


Pressure-stabilized binary compounds of magnesium and silicon

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The family of binary compounds composed of magnesium and silicon is rather rich. In addition to the well-known magnesium silicide Mg_2Si , other compounds, including MgSi_2 , Mg_4Si_7 , Mg_5Si_6 , MgSi , and Mg_9Si_5 , have also been identified and/or proposed in precipitated Al-Mg-Si solid solutions. Nevertheless, computational studies show that only Mg_2Si is thermodynamically stable at ambient conditions while certain nonzero hydrostatic pressure can stabilize Mg_9Si_5 so that it can coexist with Mg_2Si . We conduct a comprehensive search for viable binary compounds of $\text{Mg}_x\text{Si}_{1-x}$ ($1/3 \leq x \leq 2/3$), discovering numerous low-energy structures for all the compounds. On one hand, we find that MgSi_2 , MgSi , and Mg_9Si_5 are likely pressure-stabilized materials, while, on the other hand, supporting previous studies, we raise doubt on the existence of Mg_5Si_6 , and claim that the existence of Mg_4Si_7 remains an open question. Therefore, we recommend that (hydrostatic and/or nonhydrostatic) pressure should be explicitly considered when discussing the stability of these solids (and maybe other solids as well) by computations. We also find that MgSi_2 can potentially exhibit superconducting behaviors within a wide range of pressure with the critical temperature of up to 7 K.

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I. INTRODUCTION

The best-known binary compound of Mg and Si, i.e., magnesium silicide Mg_2Si , has been studied extensively due to its potential applications, e.g., infrared photonic and thermoelectric energy conversion devices [1–5]. Five other members of the Mg-Si binary family, including MgSi_2 , Mg_4Si_7 , Mg_5Si_6 , MgSi , and Mg_9Si_5 , have subsequently been identified/suggested experimentally (and occasionally studied computationally) when precipitation-hardened alloys of Al with Mg and Si were explored [6–15]. Of them, the $P4/mmm$ phase of MgSi and the $P6_3/m$ phase of Mg_9Si_5 have been confirmed experimentally [13,16] and studied computationally [9,17]. The others, e.g., MgSi_2 , Mg_4Si_7 , and Mg_5Si_6 , were proposed computationally as candidates for many (still) unknown phases of the Al-Mg-Si alloys. Specifically, Mg_5Si_6 , assumed to be in a $C2/m$ monoclinic phase, was initially proposed [11,18] as the β' precipitate of the Al-Mg-Si alloys but this proposal then caught considerable doubt [19–23]. Nevertheless, the observation of these Mg-Si binary compounds seems to contradict some first-principles calculations performed at zero pressure ($P = 0$ GPa) [6,17,24], revealing that only Mg_2Si is thermodynamically stable, while other Mg-Si binary compounds are unstable.

Among these binary compounds, Mg_5Si_6 and Mg_9Si_5 were recently predicted [25] to become stable under certain ranges of compressive hydrostatic pressure. This computational study suggests the possible role of pressure, the thermodynamic variable that may be realized in certain experimental conditions, in the observations of Mg_5Si_6 , Mg_9Si_5 , and possibly other Mg-Si binary compounds as well [25]. In fact, pressure has already been known as a key factor, stabilizing numerous new solid

materials with exotic functionalities, e.g., high energy density and high-temperature superconductivity [26–31], and inspiring a great deal of interest from the community [32–36].

Compared to Mg_2Si , not much was known [17,25,37] about MgSi , MgSi_2 , Mg_4Si_7 , Mg_5Si_6 , Mg_9Si_5 , and other possible binary compounds of this family. Recently, the thermodynamic stability and the electronic structure of Mg_5Si_6 and Mg_9Si_5 (whose hexagonal $P6_3/m$ structure was proposed [9,16,17] as the β' precipitate of the Al-Mg-Si alloy systems) have been exploited by first-principles computations [17,24,25,37]. Under compressive pressure ($P \gtrsim 10$ GPa and above), they were predicted [37] to be dynamically stable and share the metallic/semimetallic characteristics with Mg_2Si . To our best knowledge, an in-depth understanding of the other binary compounds, if realized, remains unavailable.

