated suite of computer codes for electronic structure calculations and materials modeling based on density-functional theory, plane-wave basis sets and pseudo potentials to represent electron-ion interactions [75]. It is free software distributed under the terms of the GNU General Public License (GPL). The computational procedure of the QE code includes an iterative solution of the Kohn-Sham equations and optimized charge-density mixing routines. This includes the calculation of the Hellmann-Feynman forces acting on the atoms and the stresses on the unit cell. The total energy is optimized with respect to the positions of the atoms within a unit cell.

2.6.4 The Plane-wave self-consistent field method

The set of Kohn-Sham equations is strongly non-linear and has to be solved through an iterative method. The plane-wave self-consistent field (PWScf) method implements an iterative approach to reach self-consistency, using at each step iterative diagonalization technique in the framework of the plane wave pseudo potential method. The procedure followed to do the self consistent calculation is: one first makes a trial guess for the wave functions of all electrons and calculate its effective Kohn-Sham potential, VKS. With this effective potential, the Kohn Sham equation is solved to get a new wave function. From these, a new VKS is calculated, and so on. The procedure is terminated when the charge density does not vary much anymore. At this point self-consistency is reached, meaning that the wave function and the effective potential are self-consistent with each other, i.e. the wave functions correspond to those that one would get from solving the Schrödinger equations using that potential. Both norm-conserving (NC) and ultra soft (US) pseudo potentials are implemented in the PWScf method.

There are few input parameters that are optimized to find a compromise between expediting the computational procedure to find the ground state energy, but with an appropriate accuracy. The

wave functions of a system depend on the electronic configurations of the constituent atom(s). The pseudo potential simplifies these wave functions to expedite the computational procedure. Generally, valence electrons participate in chemical reactions, bond formation, electronic structure, and thermodynamic properties of materials. Therefore, the pseudo potential approach freezes the nucleus and core electrons into an approximated potential. The wave functions of the valence electrons are only considered, and using the pseudo potential approach further simplifies these wave functions [75].

K-points are unique points used to solve the Kohn-Sham equations within the irreducible Brillouin zone. Systems with high symmetry utilize less k-point, there by expediting the computation procedure; likewise, systems with low symmetry require more k-points, which increase the computational time. The k-point is a system-dependent term, and is optimized not only to expedite the computational procedure, but to provide acceptable accurate results too. Kinetic energy cut-off (E-cut) is a system-dependent term, which is included to restrict the wave function expansion to a finite value. The E-cut term is optimized not to only expedite the computational procedure, but to provide acceptable accurate results as well.

CHAPTER THREE

METHODOLOGY

Density functional theory (DFT) is a computational quantum mechanical modeling method used in physics, chemistry and materials science to investigate the electronic structure (or nuclear structure) (principally the ground state) of many-body systems, in particular atoms, molecules, and the condense phases. Using this theory, the properties of a many-electron system can be determined by using functional, i.e. Functions of another function, which in this case are the spatially dependent electron density. DFT is among the most popular and versatile methods available in condensed-matter physics, computational physics, and computational chemistry.

In this work we apply DFT as implemented by the computer program known as QUANTUM ESPRESSO. And we used pseudo potential approximation for electronic structure calculation for determination of density of states, Fermi energy, total energy, and electronic structure along high symmetric.

We done non - magnetic calculation; we will look for different pseudo potentials from QUANTUM ESPRESSO home page; we use none relative pseudo potentials. In this work we used different software including XMGRACE FORTRAN, QUANTUM ESPRESSO XCRYSDEN others software packages.

Input File for a Simple PWScf Calculation

The input file for PWScf is constructed in a number of NAME_LISTS and INPUT_CARDS. The use of NAME_LISTS allows specifying the value of an input variable only when it is needed and to define default values for most variables that need not be specified. They are read in specific order and are ignored if not required. Three NAME_LISTS are mandatory in PWScf. The first is &CONTROL which consists of the input variable that control the flux of the calculation and the amount of input/output on disk and on the screen. Input variables specifying the systems under consideration are listed in &SYSTEM. The third mandatory

NAME_LIST is &ELECTRONS, which contains the input variables that control the algorithms used to reach the self-consistent solution of the Kohn-Sham equations for the electrons.

