Chapter

Superconductivity in Materials under Extreme Conditions: An *ab-initio* Prediction from Density Functional Theory

Thiti Bovornratanaraks and Prutthipong Tsuppayakorn-aek

Abstract

The relation between thermodynamically stable and electronic structure preparation is one of the fundamental questions in physics, geophysics and chemistry. Since the discovery of the novel structure, this has remained as one of the main questions regarding the very foundation of elemental metals. Needless to say this has also bearings on extreme conditions physics, where again the relation between structure and performance is of direct interest. Crystal structures have been mainly at ambient conditions, i.e. at room temperature and ambient pressure. Nevertheless it was realized early that there is also a fundamental relation between volume and structure, and that this dependence could be most fruitfully studied by means of high pressure experimental techniques. From a theoretical point of view this is an ideal type of experiment, since only the volume is changed, which is a very clean variation of the external conditions. Therefore, at least in principle, the theoretical approach remains the same irrespective of the high pressure loading of the experimental sample. Theoretical modeling is needed to explain the measured data on the pressure volume relationships in crystal structures. Among those physical properties manifested itself under high pressure, superconductivity has emerged as a prominent property affected by pressure. Several candidate structure of materials are explored by *ab initio* random structure searching (AIRSS). This has been carried out in combination with density functional theory (DFT). The remarkable solution of AIRSS is possible to expect a superconductivity under high pressure. This chapter provide a systematically review of the structural prediction and superconductivity in elemental metals, i.e. lithium, strontium, scandium, arsenic.

Keywords: *ab initio* random structure searching, density functional theory, superconductor, lithium, strontium, scandium, arsenic

1. Introduction

It is a long time since Kohn and Sham pave the way to the self-consistent equation, based on the exchange and correlation effects in 1965, leading the Kohn–Sham (KS) Equation [1]. This has ignited the success of quantum physics and chemistry, specifically many-body problem, owing to the KS equation can be utilized for the ground state energy. Briefly stated, the KS equation formalism of

density functional theory (DFT) described the motion of electron nuclei, which separated to be two part: the energy of electron $E_{electron}$ and the Coulomb interactions between the nuclei E_{nuclei} And what is more, the details of Ewald summations have been described extensively in Refs. [2, 3]. Apart from this, $E_{electron}$ and E_{nuclei} were performed by using the pseudopotential approximation within the KS equation. It is because of the effects of Coulomb interactions between the nuclei E_{nuclei}, as being in accordance with the the core electrons E_{core}, that the terms $E_{electron}$ and E_{core} used in the static crystal energy of materials relevant to the energies of valence electrons and pseudocores. Subsequently, the KS equation displayed the term $E_{electron}$ is from the summation of quasiparticle eigenvalues, corresponding the Kohn–Sham orbital, of occupied states.

Regarding thermodynamic properties, the Gibbs free energy is considered for the static crystal energy of materials; however, the KS equation formalism of DFT carried out at a temperature of 0 K. The Gibbs free energy therefore reduced to the Enthalpy. This, appearing at first glance to be high potential for high-pressure physics, is actually demonstrated the importance of superconductivity. According to the aforementioned theoretical findings by the KS equation formalism of DFT, resulting the exchange and correlation effects E_{xc}. Following this, Perdew et al. [4] presented a simple derivation of a simple of generalized gradient approximations (GGA) with E_{xc}. This methodology appropriated, it is well known to GGA with Perdew-Burke-Ernzerhof (PBE), for description of atoms, molecules, and solids. This is due to the fact that the GGA-PBE method give an accurate with the most energetically important. As a result of this, the role of the GGA-PBE method is key factor in achieving the ground-state energy of the static crystal materials. Herein, we preformed mainly the PBE formalism of GGA for calculations of lithium, strontium, scandium, and arsenic under high pressure.

The extensive studies of electronic structure were initiated chiefly by the KS equation formalism of DFT. In principle, one should note the quasiparticle eigenvalues of occupied states is useful for achieving the electronic band structure, density of sates, phonon dispersion. It is also interesting to note the DFT used mainly strong sides for prediction the metallicity, leading to the prediction of superconducting transition temperature. For considered the superconductivity, the PBE formalism of GGA for exchange-correlation energy is suitable for interpret the metallicity. This implied that the reliable theoretical study has quite a predictive potential, moreover, the GGA-PBE for the exchange-correlation energy give an accurate description of dynamical stability of crystal structure. One of the well-known Bardeen-Cooper-Schrieffer (BCS) theory [5] were already discussed phonon mediated superconductivity, leading to the way to vast both experimental and theoretical studies on high-pressure research. At this stage, using the KS equation formalism of DFT with the GGA-PBE for the exchange-correlation energy were used to have unique features of phonon mediated superconductivity, showing towards the evidence of superconducting materials as well.

There is alternative way to use the KS equation formalism of DFT with the GGA-PBE. It is well known to *ab initio* random structure searching (AIRSS). The AIRSS method have been described extensively in Refs. [6, 7]. Especially, the AIRSS method is useful in achieving the high-pressure research owing to it can predict novel structure under compressed conditions. The reliable theory for ground-state structure can help to interpret experimental data. In fact, there is also quite some experimental observation cannot identify the atomic position and crystal symmetry. The AIRSS method is powerful tool and it can guide further experimental studies.

