Computational study of pressurized tetragonal magnesium hydride (MgH4) as a potential candidate for high-temperature superconducting material

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Keywords: electron-phonon coupling, electronic band, high-temperature superconductivity, magnesium hydrides, metalization pressure, phonon band dispersion

Abstract
The dream of realizing room temperature superconductivity is one of the most challenging problems in condensed matter physics. Currently, materials with dense hydrogen contents at high pressures hold great promise for realizing room temperature superconductivity. In particular, pressurized alkaline earth metal hydrides received particular attention following the recently predicted sodalite-like calcium hydride (CaH6) with predicted Tc about 261 K above a pressure of 150 GPa; and magnesium hydride (MgH6) with predicted Tc about 270 K above 300 GPa. In this paper, we studied magnesium hydride (MgH4) with tetragonal (I4/mm) type symmetry, and we found that this structure shows the highest Tc ≈ 313 K at a pressure of 280 GPa which is higher than that of MgH6. Using density-functional perturbation theory (DFPT), the superconducting transition temperature, electron-phonon coupling, Eliashberg spectral function, and the logarithmic average frequency were computed. Our results reveal that, the computed values are reasonably in agreement with previous estimates.

1. Introduction
Superconductivity, as complete disappearance of electrical resistance of a material upon cooling below a characteristic temperature, the so-called superconducting transition temperature (Tc), was discovered in 1911 by Kamerlingh Onnes [1]. In superconducting materials, there will be no wastage of heat (or electrical power) and such peculiar materials can conduct unlimited electricity without any wastage of electrical power. After Kamerlingh Onnes’s discovery, no fundamental theory of superconductivity was developed for almost half of a century. In 1957, the microscopic theory of superconductivity proposed by Bardeen, Cooper, and Schrieffer (BCS theory) came based on the fact that superconducting phenomena occur when pairs of electrons (or fermions) with opposite spins paired together [2]. After this discovery, many new superconducting materials were discovered, but with small values of critical temperatures. Based on their Tc values, superconducting materials can be grouped into conventional (low Tc) and unconventional (high Tc) superconductors. A superconductor is considered as an unconventional (high Tc) if it cannot be explained by BCS theory. Generally, high Tc superconductors are thought of as unconventional superconductors. The practical technological application of conventional (low Tc) superconductors is very limited due to the very low operating value of the critical temperature. For only conventional (low Tc) superconductors, the mechanism of superconductivity can be fully explained by the well-known BCS theory [2]. Because of the need for dissipationless energy (electrical power) in the daily life of mankind and for other practical technological applications, the need to discover (and to realize) new materials having high Tc superconductors become an important task for many scientists around the globe. In particular, the dream of realizing room-temperature superconductivity (RTS) has become an active area in the field of condensed matter physics. In the scramble to find new high Tc superconductors, some
materials exhibiting high Tc superconductors were discovered by different scholars at different times. In the past few years, some of the materials discovered for high Tc superconductivity include magnesium diborides (MgB$_2$) [3], cuprates [4], and iron-based materials [5]. But, since all these superconductors have small Tc values, their technological application is limited. In magnesium diborides (MgB$_2$), the maximum transition temperature was about 39 K [3], which is very much lower than room temperature. In cuprate superconductors, the constituents of the chemical compounds are mostly ceramics which have complex electronic structure; and the maximum value of Tc was about 164 K [4]. In the case of iron-based superconductors, the maximum value of Tc was about 56 K [5, 6]. Another problem in the case of cuprates and iron-based superconductors is, in addition to superconducting state, additional competing state; for example, such as charge density wave (CDW) state, which competes with superconductivity also exists [7]. In such competing quantities, one can suppress the other. Due to the presence of such competing parameters, the mystery of unlocking high Tc on these materials is made difficult and the value of Tc remains small.