This paper addresses these two points. By searching for low-energy structures of 13 Mg-Si binary compounds (with varying Mg content) at the level of density-functional theory (DFT) [38,39], we identified numerous structures that are significantly lower in energy than those currently recognized. Because the number of Mg-Si binary compounds considered in this comprehensive paper is sufficiently large, the stability of these compounds can be better accessed. From this analysis, we suggest that MgSi_2 , MgSi , and Mg_9Si_5 are likely pressure-stabilized materials while confirming (and suggesting) the thermodynamical instability of Mg_5Si_6 [19–23] (and Mg_4Si_7). We recommend explicitly considering external pressure when discussing the thermodynamical stability of Mg-Si based solids, and presumably other solids as well. For those identified to be thermodynamically stable, their dynamical stability, electronic structure, and possible superconductivity were studied using DFT computations.

In addition to the aforementioned results, the data set of 358 low-energy structures identified herein is also useful

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TABLE I. Summary of the Mg-Si binary compounds on which the searches were performed in this work. For each binary, the Mg concentration x and N_{\max} , the maximum number of atoms of the cells used for the search, are given.

Materials	x	N_{\max}	No. f.u.	No. structs.
MgSi ₂	0.333	24	8	65
Mg ₅ Si ₉	0.357	28	2	14
Mg ₄ Si ₇	0.364	22	2	26
Mg ₂ Si ₃	0.400	20	4	29
Mg ₃ Si ₄	0.429	28	4	43
Mg ₅ Si ₆	0.455	22	2	32
MgSi	0.500	24	12	34
Mg ₆ Si ₅	0.545	22	2	15
Mg ₄ Si ₃	0.571	28	4	41
Mg ₃ Si ₂	0.600	20	4	9
Mg ₇ Si ₄	0.636	22	2	15
Mg ₉ Si ₅	0.643	28	2	14
Mg ₂ Si	0.667	24	8	21

for the community in the context of the emerging age of materials informatics [40–42]. Because this data set was prepared by exhaustive low-energy structure searches, it provides a large number of reliable materials structures. Generally, data sets prepared in this way [43,44] are a good complement to the established materials databases such as Materials Project [45], Open Quantum Materials Database [46], AFLOW [47], and Polymer Genome [48].

II. COMPUTATIONAL DETAILS

Our first-principles calculations were performed at the level of DFT, using specifically the version implemented in VIENNA AB INITIO SIMULATION PACKAGE [49–52]. We used the kinetic energy cutoff of 500 eV for the plane-wave basis set, and the generalized gradient approximation Perdew-Burke-Ernzerhof functional [53] for the exchange-correlation (XC) energies. The Brillouin zone of the examined structures was sampled by a Monkhorst-Pack k -point mesh [54] with a spacing of 0.1 \AA^{-1} in the reciprocal space.

Low-energy structures of the possible Mg-Si binary compounds was searched using the minima-hopping method [55–57], which has been successfully used for different material classes [25,58–61]. This method relies on exploring the DFT energy landscape by alternating molecular-dynamics runs for escaping the current local minimum and geometry optimization runs for identifying the next local minimum. As the energy landscapes of the examined materials are constructed at the DFT level, the searches are reliable but generally expensive. In principle, searches can be performed at any pressure, as performed in Ref. [25]; however, given that the number of binary compounds considered is large (13) and that the pressure window of interest is unknown, the searches for each Mg-Si binary were conducted only at zero pressure for some certain numbers of formula units (and equivalently, number of atoms—see Table I for details). The structures within a window of 200 meV/atom from the lowest-energy structure were selected and studied at varying elevated pressures.

This procedure, as will subsequently be shown in this paper, captures the stable stoichiometries of the Mg _{x} Si _{$1-x$} identified within 0–30 GPa, the pressure range of our current interest. Their symmetry was analyzed using FINDSYM [62] while VESTA [63] was used for visualization. The (crystallographic information format) structure files were prepared with PYMATGEN [64].