High pressure physics is important for structural phase transitions in materials [8–18]. Regarding a crystal structure of materials under high pressure, it can enhance electronic properties of materials [19–21]. Nowadays, superconductivity is

one of the most charming in physical properties. Many materials were predicted to be a superconducting transition temperature (T_c), such as SH_3 [22–25], LaH_{10} [26–28], YH_{10} [28–30], CeH_{10} [17, 31]. It is worth note that hydrogen (H) is a role important for promoting a T_c. For example, the case of LaH_{10} was shown that the T_c reached 250 K at 170 GPa [26]. The existence of H displayed that it can support pure element lanthanum (La), one can see that the T_c of pure element lanthanum is 5.88 K [32]. It is interesting to note that the physical property of pure elemental metal should be mentioned.

As mentioned above, a structural prediction is a key factor for achieving a T_c. We referred the original predictions regarding superconductivity in strontium (Sr), it is beginning to show that the T_c of the predicted phase increased with a increasing pressure [33]. The case of strontium is interested. At high pressure, Sr. displayed structural phase transition from a simple structure to a complex structure [34–37]. We can see that Sr. is a normal metal at ambient pressure, with a increasing pressure, Sr. is a metallicity, indicating that it is a superconductivity [33]. Moreover, Sr. is not only superconducting phase at high pressure, but also calcium (Ca) indicating possible increasing of the T_c also at high pressure [38].

A curious aspect of a T_c increased with increasing pressure. We found that Ca is one of a periodic table, indicating the highest T_c among the periodic table [38–40]. Moreover, it is not always clear whether or not that the increased pressure and T_c are increased. We note that scandium (Sc) [14] and arsenic (As) [12], shown a possible decreasing of T_c with a increasing pressure [12, 14]. Hence, the focus is on pure elemental metals are interesting. This is because that the prediction discovered to novel structure [12, 14], leading to the superconductivity at high pressure.

According to the aforementioned superconductor findings, the characteristic of electronic structure is often attributed to the T_c [14, 17, 41]. It is interesting that Lithium (Li) has the second highest T_c among the elemental metals [42–45]. The electron localization function (ELF) is one of the tools can determine the T_c [14, 17]. The nature of chemical bonding is directly shown in the ELF, it is considered to be consistent with the highest T_c; this implies that a strong bonding supports the T_c of the metals [46].

Regarding superconductivity in the metals [12, 14, 17, 41], a lattice dynamic is a key factor for consideration a stable structure. In practice, we can achieve the superconducting structure through electron–phonon coupling (EPC) [12, 14, 17, 41]. For example, recent work on LaH_{10} has shown that the quantum effect is important for the stabilization and destabilization [27]. In fact, both thermodynamically and dynamically structures have to consistent. Generally, the solution of dynamically structure is a harmonic phonon but the case of LaH_{10} shown that it displayed an anharmonic phonon. This because the EPC exhibited the destabilized structure. Hence, it is worth to note that Sr. is possible to be an anharmonic phonon in the Sr-III structure (the β-tin structure) At this point, we found that there is a discrepancy between a experimental observation and a theoretical study [33–37, 47]. Herein we review the superconductivity in the elemental metals both the experimental observation and the theoretical study under high pressure. In this review, we provide the success of the metals [12, 14] is BCS-type superconductor [12, 14, 17, 19, 41, 48–53]. Also, we hope that this review is useful for those interested readers in superconductivity in elemental metal under high pressure.

2. Methodology

In considered in the present work, we performed the first-principles calculations, based on the density functional theory, to examine the thermodynamic

stability as a function of pressure. The static crystal energy of materials was considered at a temperature of 0 K. The calculation details of stable structure were determined by neglecting the entropy contributions. This is because the calculations were carried out at 0 K, indicating that the ground-state energy can confirm phase stability. Here, the KS equation formalism of DFT with the GGA-PBE for the exchange-correlation energy were used for Li, Sr., Sc, and As. For further details of the energy cutoff for plane waves and the Monkhorst–Pack k-point mesh as well as the DFT software have been described extensively in Refs. [10, 12–14]. Our works used the AIRSS technique, based on the density functional theory, to predict the novel structure. Following the AIRSS method, we calculated the enthalpies of the phases at any pressure using the simple linear approximation [7]. For each relaxed structure, the structures were simulated to be a non-symmetry and randomly placed in atomic position. During the calculations of the structures, it started to relax from bias until it reaches unbias. The shape is generating by shaking within a reasonable pressure range. It led to higher-symmetry space groups obtained in a search. The AIRSS technique is the approach in the local minima by giving the lowest enthalpy. We have studied the phonon mediated superconductivity by using isotropic Eliashberg theory, as implemented in the quantum espresso (QE) [54, 55]. Following the result of isotropic Eliashberg theory, the Allen-Dynes modify McMillan Equation [56] was used to estimated the superconducting transition temperature.

3. Result and discussion

3.1 Lithium

According to the aforementioned in the introduction, high pressure physics is useful in achieving a novel structure and superconductivity [12–14, 17, 33, 57–59]. Li is one of the challenging to find a novel structure [43, 60–63]. Since it is interesting that there is complex structures were discovered in alkali metal, i.e. sodium (Na) [64], potassium (K) [65–68], and rubidium (Rb) [69, 70]. Therefore, Li might be expected to possible to be a complex structure at high pressure. For the transitions sequence of Li, we found that the Im-3 m structure transformed into the Fm-3 m structure at pressure 8 GPa. Next, the Fm-3 m structure transformed into the R-3 m structure at pressure 39 GPa. With increasing pressure, the R-3 m structure transformed into the I-43d structure at pressure 44 GPa, then it transformed into C2mb at pressure 73 GPa. On further compression, the C2mb structure transformed into the C2cb structure at 80 GPa. Finally, it transformed into Cmca 120 GPa. It is interesting that there is no found the incommensurate host-guest structure at any pressure among such sequence [43, 60–63, 71].