INPUT_CARDS on the other hand are used to provide input data that are always needed and would be boring to specify with the variable-name = variable-value syntax used by NAME_LISTS. Similarly, there are three mandatory INPUT_CARDS. The name, mass, and pseudo potential used for each atomic species present in the system are specified in ATOMIC_SPECIES. ATOMIC_POSITIONS is where the type and coordinates of each atom in the unit cell are specified. K_POINTS is the last mandatory INPUT_CARD that contains the coordinates and weights of the k-points used for the Brillouin zone integration. To estimate critical temperature of Lanthanum hydrides superconductor use parameter μ^* is coulomb pseudo potential (0.13) and Debye temperature 3000K [62].

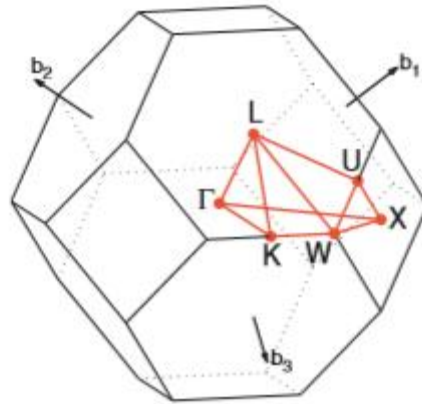


Figure 10: Brillouin zone of FCC lattice Path: Γ -X-W-K- Γ -L-U-W-L-K-U-X.

CHAPTER FOUR

RESULT AND DISCUSSION

4.1. Electronic band structure and density of state (DOS) of LaH_x ($x=1, 3, 4, 6$)

In this thesis we present the simulation result of the electronic band structure, crystal structure and density of electron state (DOS) of Lanthanum hydrides (LaH_1 , LaH_3 , LaH_4 , LaH_6). We start by discussing the lowest hydride LaH_1 and LaH_3 which is well studied under pressure at by the system and at low pressures. Figure9 is crystal structure of LaH_3 which was obtaining by XCRYSDEN and the guessed Brava is type p- cubic. Face center cubic phase.

In the figure 10a: and figure 11 a, we present the band structure obtained along high symmetry (Γ -X-W-K- Γ -L-U-W-L-K) direction of LaH_1 and LaH_3 . We found that the band structure of LaH_1 (fig 10a) and LaH_3 (fig 11a) are not crossing the Fermi level. These bands and DOS (Fig 10b, fig 11b) confirm that LaH_1 and LaH_3 are an insulator from nature of their electronic band structure. LaH_1 and LaH_3 are not superconductors in agreement with the experimental report.

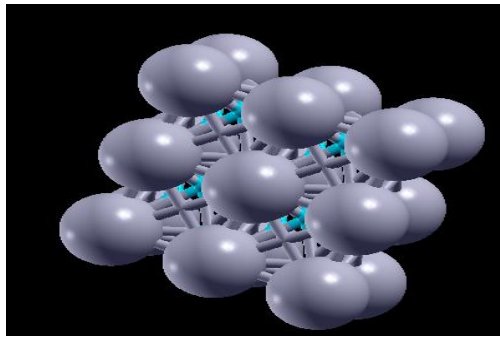


Figure11: predicted Crystal Structure of LaH_3 .