Phonon-related calculations reported herein, including those related to the phonon-mediated superconductivity of the predicted structures as discussed subsequently, were performed using the linear response approach [65,66] as implemented in ABINIT [67], employing the Hartwigsen-Goedecker-Hutter norm-conserving pseudopotentials [68], a plane-wave cutoff energy of 40 Hartree ($\simeq 1,100\text{eV}$) and the PBE XC functional. In fact, because of some intractable uncertainty, material structures determined computationally or experimentally may actually be dynamically unstable and, in this case, proper phonon calculations may be used to refine them [60,69]. The phonon band structure reported in this paper are used to track the dynamical stability of the structure predicted. Correction to the energy from the lattice vibrations, which can be computed from the phonon density of states (as performed in Refs. [25,60,61]), was not considered here because of two reasons. First, the computational resource required for more than 300 structures at different values of pressure is prohibitively enormous, and second, zero-point energy corrections tend to cancel out, leaving only a part of such a small

TABLE II. Summary of the new structures predicted for Mg-Si binary compounds. For those predicted in this paper, ΔH_{DFT} is the enthalpy of formation, given in meV/atom.

Mater.	Literature		This Paper	
	Symmetry	Refs.	Symmetry	ΔH_{DFT}
$P = 0 \text{ GPa}$				
MgSi ₂	<i>Imma</i>	[6]	$R\bar{3}m$	−90.2
Mg ₄ Si ₇	<i>C2/m</i>	[6,7]	<i>P1</i>	−6.1
Mg ₅ Si ₆	<i>C2/m</i>	[11,12]	<i>C2/m</i>	−5.3
MgSi	<i>P4/mmm</i>	[13,17]	<i>P2₁/m</i>	−140
Mg ₉ Si ₅	<i>P6₃/m</i>	[9,16]	$R\bar{3}c$	−3.0
$P = 10 \text{ GPa}$				
MgSi ₂	<i>Imma</i>	[6]	<i>Imma</i>	−1.1
Mg ₄ Si ₇	<i>C2/m</i>	[6,7]	<i>P1</i>	−6.2
Mg ₅ Si ₆	<i>C2/m</i>	[11,12]	<i>C2/m</i>	−0.8
MgSi	<i>P4/mmm</i>	[13,17]	<i>C2/m</i>	−38.5
Mg ₉ Si ₅	<i>P6₃/m</i>	[9,16]	$R\bar{3}c$	−0.8
$P = 20 \text{ GPa}$				
MgSi ₂	<i>Imma</i>	[6]	<i>P6/mmm</i>	−3.2
Mg ₄ Si ₇	<i>C2/m</i>	[6,7]	<i>Pm</i>	−28.1
Mg ₅ Si ₆	<i>C2/m</i>	[11,12]	<i>Cm</i>	−5.2
MgSi	<i>P4/mmm</i>	[13,17]	<i>P4/mmm</i>	0
Mg ₉ Si ₅	<i>P6₃/m</i>	[9,16]	$R\bar{3}c$	−1.0
$P = 30 \text{ GPa}$				
MgSi ₂	<i>Imma</i>	[6]	<i>P6/mmm</i>	−6.7
Mg ₄ Si ₇	<i>C2/m</i>	[6,7]	<i>Cm</i>	−107
Mg ₅ Si ₆	<i>C2/m</i>	[11,12]	<i>Cm</i>	−46.7
MgSi	<i>P4/mmm</i>	[13,17]	<i>P4/mmm</i>	0
Mg ₉ Si ₅	<i>P6₃/m</i>	[9,16]	$R\bar{3}c$	−4.3