Li was observed by optical spectroscopic through diamond anvil cells (DAC) [72]. The solution of the experimental study revealed that there is unknown phase above 50 GPa. Moreover, the characteristic of the high frequency band, i.e. Li-Li vibration, can interpret to be an incommensurate host-guest structure. The commensurate host-guest structure is defined by the different the number of the guest atoms in channels in along the c axis of the host structure, referring to the commensurate value c_H/c_G, also known as γ. At this point, it is interested to examine the unknown structure by following the Ref. [72].

As mentioned above, the unknown structure can be identified by a random search techniques. The random search technique is the high performance for the prediction of the materials. For elemental Li, the *ab initio* random structure searching (AIRSS) technique [6] is employed for determination the unknown

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structure. The remarkable result shown that Li is predicted to be the incommensurate host-guest structure above 50 GPa. Tsuppayakorn-aek et al. [13] was pointed out that structural phase transitions of Li might be considered to be different origins in two-phase transition sequences (**Figure 1**). Interestingly, one of two transition sequences can be obtained the incommensurate host-guest structure, indicating that it is energetically stabilized above 50 GPa and Li is likely to crystallize in the incommensurate host-guest structure at high temperature.

The existence of the incommensurate host-guest structure can be considered from the ELF calculation. As a possible cause of this, one might think of there is the s-pμ hybridization between the host–host atoms at 150 GPa (**Figure 2**) [13]. The study useful to point out that the possibility of the incommensurate host-guest structure is stable. Moreover, the nature of chemical bonding shown that the

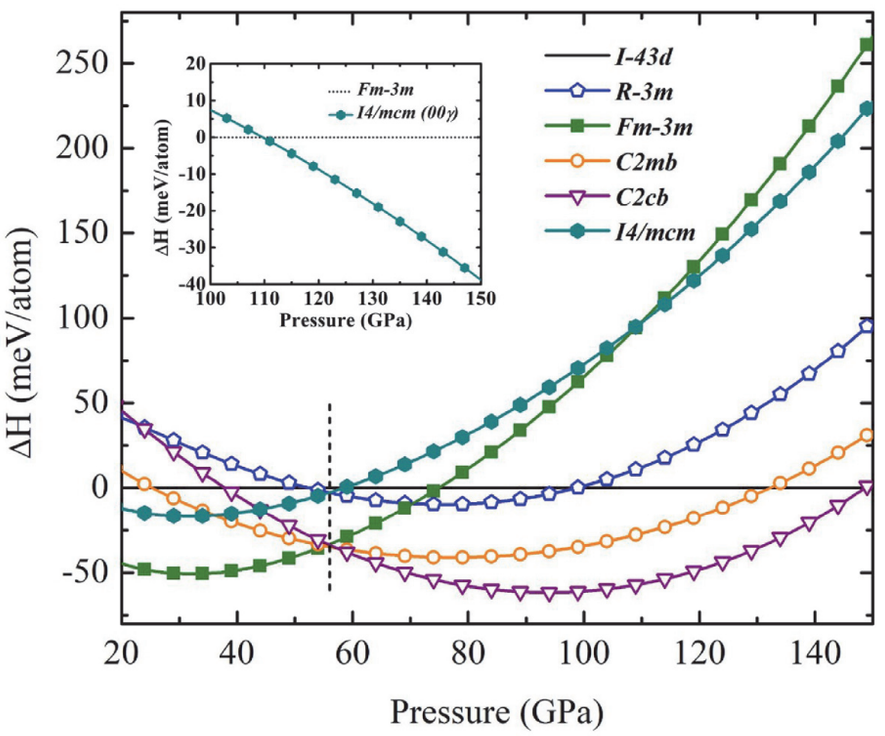

Figure 1.
The relative enthalpy of Li as a function of pressure.

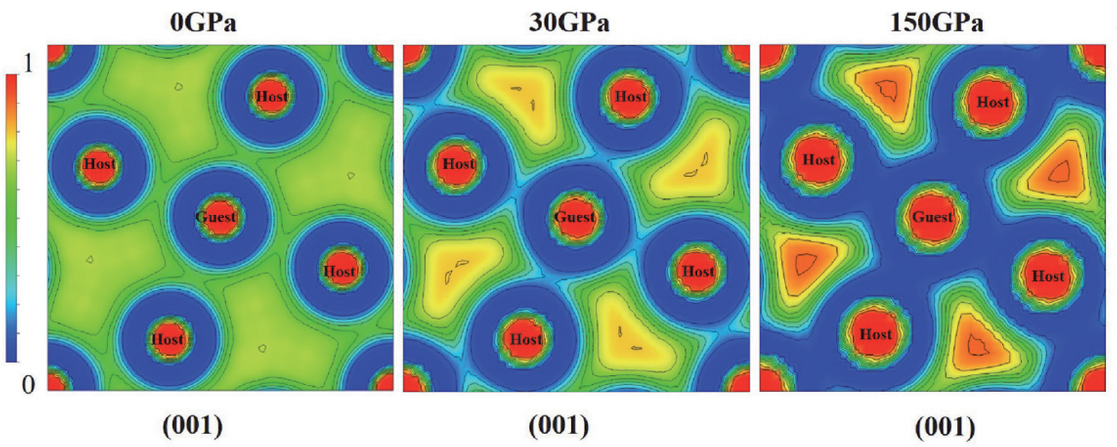

Figure 2.
The electron localization function (ELF) of the host-guest structure of Li is calculated in the (001) atomic plane.

incommensurate host-guest structure has tend to favor superconductivity at higher pressure. It is worth to note that the nature of the chemical bonding of the host–host atoms, i.e. the μ bonging, might be considered to be a superconducting phase.