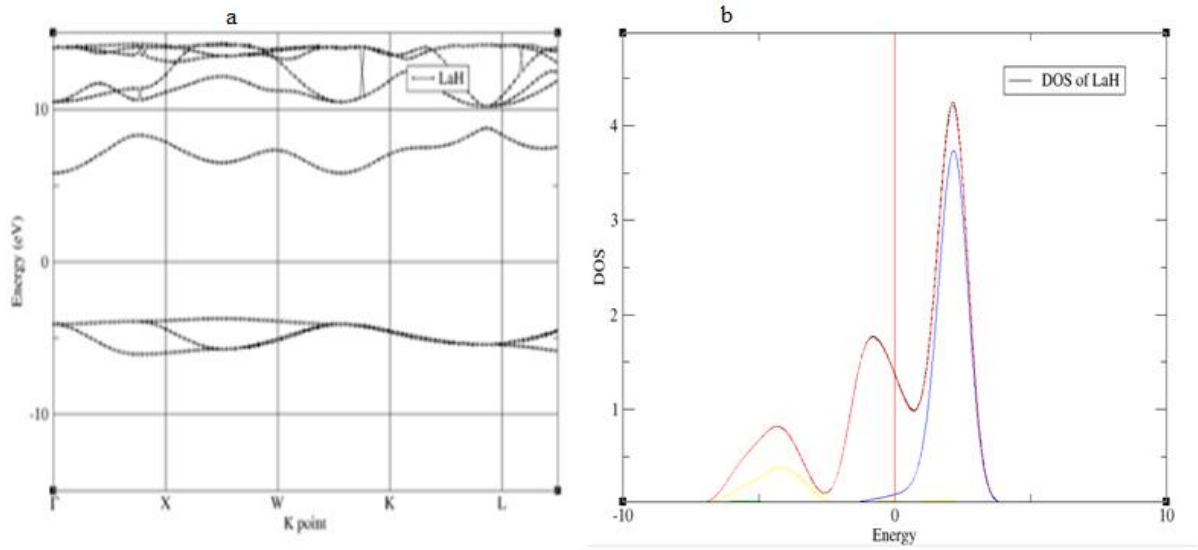


Figure 12: a, electronic band structure LaH_1 ; b, density of state of LaH_1

Figure 12: a, electronic band structure LaH_1 ; b, density of state of LaH_1 (red line is for total density, blue line for lanthanum and yellow line for hydrogen)

We compared the band width from the Fermi level, for example, in Figure 10a the band width is far from Fermi energy. When we see at some particular k point (at X k point) is 7.87815 and Fermi energy is lie between -15 eV to 15 eV.

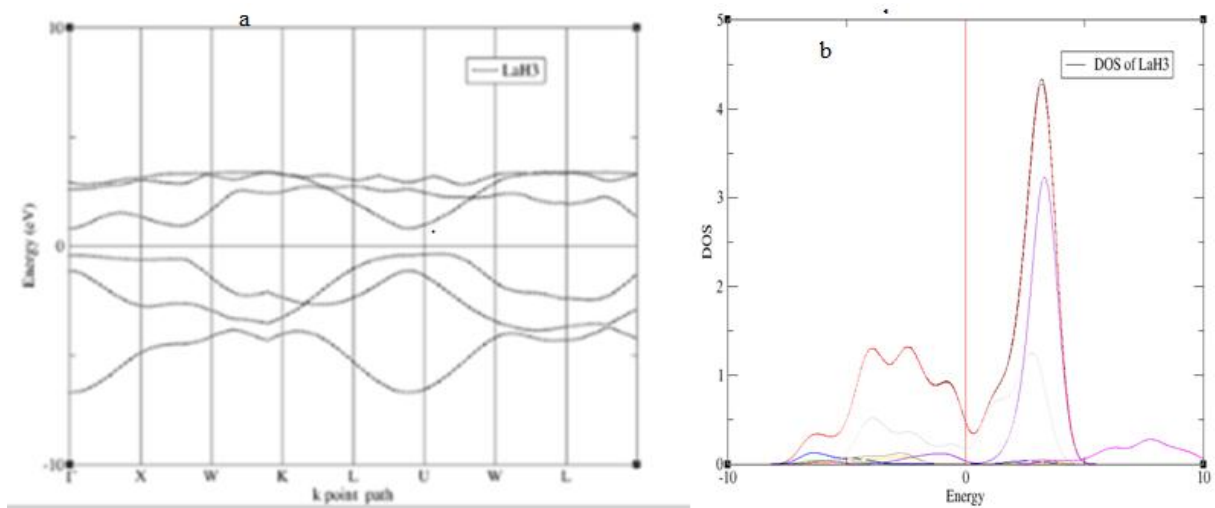


Figure13: a, Electronic band structure; b, density of state of LaH_3 .