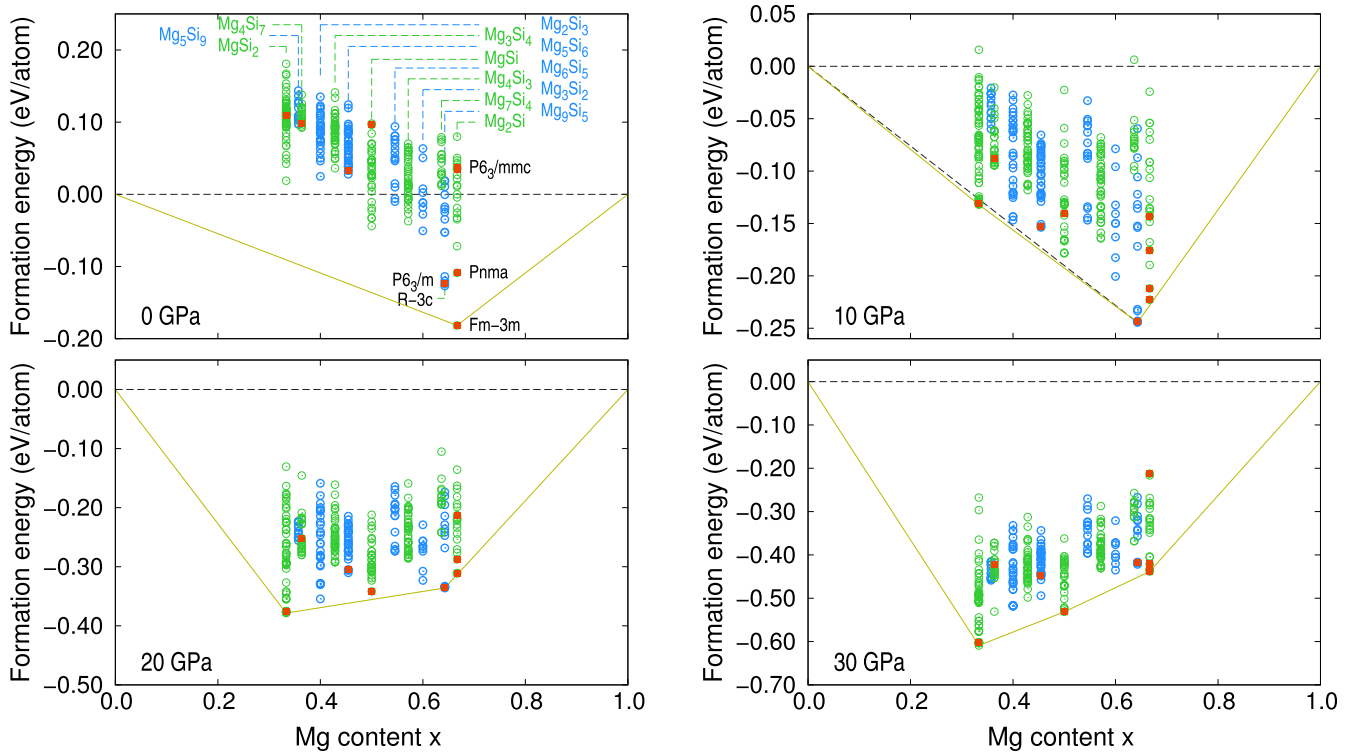


FIG. 1. Convex hull constructed from the DFT enthalpy of formation ΔH_{DFT} defined in Eq. (1) for $\text{Mg}_x\text{Si}_{1-x}$ binary compounds. Alternative colors are used to label the binary compounds while red squares are used for the structures obtained either experimentally or computationally in the literature.

amount contributing to the relative energy difference between structures.

III. RESULTS AND DISCUSSIONS

A. Thermodynamic stability

A summary of the low-energy structures identified in this paper is given in Table II while their detailed crystallographic information is provided in the Supplemental Materials [70]. Except Mg_2Si , new “ground state” structures were identified for the others at $P = 0$ GPa. For MgSi_2 and MgSi , the new lowest-energy structures ($R\bar{3}m$ and $P2_1/m$) are significantly lower than the previously reported counterparts in E_{DFT} by $\simeq 90$ meV/atom and $\simeq 140$ meV/atom, respectively. For Mg_4Si_7 , Mg_5Si_6 , and Mg_9Si_5 , the advance in E_{DFT} of the new structures is smaller but remains noticeable.