3.2 Strontium

Structural phase transitions in alkaline earth metal under high pressure is interested among the periodic table. Nowadays, there are several works reported a transition sequences [33, 37, 40, 47, 58]. It is interesting to consider that a transition sequences of Ca and Sr. are similar. Ca shown that it exhibited stable structure at high temperature and low pressure through compression [58, 73]. The experimental observations [74] and the theoretical study [58, 73] reported that the simple cubic (sc) structure is stable at room temperature. At this point, the solution of theoretical study revealed that the sc structure is stable by performing a molecular dynamics (MD) calculation [73]. This is because the MD calculation can include a temperature via *ensemble*. However, the sc structure is considered by a lattice dynamics calculation [75], indicating that it is unstable structure. This is due to that fact that the sc structure is not a harmonic phase, but it is anharmonic phase [75]. Here, the sc structure is difficult to estimate the T_c by theoretical study.

In 2009, Ca was reported a novel structure at high pressure that it is the β-tin structure [58]. Here, it is worth to note that the transitions sequence of Ca is similar Sr. (the Fm-3 m structure transformed into the Im-3 m structure, then it transformed into the β-tin structure) Here, the β-tin structure is found that it is stable at high pressure and low temperature [58]. The T_c of the β-tin structure was estimated to be 5 K at 40 GPa. The case of Ca is interesting due to the d electrons are important for the estimated T_c. As a possible cause of this, one might think of the d electron is dominated near the Fermi level.

It is interesting to note that structural phase transitions in Sr. [33–37, 47]. The remarkable studies revealed that there are discrepancy between the experimental observations [34–36] and the theoretical studies [33, 37, 47]. The experimental observations were reported that the Fm-3 m structure transformed into the Im-3 m structure, then it transformed into the β-tin structure. Next, the β-tin structure transformed into the Sr-IV, finally, the Sr-IV structure transformed into the Sr-V structure. On the contrary, the theoretical studies were reported that the Fm-3 m structure transformed into the Im-3 m structure, then it transformed into the Sr-IV structure, showing that the the β-tin structure is not energetically favored over the Sr-IV structure.

In 2012, Sr. was predicted that there is a candidate structure [33]. The relative enthalpy of Sr. was reported that the Cmcm structure is thermodynamically favored over the Fm-3 m structure, the Im-3 m structure, and the β-tin structure. In addition, the Cmcm structrue was displayed that it can transform into the hcp structure as well. The Cmcm structure was investigated superconductivity, showing that the T_c of the Cmcm is estimated to be 4 K. The remarkable result manifested that the predicted T_c values are in good agreement with experiment [76, 77].

However, the discrepancy between the experimental observations and the theoretical studies were not solved yet. In 2015, the discrepancies in transition sequence between the experimental and theoretical works was explained by Tsuppayakornaek et al. [10]. Regarding transition sequence in Sr., it was investigated by the hybrid exchange-correlation functional, i.e. screened exchange local density approximation (sX-LDA) [78–80]. The stable structure of the β-tin was corrected by sX-LDA functional. In fact, the sX-LDA functional is important for the d electrons. At this point, it is interesting to compare the experimental observation and the theoretical study [10] by considering the energy levels in each electron

configuration of isolate strontium (**Figure 3**). The solution of the energy levels indicated that the sX-LDA functional is in good agreement with the experiment [81].

The remarkable result of the Ref. [10] shown that the β-tin structure is thermodynamically favored over the hcp structure by sX-LDA functional (**Figure 4**). The Ref. [10] manifested that the Im-3 m structure transformed into the β-tin structure,