Figure 13 at this band structure band width is from Fermi energy when we see at some particular k point (at X k point) is at this band structure band width is relatively not far from Fermi energy when we see at some particular k point (at X k point) is the measured value is 1.33053; Fermi energy lie between -10 eV to 10 eV .s

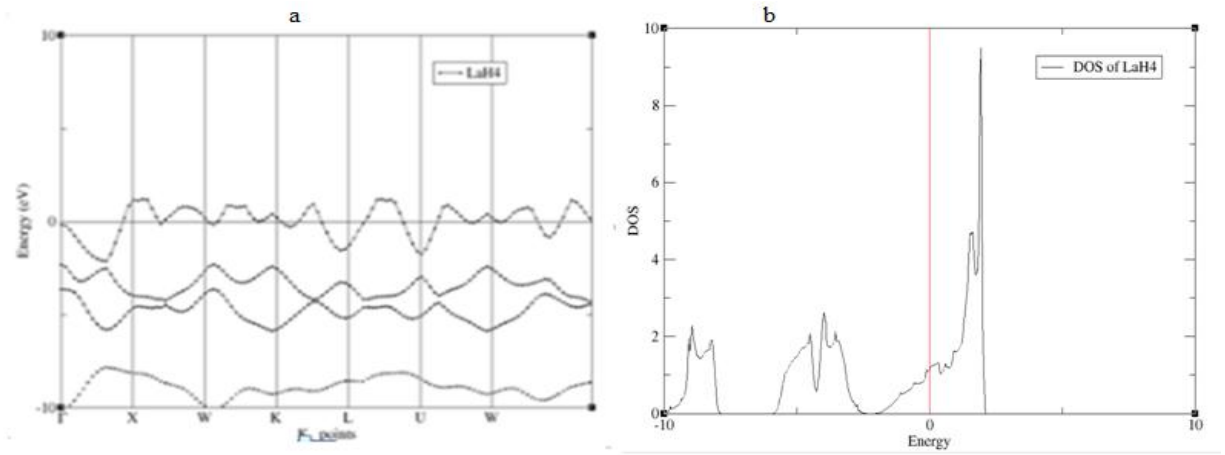


Figure 14: a, Electronic band structure b, density of state of LaH₄

Figure 14a and 14a are the band structure of LaH₄ and LaH₆. One can see that there are bands that cross the Fermi level. This is one of the indications for their superconducting nature. The Fermi level is reduced compared to LaH₁ and LaH₃. As it is already known the increment of Hydrogen atom improves the critical temperature. This may be due to the change in the band structure and the density of state (Fig 12b and Fig 13b).

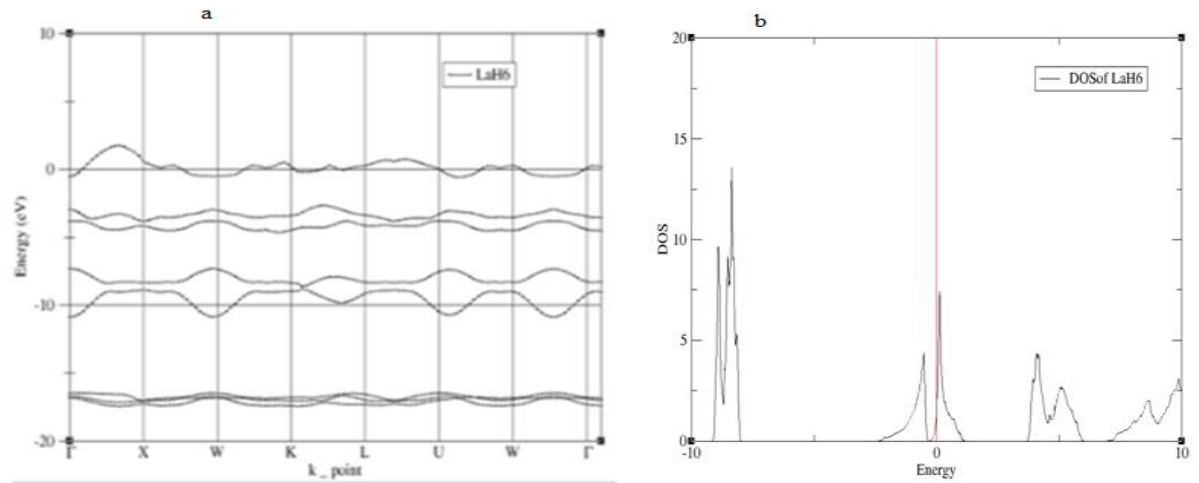


Figure15: a, Electronic band structure; b, density of state of LaH₆

Table 2 and Table 3 are the result obtained from the above electronic band structure and Density of state (DOS) simulation. as it is clearly presented in table2, increment of Hydrogen result in reducing the bandwidth from the Fermi level. In table 3, the density of state is found increasing.