The thermodynamic stability of the identified structures are examined by four convex hulls shown in Fig. 1. They were constructed at $P = 0, 10, 20,$ and 30 GPa from the formation DFT enthalpy ΔH_{DFT} , defined as

$$\Delta H_{\text{DFT}} = H_{\text{DFT}}(\text{Mg}_x\text{Si}_{1-x}) - [x H_{\text{DFT}}(\text{Mg}) + (1-x)H_{\text{DFT}}(\text{Si})]. \quad (1)$$

Here, $H_{\text{DFT}}(\text{Mg}_x\text{Si}_{1-x})$, $H_{\text{DFT}}(\text{Mg})$, and $H_{\text{DFT}}(\text{Si})$ are the DFT enthalpies computed for $\text{Mg}_x\text{Si}_{1-x}$, the ground state hexagonal $P6_3/mmc$ structure of Mg, and the ground state cubic $Fd\bar{3}m$ structure of Si. In the definition $H_{\text{DFT}} \equiv E_{\text{DFT}} + PV$ of the DFT enthalpy, the DFT energy E_{DFT} and the volume

of the simulation box V were computed at the hydrostatic pressure P .

Consistent with previous reports [6,17,24,25], only Mg_2Si is thermodynamically stable at $P = 0$ GPa. Starting from $P \simeq 10$ GPa, MgSi_2 becomes stable in different phases, i.e., $Imma$ and $P6/mmm$ at $P = 10$ and ≥ 20 GPa, respectively. The predicted $Imma$ structure (with $a = 4.12$ Å, $b = 5.64$ Å, $c = 7.64$ Å) is about 1 meV/atom lower than the previously proposed $Imma$ structure [6] (with $a = 4.00$ Å, $b = 5.88$ Å, $c = 7.60$ Å) but they appear to be just slightly different when the motifs are visualized. At 20 GPa and 30 GPa, the predicted $P6/mmm$ structure of MgSi_2 is new, as shown in Fig. 2. Similarly, the predicted $R\bar{3}c$ structure of Mg_9Si_5 (summarized in Table II) is lower than the $P6_3/m$ structure previously proposed [9,16] (and studied computationally [37]) by $\simeq 1-4$ meV/atom but a closer investigation indicates that the difference between them is also small (see Supplemental Materials [70] for a visualization). Considering the small energy difference, the recent conclusion that between 6 and 24 GPa, Mg_2Si can decompose into Mg_9Si_5 and Mg without energy cost [25] remains valid, as shown in Fig. 1. For MgSi , the previously proposed $P4/mmm$ structure [13,17] is higher than the predicted $P2_1/m$ structure by $\simeq 140$ meV/atom at $P = 0$ GPa. However, this shortcoming is rapidly diminished as P increases, and starting from $P \simeq 20$ GPa, the $P4/mmm$ structure of MgSi becomes lowest in H_{DFT} .

The above observation strongly hints that MgSi_2 [6], and specifically MgSi [13,17] and Mg_9Si_5 [9,16], whose experimentally observed structures become lowest in enthalpy within some ranges of pressure, are indeed pressure-stabilized materi-

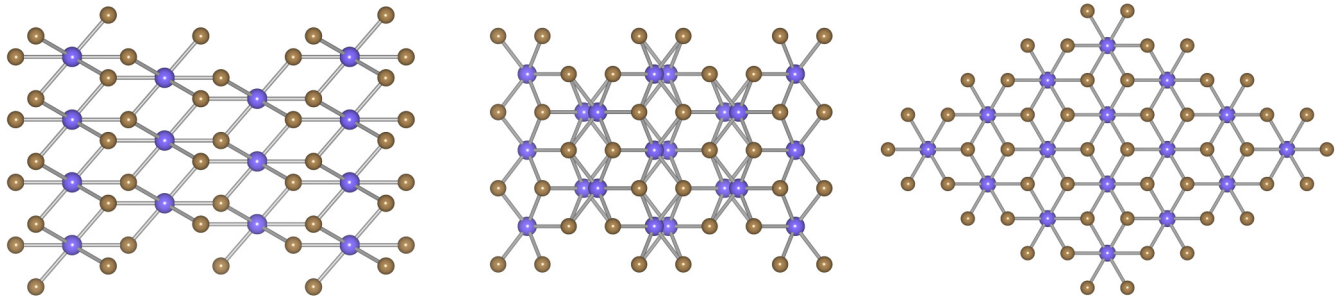


FIG. 2. Structures of MgSi_2 at 0 GPa ($R\bar{3}m$, left), 10 GPa ($Imma$, center), and 20 GPa ($P6/mmm$, right). The structure at 30 GPa is similar to that at 20 GPa. Magnesium and silicon atoms are shown in olive and medium slate blue colors, respectively.