Other important classes of materials for realizing RTS are hydrogen dominated materials (hydrides) under high pressure [8–10]. Under high pressures, hydrides hold a great promise to exhibit high-temperature superconductivity [11–13]. The idea of metallization of hydrogen under high pressure was suggested around 1935 [14]. Later, in 1968, Ashcroft suggested that at high pressures, metallic hydrogen can be a superconductor [15]. Hydrogen is the lightest atom in the periodic table, and it is abundant in the Universe. At high pressures, when this light element interacts with other metallic or non-metallic elements, there will be high phonon frequency and a high density of states at the Fermi surface. The high phonon frequency and high phonon density of states at the Fermi surface can lead to superconductivity at high temperatures. Pressurized hydrides show many interesting and peculiar properties. Few of the important properties are: change of phase (metallization) property; formation of new polyhedral type structural units; formation of Fermi surface nesting, etc. Recently, superconductivity with a critical temperature of 203 K was discovered in sulfur hydride under high pressure [16]. This discovery of high Tc in pressurized sulfur hydride opened a new era for the search for additional hydrides with higher Tc values. Currently, there are some theoretically predicted hydrides that exhibit high Tc values at high pressures [17–19]. In the high-pressure search, a number of hydrides with high Tc values were theoretically predicted by different authors. Table 1 below lists some of the predicted hydrides that exhibit high-temperature superconductivity.

In alkaline earth metal hydrides, the highest Tc predicted was in similar sodalite-like magnesium and calcium hydrides [20, 21]. In the family of calcium hydrides, the highest Tc predicted was about 261 K in CaH$_6$ above 150 GPa; and in the family of magnesium hydrides, the highest Tc predicted was about 270 K in MgH$_6$ above 300 GPa. Calcium and magnesium have similar properties, and the prediction of high Tc in MgH$_6$ came

### Table 1. Some theoretically predicted superconducting hydrides at high pressure.

| Crystal hydride | Symmetry of the crystal | Pressure (GPa) | Tc (k) | References |
|-----------------|------------------------|---------------|-------|------------|
| YH$_6$         | Im-3m                  | 166           | 224   | [10]       |
| Carbonaceous   |                        |               |       |            |
| Sulfur hydride (C-S-H) |            |               |       |            |
| H$_2$S         | Im-3m                  | 200           | 203   | [16]       |
| MgH$_6$        | Im-3m                  | Above         | 270   | [20]       |
| CaH$_6$        | Im-3m                  | Above         | 261   | [21]       |
| LaH$_{10}$     | Fm-3m                  | 250           | 250   | [22]       |
| ThH$_{10}$     | Fm-3m                  | 100           | 241   | [23]       |
| ThH$_7$        | P2$_1$/c               | 100           | 65    | [23]       |
| SrH$_6$        | R-3m                   | 250           | 156   | [24]       |
| TaH$_3$        | Fdd2                   | 300           | 136   | [25]       |
| AsH$_3$        | C2/c                   | 450           | 152   | [26]       |
| T$_{12}$H$_{13}$ | Immm                  | 350           | 149   | [27]       |
| YH$_8$         | P6$_3$/mmc             | 201           | 243   | [28]       |
| ScH$_9$        | Cmcm                   | 300           | 169   | [29]       |
| ScH$_9$        | I4$_1$md               | 300           | 163   | [29]       |
| ScH$_{12}$     | Immn                   | 350           | 141   | [29]       |
after the discovery of CaH6 [21]. In the family of magnesium hydrides, MgH2 structure was predicted to metalize in different phases (low and high-pressure phases) [18]. In addition, the MgH4 structure which belongs to the Cmcm type symmetry was predicted to be stable above 100 GPa with a predicted Tc of 29–37 K [18].

2. Content organization

The contents of this paper are organized as follows. Section-3 presents general theoretical formulation of the study. In section-4, computational details of the paper are presented. The results of our findings and discussions of the results are provided in section-5. Finally, conclusion is drawn in section-6.

3. Theoretical formulation

Under the application of high pressure, the initial symmetry of a given crystal structure can be changed into another new different crystal symmetry [30–36]. In this change, the initial liquid or gas phase can be changed into solid; or non-metallic phases can be changed into metallic phases. For a given hydride to become superconductor under applied pressure, its crystal structure must be dynamically stable. Dynamical stability means the absence of negative or imaginary frequency throughout the Brillouin zone of the crystal in the phonon band dispersion curves. In some elements, some factors which govern the amount of pressure required for metallization are: atomic radius, nearest neighbor distance, binding energy, ionization potential, etc. This means that, in most cases, the amount of metallization pressure of some simple elements can be compared from the knowledge of their position across a particular group (or period) of the periodic table. For hydrides of similar metals in the same group of the periodic table, with the same crystal symmetry; and with the same number of hydrogen atoms; we argue that the amount of pressure required to metalize for a given hydride should progressively increase upward in the same group of the periodic table. Calcium and magnesium are found in the same group of the periodic table and have similar properties. In previous works, sodalite–like structure CaH6 was predicted to metalize above 150 GPa with an approximate Tc of about 261 K [21]. Similarly, sodalite–like structure MgH4 was predicted to metalize above 300 GPa with an approximate Tc of about 270 K [20]. Here, we see that, the metallization pressure of MgH4 is higher than that of CaH6; showing that, the amount of metallization pressure progressively increases upward in the same period of the periodic table. Another example that supports this fact is that in the case of H3S and H3Se [37]. As reported in [37], H3S and H3Se were predicted to be superconductors for the same Im-3m type structure symmetry. But, the metallization pressure of H3S is higher than that of H3Se, which correctly shows us that, the amount of metallization pressure progressively increases upward for similar S and Se hydrides in the periodic table.