No	System	Bandwidth
1	LaH ₁	7.87815
2	LaH ₃	1.33053
3	LaH ₄	1.18537
4	LaH ₆	0.576859

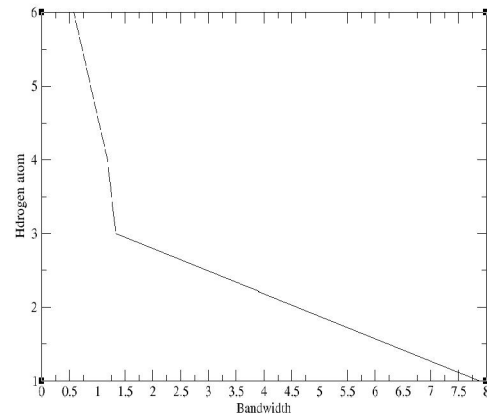


Table 2: Bandwidth measured at X k_{point} Graph 1: The graph of hydrogen atom VS Bandwidth

No	System	Value
1	LaH ₁	0.101541
2	LaH ₃	0.402661
3	LaH ₄	1.11345
4	LaH ₆	1.14166

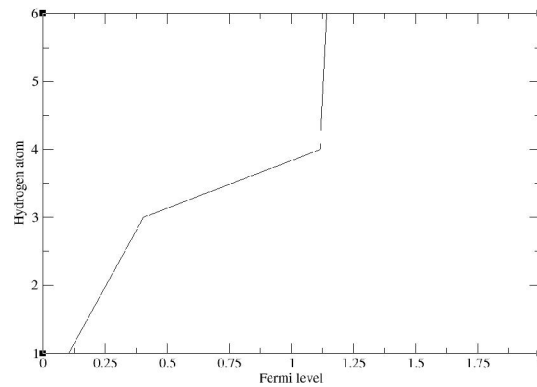


Table 3: density of state from Fermi level

Graph 2: the graph of hydrogen atom VS Fermi level

4.2 Calculation of Superconducting critical temperature (T_c)

Experimental report [69] indicated that Lanthanum based hydrogen rich compound shows BCS type. With this understanding and using the density of state result we calculated the critical temperature. The critical superconducting transition temperature was calculated with reasonable approximation using the following well know formula for LaH₄ and LaH₆.

$$T_C = \frac{\omega_D}{1.45} \exp \left[-\frac{1.04(1 + \lambda)}{\lambda - \mu^* (1 + 0.62\lambda)} \right]$$

For LaH₄ where λ electron - phonon coupling parameter is 1.11345 and μ^* is coulomb pseudo potential (0.13) ω_D is Debye temperature 3000K

$$T_C = 2068.96K \exp [-2.197988/0.89370593]$$

$$T_C = 2068.96K [0.085455]$$

$$T_C = 176.87K$$

For LaH₆ where λ electron - phonon coupling parameter is 1.14166 and μ^* is coulomb pseudo potential (0.13) ω_D is Debye temperature 3000K

$$T_C = 2068.96K \exp [-2.2273264/0.919642139]$$

$$T_C = 2068.96K \exp [-2.4219490447]$$

$$T_C = 183.6K$$

When we compare critical temperature of LaH₄ and LaH₆; the value increases from 176.7K to 183.6K. This is due to the effect of increasing hydrogen atom.

CHAPTER FIVE

CONCLUSION

The increment of T_c to near to room temperature in metallic hydrogen, or hydrogen rich compounds arose the interest of many scientists. Most of the report has been done under pressure. The researcher was interested to work on hydrogen rich compound to understand the nature of the band structure and the density of state. Since first principle Method (DFT) on superconductivity predictions have played a crucial role in guiding these experimental discoveries, we applied it as implemented in QUANTUM ESPRESSO. The electronic band structure, density of state and superconducting properties of LaH_X with $X = 1, 3, 4, 6$ were studied within the density functional theory which gives possible explanations of the observed superconducting critical temperature 176.8K and 183.6K. We also confirmed that as the number of Hydrogen increases the band structure and the density of state changes. The change is in agreement with the experimental reported result.

Recommendation: Due to the existence of many bands far from the Fermi level we suggest further study on the role of these bands for the mechanism of high TC.

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