als. From the computational point of view, (hydrostatic and/or nonhydrostatic) pressure should be explicitly considered when discussing the thermodynamic stability of the Mg-Si binary compounds. This conclusion, which places MgSi_2 , MgSi , and Mg_9Si_5 into a class of (pressure-stabilized) metastable materials like $\text{LiK}(\text{BH}_4)_2$ [32,33], aligns well with the recent rising role of pressure that has been extensively discussed in the literature of materials discovery [34–36].

On the other hand, Table II and Fig. 1 show that Mg_4Si_7 and Mg_5Si_6 , which have also been reported previously [6,7,11,12], are thermodynamically unstable at pressure P up to 30 GPa. For both of them, their lowest-enthalpy structures are always about 100–200 meV/atom above the convex hulls. This observation is consistent with more recent findings [19–23] that the β'' phase of Al-Mg-Si is not Mg_5Si_6 as previously conjectured. In case of Mg_4Si_7 , the theoretically proposed structures [6,8] were shown [8] to have positive formation energy at 0 GPa. These results, together with what’s revealed by Fig. 1, that ΔH_{DFT} of Mg_4Si_7 is significantly higher than the convex hulls at any P , suggest that the existence of Mg_4Si_7 is an open question.

Among the other binary compounds examined, Mg_2Si_3 and Mg_3Si_2 are “nearly” stable within 10–20 GPa, where their lowest-enthalpy structures are just about 1–5 meV/atom about the convex hulls. Although no direct report for these compounds are currently available, there are, however, a fair number of phases of the Al-Mg-Si alloys that have yet to be resolved [17]. As summarized by Table II and Fig. 1, pressure strongly alters the energetic ordering of the low-lying structures, being an important factor leading to the significant complexity of the systems.

B. MgSi_2

Although MgSi_2 is not thermodynamically stable at 0 GPa, it becomes stable at $P \simeq 10$ GPa and above. For completeness, we studied the lowest-lying structures of this compound at 0 GPa ($R\bar{3}m$), 10 GPa ($Imma$), 20 GPa, and 30 GPa (both $P6/mmm$). These structures, which are visualized in Fig. 2, are all dynamically stable, as demonstrated by the computed phonon band structures shown in the Supplemental Material [70]. Their computed electronic structures are given in Fig. 3, showing that these phases are all metallic. At 0GPa, the $R\bar{3}m$ phase features profound local maximum of the density of electron states right above the Fermi level E_F while at 10 GPa, 20 GPa, and 30 GPa, such local maxima ($\simeq 3$ states/eV

for $Imma$ phase at 10 GPa) are exactly at the Fermi level. The conduction bands contributing to these local maxima are primarily characterized by π -type bonding between adjacent Si atoms. They cross E_F several times, having multiple extremities and/or saddle points exactly at E_F , leading to the van Hove singularities. Such “flat band-steep band character,” which is a signature of possible superconductivity [71], has been widely