In the case of calcium hydrides, the structure CaH4 which belongs to the crystal symmetry I4/mmm was predicted to be stable above 50 GPa [38]. So, a similar structure of magnesium hydride with similar symmetry type I4//mmm MgH4 should also metalize at higher metallization pressure than CaH4. This paper correctly answers this type of question. This study can benefit researchers in the field of condensed matter physics. In particular, this study can help researchers whose focus is on searching room-temperature superconductivity.

4. Computational details

In this paper, first-principle calculations were performed. Electronic structure calculations such as structural optimizations, electronic band structure calculations, electronic density of states, etc.; we employed QUANTUM ESPRESSO computational package [39]. QUANTUM ESPRESSO is a distribution of software for electronic–structure calculations based on density-functional theory (DFT), plane wave self-consistent field (PWscf), and pseudopotentials. The calculations were performed within the frame work of density functional theory (DFT) using generalized gradient approximation (GGA) functional specifically with Perdew–Burke–Ernzerhof (PBE) type pseudopotentials [40, 41]. The structure was fully optimized until all forces acting on the atoms become zero. After obtaining the most stable structure, band structure calculation was carried out for the optimized structure. In the initial step, using unshifted (Γ–centered) k-point mesh, the structure was optimized using k-point mesh 9 × 9 × 6 with kinetic energy cutoff 80.0Ry; and energy for charge density 640.0Ry. Next, electronic band structure calculation was carried out using denser k-point 24 × 24 × 24. Here, we have used Methfessel–Paxton (mp) type smearing with smearing width of 0.01. After analyzing electronic band structures, we next studied the superconducting and vibrational properties. The superconducting parameters such as electron–phonon coupling, Eliashberg spectral function, logarithmic average frequency, superconducting transition temperature, phonon band dispersion, phonon density of states (phDOS), etc.; were studied with the method of density-functional perturbation theory (DFPT) [42–44]. This method is efficient, powerful, and
flexible way for calculating vibrational and superconducting properties. In our work, by varying the lattice parameters for different targeted pressures, PWscf calculations were carried out using the open-source QUANTUM ESPRESSO computational package. From each PWscf calculation, each pressure was noted down. At each of the noted pressure obtained from the PWscf calculation, phonon calculations were performed. From the phonon calculation results, we obtained electron-phonon coupling constant \( \lambda \) and Eliashberg spectral function. Next, \( T_c \) was estimated by using the well-known Allen - Dynes formula [45] for calculating \( T_c \). The Allen - Dynes formula for calculating \( T_c \) is given by:

\[
T_c = \frac{\omega_{\text{lo}} \log 1.2}{1.2} \exp \left( \frac{-1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)} \right).
\]  

(1)
Where, \( \omega_{\text{log}} \) is the logarithmic average frequency of the phonon modes that is given by:

\[
\omega_{\text{log}} = \exp \left( \frac{2}{\lambda} \int_{0}^{\infty} \frac{d\omega}{\omega} \alpha^2 F(\omega) \log(\omega) \right).
\]  

The electron-phonon coupling constant \( \lambda \) which represents a dimensionless measure of the strength of the Eliashberg spectral function \( \alpha^2 F(\omega) \) is written in the form:

\[
\lambda = 2 \int_{0}^{\infty} \frac{d\omega}{\omega} \alpha^2 F(\omega).
\]

where, the term \( \alpha^2 F(\omega) \) stands for the well-known Eliashberg spectral function.