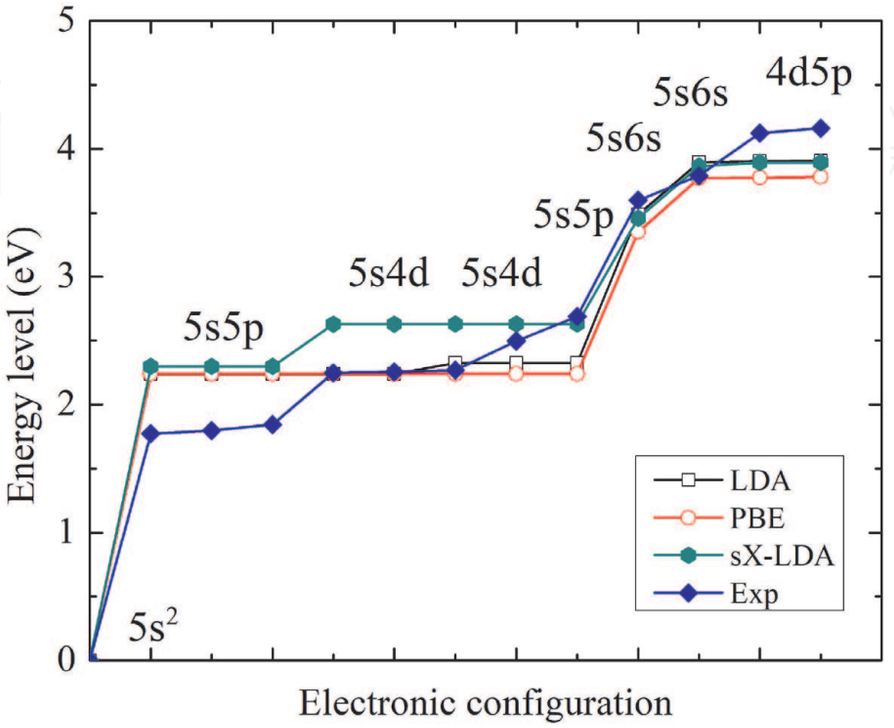

Figure 3.
The energy level each electron configuration of isolate Sr.

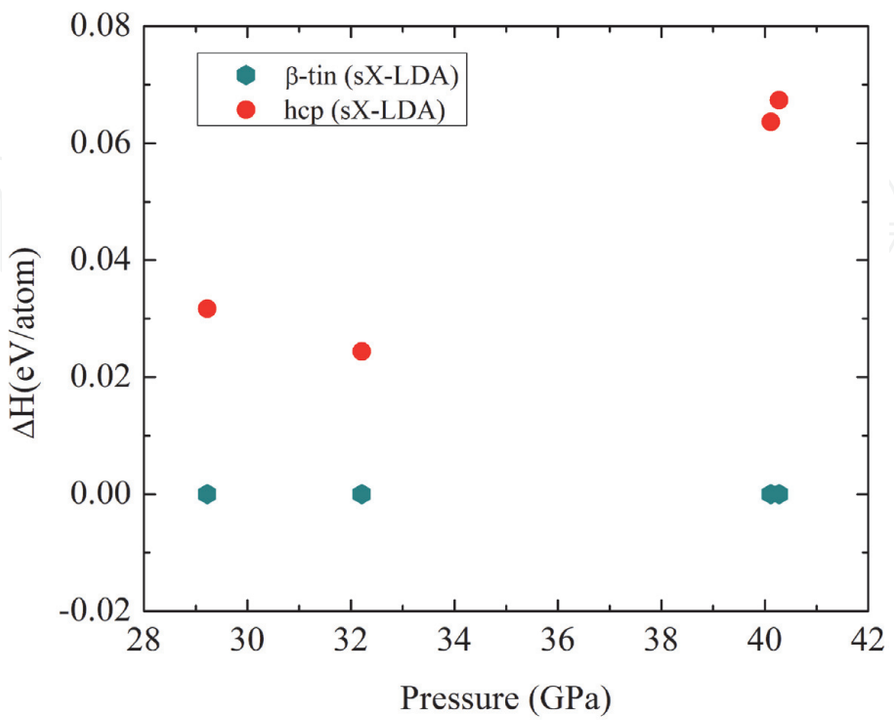

Figure 4.
The relative enthalpy of Sr. as a function of pressure by sX-LDA functional.

showing that the theoretical study is in good agreement with experimental observations [34–36].

Regarding the superconductor in the β-tin structure is interesting. Although the β-tin structure is thermodynamically stable by sX-LDA functional, it is not calculated the T_c. This because the sX-LDA functional is not implemented for the T_c calculation. However, other hybrid exchange-correlation functionals, i.e. PBE0 or HSE06, are possible for investigation the stability of the β-tin structure, leading to find the T_c.

3.3 Scandium

Structural prediction at high pressure is suitable for identifying unknown structure. Scandium (Sc) is one of d-transition metal, showing that there is an unknown structure (Sc-III) at high pressure [82]. The transition sequences is found that the hcp structure transformed into the host-guest structure [83, 84]. The host-guest structure is thermodynamically stable up to 70 GPa [85]. It is interesting to note that what is the unknown structure beyond the host-guest structure above 70 GPa. In 2018, Tsuppayakorn-aek et al. [14] was identified the unknown structure by *ab initio* random structure searching (AIRSS). The predicted structure was manifested that Sc-III is the tetragonal structure with space group $P4_12_12$. The $P4_12_12$ structure was shown that it is thermodynamiclly stable favored over the hcp structure and the host-guest structure above 93 GPa (**Figure 5**) [14]. Also, the $P4_12_12$ structure was found that it is dynamically structure at 120 GPa, as shown in (**Figure 6**). Moreover, the solution of the simulated XRD pattern [14] is in good agreement with the observed XRD pattern from the experimental study [82]. Structural phase transitions of Sc was reported that the hcp structure transformed into the host-guest structure, and then, it transformed into the $P4_12_12$ structure.