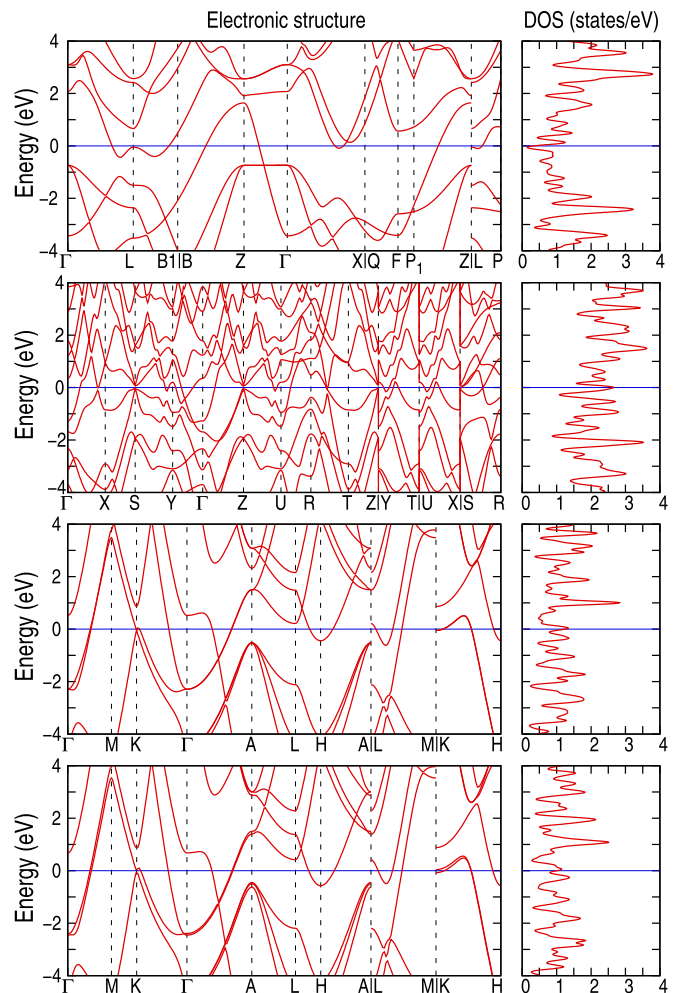


FIG. 3. Electronic structures of the lowest-enthalpy structures of MgSi_2 at, from top to bottom, 0 GPa ($R\bar{3}m$), 10 GPa ($Imma$), 20 GPa ($P6/mmm$), and 30 GPa ($P6/mmm$). The Fermi level (blue line) is placed at zero.

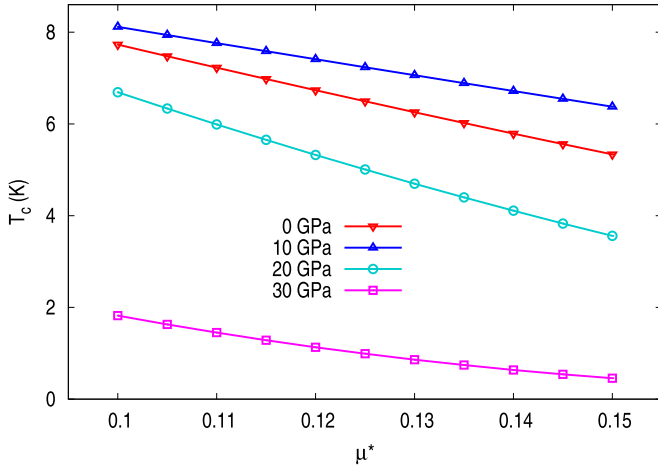


FIG. 4. Superconducting critical temperature calculated for MgSi_2 at 0 GPa ($R\bar{3}m$ phase), 10 GPa ($Imma$ phase), and 20 GPa and 30 GPa (both $P6/mmm$ phase).

used [28–30] in the literature as a screening criterion when predicting superconducting structures of solids.

The phonon-mediated superconducting properties of these predicted structures were computed with ABINIT package [67], employing the linear response approach [65,66]. In short, we estimated the critical temperature T_c using the Allandynes modified McMillan’s approximation of the Eliashberg equation according to [72,73]

$$T_c = \frac{\langle \omega_{\log} \rangle}{1.2} \exp \left[-\frac{1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)} \right]. \quad (2)$$

Here, λ is the overall electron-phonon coupling strength that can be computed from the frequency-dependent Eliashberg spectral function, $\langle \omega_{\log} \rangle$ the logarithmic average phonon frequency, and μ^* the Coulomb pseudopotential, for which the typical range of value (from 0.10 to 0.15) [72] was explored. For the $R\bar{3}m$ and $P6/mmm$ structures (three atoms per primitive cell), the k -point mesh was chosen to be $15 \times 15 \times 15$ while for the $Imma$ with larger primitive cell (six atoms), the k -point mesh was $12 \times 12 \times 12$. For all of these phases, the q -point mesh was $3 \times 3 \times 3$. We found that the experimentally realized $Imma$ phase of MgSi_2 is superconducting at $T_c \simeq 6.9$ K. The other structural phases of this compound, i.e., $R\bar{3}m$ and $P6/mmm$, also display superconducting characteristics at the critical temperatures T_c up to $\simeq 7$ K, as shown in Fig. 4.