5. Results and discussion

Initially, we put the Mg atoms at the Wyckoff position 2b (0.000, 0.000, 0.5000), and the H atoms at the Wyckoff position 4e (0.000, 0.000, 0.570) and 4d (0.000, 0.5000, 0.2500) so that the structure contains 10 atoms. The optimized structure of this I\(_4\)/mmm type MgH\(_4\) is shown in figure 1. The structural parameters obtained from the optimization are: \( a = b = 3.5448\text{Å} \), \( c = 5.4133\text{Å} \). The final optimized structure belongs to the space group number-139 with Bravais lattice type tI2 and Pearson symbol tI10. This structure can be considered as a
tetragonal crystal system with space group label I4/mmm. The optimized structure of this MgH4 (I4/mmm—type symmetry) forms polyhedral structure as shown in figure 2.

The H atoms are located at all the corners and faces of the cube; and the Mg atoms at the four sides and two faces of the cube. The experimental bond length of H2 molecule is 0.074Å [46–48]. In our optimized structure for this I4/mmm type MgH4, the bond length of the H2 molecule inside the cube is 0.076Å. Therefore, structural parameters of our optimized structure are reasonably in close agreement with experimental result, showing that our DFT calculation is correct.

To obtain the band structure of this optimized tetragonal-type MgH4, the appropriate k-point path for the high-symmetry points is \( \Gamma \rightarrow X \rightarrow P \rightarrow N \rightarrow \Gamma \rightarrow M \rightarrow S \rightarrow \Gamma \rightarrow X \rightarrow R \rightarrow G \rightarrow \Gamma \). With the use of XCrySDen viewer [49], we plotted the path of these high-symmetry points as shown in figure 3(b) below.

The electronic structure of MgH4 (I4/mmm) at 0 GPa is shown in figure 4. From figure 4(a), we see that, there are many bands in the vicinity of the Fermi level. Also, there are bands crossing the Fermi level in every direction of the high symmetry points: \( \Gamma \rightarrow X, X \rightarrow P, P \rightarrow N, N \rightarrow \Gamma, \Gamma \rightarrow M, M \rightarrow S, S \rightarrow \Gamma, \) and \( G \rightarrow M \). This information tells us that there are many mobile charge carriers in the Fermi surface of this tetragonal type MgH4 structure. Also, there is no gap between the valence and conduction bands. Clearly, this structure is metallic. Similarly, the projected density of states for this I4/mmm type MgH4 structure is presented in figure 4(b). From the figure, we...
see that, the contribution to the total density of states arises from all orbitals (H\textsubscript{s} orbital, Mg\textsubscript{s} orbital, and Mg\textsubscript{p} orbital). The largest contribution to the total density of states is from both H\textsubscript{s} and Mg\textsubscript{p} orbitals.

At 0 GPa, the charge density map of tetragonal-type I\textsubscript{4}/mmm MgH\textsubscript{4} structure is shown in figure 5. From the charge density map, we see that there is a strong interaction between the hydrogen molecules situated between the magnesium atoms. As indicated in figure 5(a), in the crystal of MgH\textsubscript{4}, the magnesium atoms are in between bonded hydrogen molecules inside the cube. This interaction is rather high and it is clearly shown in figure 5(b) as a charged cloud.

Our next task is to study the vibrational and superconducting properties of this I\textsubscript{4}/mmm type MgH\textsubscript{4}. By varying the lattice parameters for different pressures starting from 0 GPa, phonon calculations were carried out to find the range of dynamical stability for this I\textsubscript{4}/mmm type MgH\textsubscript{4}. The phonon calculations were carried out with k-point mesh of 16 × 16 × 16, and q-point mesh 4 × 4 × 4. According to our phonon calculation results, it is found that, this tetragonal type (I\textsubscript{4}/mmm) MgH\textsubscript{4} is dynamically stable above 190 GPa. In the range of pressures from 190 GPa up to 360 GPa, I\textsubscript{4}/mmm type MgH\textsubscript{4} shows dynamical stability. However, above 360 GPa, dynamical stability of the structure disappears. As a model result, phonon band dispersion of this tetragonal type MgH\textsubscript{4} at a pressure of 280 GPa is shown in figure 6. In the phonon band dispersion shown in figure 6, we see that there is no negative frequency in the whole Brillouin zone, showing that the structure is

Figure 7. Phonon density of states for the MgH\textsubscript{4} (I\textsubscript{4}/mmm) at a pressure of 280 GPa.