Regarding superconductor of the $P4_12_12$ structure, it was found to be the metallicity by considering density of state (DOS), leading to investigate the T_c. The $P4_12_12$ structure displayed that the estimated T_c is 8.36 K at 110 GPa. While, the

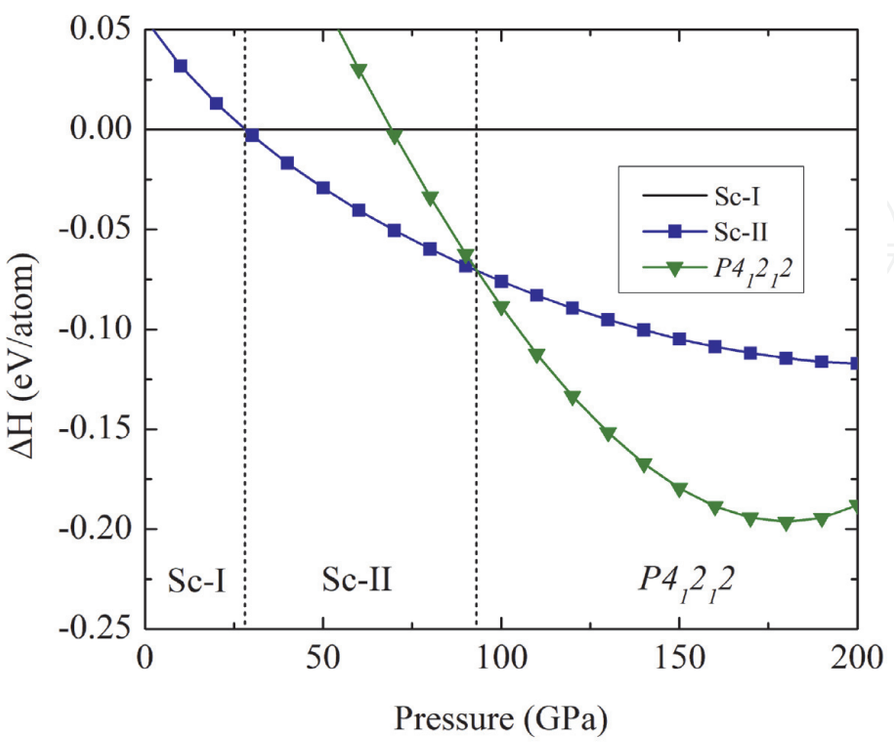

Figure 5.
The relative enthalpy of Sc as a fucntion of pressure.

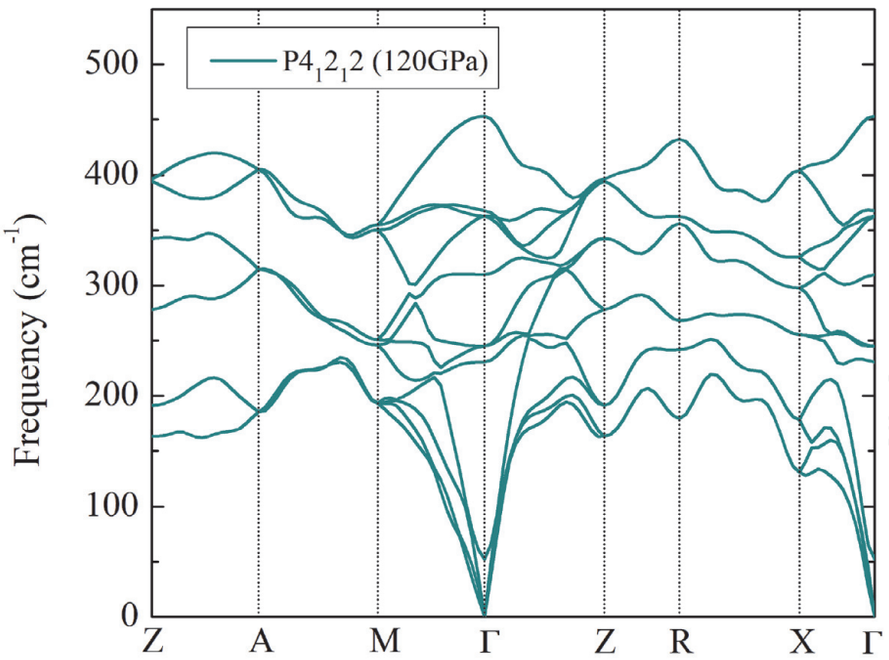

Figure 6.
The phonon dispersion of the $P4_12_12$ structure.

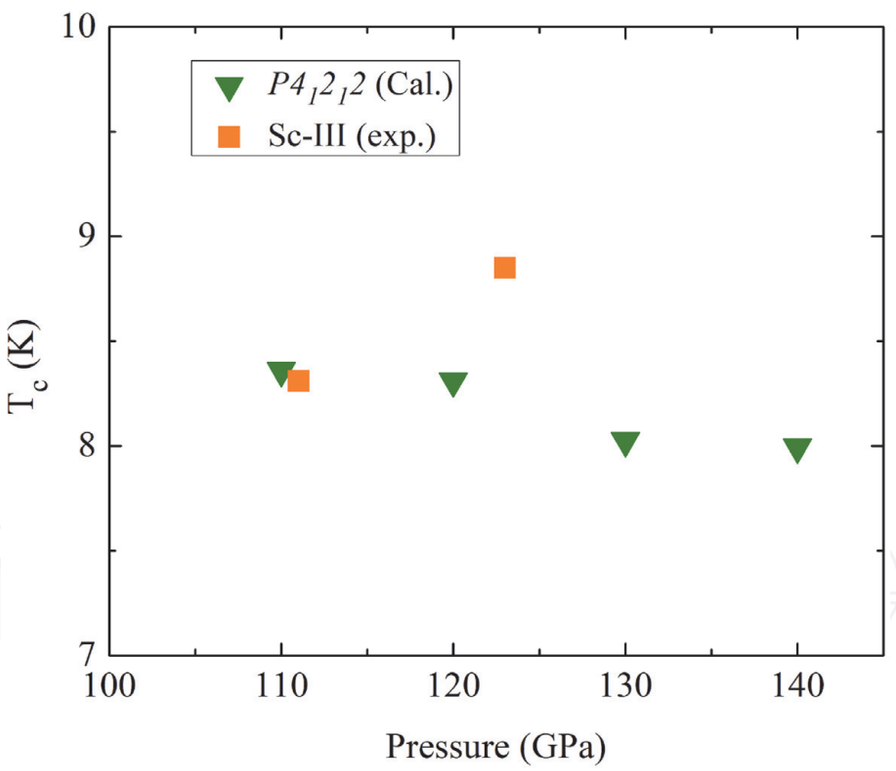

Figure 7.
The T_c of the $P4_12_12$ structure compare the T_c of Sc-III phase.

experimental study was reported the T_c is 8.31 K and 111 GPa [86]. Moreover, the $P4_12_12$ structure was explored the T_c above 130 GPa. Also, it was found that the T_c decreased monotonically with increasing pressure (**Figure 7**). In addition, the EPC strengths decreased with increasing pressure as well.

Tsuppayakorn-aek et al. [14] was revealed in that the T_c of the $P4_12_12$ structure decreased with increasing pressure occurred from the mechanical of the DOS. It can be easily understood by considering the partial-density of state. They were shown that the p-electron decreased with increasing pressure. In contrast, the s electron

increased with increasing pressure. In addition, the decreasing of T_c value is supported by the ELF calculation. The ELF is displayed in the (110) atomic plane of the $P4_12_12$ structure, showing that the characteristic of electron state. One can see that the p-electron is accumulated between Sc atoms, indicating that the nature of the chemical bonding is the weak bonding. On increasing pressure, the p-electron transferred into the s and d electrons. This implied that the decreasing of the p-electron might affect the T_c value.

Sc is one of the group-IIIB element was shown that structural phase transformation displayed the complex to simple transition. Also, it promoted the superconducting temperature transition to be 8.36 K at 110 GPa, which it is in good agreement with the experimental observation.

3.4 Arsenic

The group-V element is one of central interest in superconductor. It is interesting to note that arsenic (As), antimony (Sb), and bismuth (Bi) share the remarkable similarity of structural and property [87, 88]. Structural of the group-V element was reported that As-III, Sb-IV, and Bi-III are the incommensurate host-guest structure [89–92]. Also, it is worth to note that the Im-3 m structure is thermodynamically stable favored over the incommensurate structure [87, 88].

Tsuppayakorn-aek et al. [12] was explored the high-pressure phase in As. This because it is interesting to find the high-pressure phase, leading to go beyond the Im-3 m structure. The structural prediction was investigated up to 300 GPa. The predicted structure was shown that the body-centered tetragonal (bct) structure with space group $I4_1/acd$ to be the stable structure at high pressure. The $I4_1/acd$ structure is energetically and dynamically stable. Also, it is thermodynamically favored over the host-guest structure. The $I4_1/acd$ structure displayed that it compete with the Im-3 m structure. Moreover, The $I4_1/acd$ structure and the Im-3 m structure are very closed in enthalpy from 100 to 300 GPa. Also, the $I4_1/acd$ structure is sub-spacegroup of the the Im-3 m structure. It is possible that the $I4_1/acd$ structure is coexistence phase with the Im-3 m structure.

Here, the $I4_1/acd$ structure was discovered to be the metallicity, indicating that it is superconducting phase. As already mentioned, the $I4_1/acd$ structure and the Im-3 m structure are wonderfully closed in enthalpy. It is interesting to investigate the superconducting phase of both of them. An important and a fundamental of the spectral function led to consider superconductor. In fact, the spectral function is associated with the electron–phonon coupling (EPC). The $I4_1/acd$ structure was regarded in superconductor, it was found that the estimated T_c is 4.2 K at 150 GPa. On increasing pressure, the T_c of the $I4_1/acd$ structure decreased with the EPC. Likewise, the T_c of the Im-3 m is likely to decrease, where a pressure increasing. It is worth to note that the $I4_1/acd$ and Im-3 m structures are very similar in the T_c [12].

The remarkable results of the T_c value were shown that the T_c of the $I4_1/acd$ structure has higher than the Im-3 m structure at 150 GPa. The reason can be considered by the spectral function (α^2F) (**Figure 8**). The contribution of the α^2F shown that the $I4_1/acd$ structure is higher than those of the Im-3 m structure around middle frequency regime (6–13 THz).

Now, it is worth to note that the $I4_1/acd$ structure hold the metallic state at 300 GPa. Tsuppayakorn-aek et al. [12] suggested that the $I4_1/acd$ structure is not favored superconductor above 300 GPa, indicating that it is likely to transform into a normal metallic state (**Figure 9**). As a possible cause of this, one might think of phase transformation [19]. Moreover, the EPC of the $I4_1/acd$ structure is very poor characterized by compression. At this point, it is possible that a novel phase might occur above 300 GPa.