Figure 8. Eliashberg spectral function for the MgH\textsubscript{4} (I\textsubscript{4}/mmm) at a pressure of 280 GPa.
dynamically stable. The phonon density of states (phonon DOS) for this structure at a pressure of 280 GPa is presented in figure 7. At this pressure, the vibrational phonon frequency is rather high reaching up to 4250 cm$^{-1}$. This structure has very high frequencies of bending and stretch modes. The lowest frequencies ranging up to 750 cm$^{-1}$ are the modes due to translations and rotations. The higher frequencies indicated at about 4250 cm$^{-1}$ are due to bending and stretch modes.

The Eliashberg spectral function, $\alpha^2F(\omega)$, at a pressure of 280 GPa is shown in figure 8. The spectral function at this pressure is sharp and has large values.

At a pressure of 280 GPa, the value of the electron-phonon interaction ($\lambda$) obtained from our phonon calculation is 1.95437, and the average logarithmic frequency ($\omega_{\log}$) is 2208.524 K. Then, using Coulomb pseudopotential $\mu^* = 0.10$, and Allen Dynes formula [45], the estimated value of the transition temperature is 313.399 K. This value of Tc is very high; even higher than the value predicted for sodalite-like MgH$_6$ [20]. To see the influence of the superconducting temperature by the pressure, various PWscf calculations were performed.

Figure 9. Variation of Tc with pressure for the MgH$_4$ (I4/mmm).

Figure 10. Variation of electron-phonon interaction with pressure for the MgH$_4$ (I4/mmm).
by varying the lattice parameters for different pressures. For each of these pressures, phonon calculation was carried out. Finally, with the help of the well-known Allen-Dynes formula given in equation (1), we estimated the value of $T_c$. This variation of $T_c$ with pressure is shown in figure 9. The variation of $T_c$ as a function of applied pressure shows that, the graph of $T_c$ versus pressure for this I4/mmm type MgH$_4$ has no monotonic behavior.

The variation of the electron-phonon coupling with pressure is also plotted in figure 10. On the pressure range 190 GPa - 250 GPa, the value of the electron-phonon interaction decreases with pressure. However, above 250 GPa, it starts to increase with pressure. From figure 10, we see that the variation of the electron-phonon coupling for this I4/mmm type MgH$_4$ has no monotonic behavior on the indicated range of pressures.

The influence of pressure on the average logarithmic frequency ($\omega_{log}$) is shown in figure 11. Clearly, the figure shows that the average logarithmic frequency increases with pressure on the range 190 GPa - 260 GPa.

At 280 GPa, electronic band structure of I4/mmm type MgH$_4$ is presented in figure 12(a); and the projected density of states at that pressure in figure 12(b). From the band structure shown in figure 12(a), we see that, there are bands crossing the Fermi level in the high-symmetry directions N-Γ, Γ-M, M-S, X-R, and G-M.
Furthermore, there is no gap between the valence and conduction bands. In this case, at this pressure, the structure is still metallic. The density of states at 280 GPa is slightly decreased from its optimized (0 GPa) structure. At a pressure of 280 GPa, the largest contribution to the total DOS arises from both hydrogen s and magnesium p orbitals. According to the charge density map of MgH₄ shown in figure 13, at a pressure of 280 GPa, hat-like shapes are formed around the hydrogen and magnesium atoms.

6. Conclusion

In this paper, we studied a new stable phase tetragonal-type I₄/mmm MgH₄ as a potential candidate for high-temperature superconductivity using first-principle calculations. The amount of pressure required for dynamical stability of I₄/mmm type structure CaH₄ as reported in [38] is above 50 GPa. In this study, however, we have found that the pressure required for dynamical stability of similar I₄/mmm type structure MgH₄ is above 190 GPa. This information correctly proves the fact that, for similar hydrides of the same group in the periodic table, the amount of pressure required to metalize for a given hydride is progressively increasing upon moving towards the top of a particular group. For this I₄/mmm type MgH₄, the highest Tc calculated is about 313 K at a pressure of 280 GPa. This value of Tc is higher than that of the recently predicted MgH₆. Additional advantage of this superconductor MgH₄ is that, this structure requires less metallization pressure than that of MgH₆.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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Figure 13. Charge density for MgH₄ (I₄/mmm) at a pressure of 280 GPa: (a) interaction between Mg and H in the crystal, and (b) the charge density map as viewed in the z-plane.
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