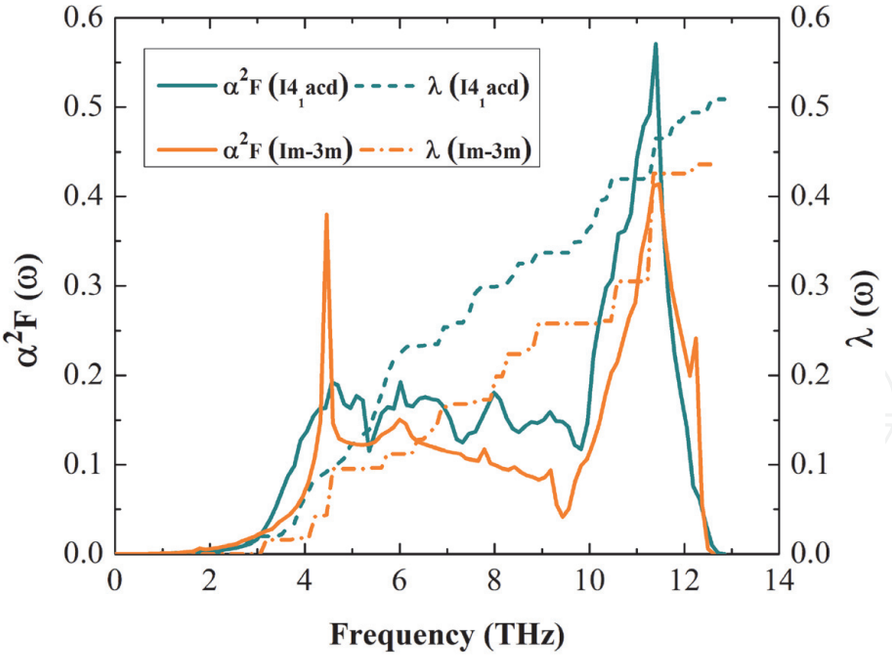

Figure 8.
The spectral function of the $I4_1/acd$ and Im-3 m structures at 150 GPa.

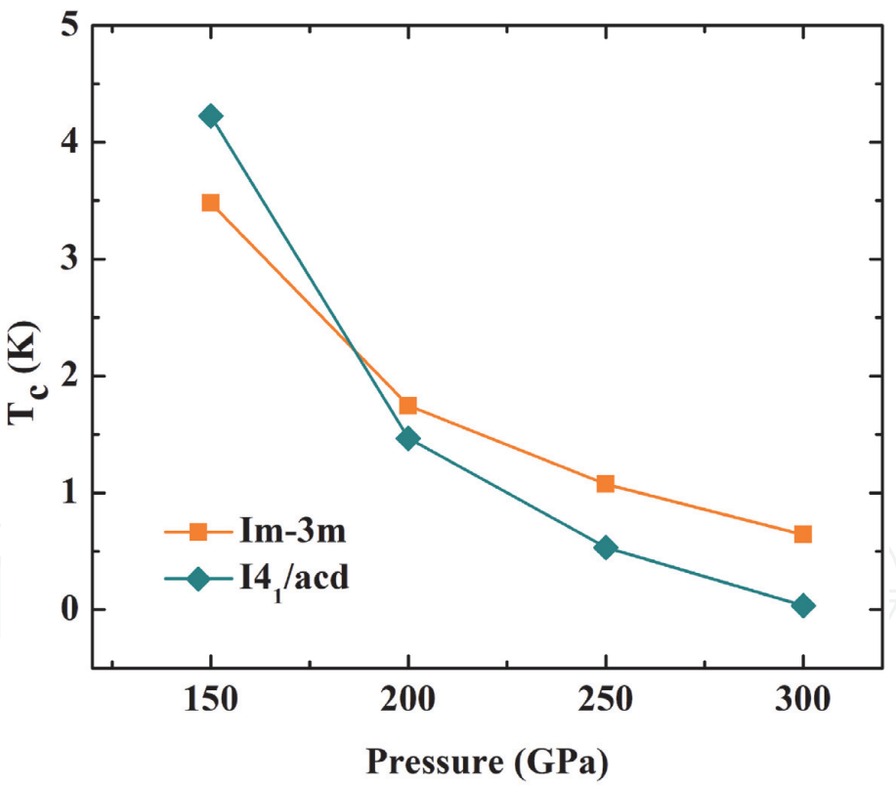

Figure 9.
The T_c of the $I4_1/acd$ and Im-3 m structures as a function of pressure.

4. Conclusion

Ab initio random structure searching is combined with density functional theory has been use to predict a candidate structure in lithium, strontium, scandium, and arsenic under high pressure. The predicted host-guest structure in lithium is expected to be superconductor, where the electron localization function is

considered. The discrepancy between the experimental observations and the theoretical studies in strontium is solved by hybrid exchange-correlation functional. Moreover, the β-tin structure is worth to explore a superconductor by performing hybrid exchange-correlation functional. The role of the electron phonon coupling displays that it is crucial for scandium ans arsenic under compression. The remarkable result of the superconducting transition temperature of scandium and arsenic share to a similar character, indicating that the superconducting transition temperature of both of them is likely to decrease with increasing pressure.

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Conflict of interest

The authors declare no conflict of interest.

Author details

Thiti Bovornratanaraks[1,2*] and Prutthipong Tsuppayakorn-aek[1,2]

1 Extreme Conditions Physics Research Laboratory (ECPRL) and Physics of Energy Materials Research Unit, Department of Physics, Faculty of Science, Chulalongkorn University, Bangkok, Thailand

2 Thailand Center of Excellence in Physics, Ministry of Higher Education, Science, Research and Innovation, Bangkok, Thailand

*Address all correspondence to: thiti.b@chula.ac.th

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