C. MgSi

The proposed $P4/mmm$ structure of MgSi is composed of alternating Mg and Si rows along [100] direction [13,17]. At 0 GPa and 10 GPa, it is higher than the $P2_1/m$ and $C2/m$ structures predicted herein by $\simeq 140$ meV/atom and $\simeq 38$ meV/atom, respectively. At higher pressure, the $P4/mmm$ structure becomes lowest in energy compared to the other structures of MgSi . This phase is about 0.1 meV/atom above the convex hull at 20 GPa while at 30 GPa, it is thermodynamically stable. Crystallographic information, visualizations, and calculated phonon structures of these phases are given in the Supplemental Material, showing that they are distinct and dynamically stable [70].

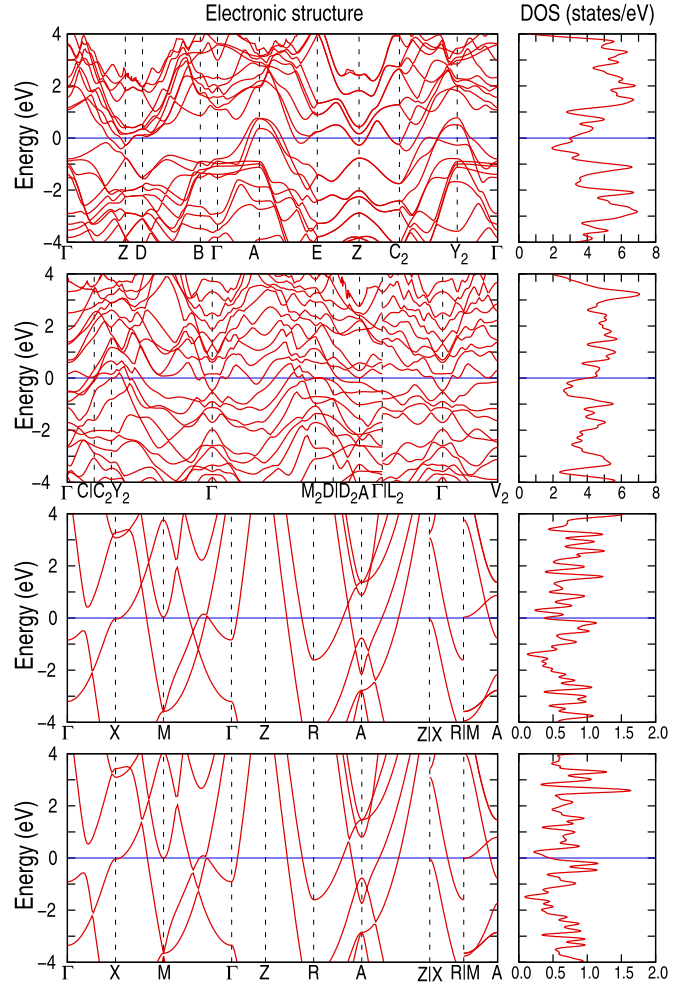


FIG. 5. Electronic structures of the lowest-enthalpy structures of MgSi at, from top to bottom, 0 GPa ($P2_1/m$), 10 GPa ($C2/m$), 20 GPa ($P4/mmm$), and 30 GPa ($P4/mmm$). The Fermi level (blue line) is chosen to be zero.

All of these phases are metallic, as revealed in Fig. 5, for their calculated electronic structures. At 0 GPa and 10 GPa, the $P2_1/m$ and $C2/m$ structures feature quite high density of electron states at the Fermi level E_F , i.e., $\simeq 2.0$ and $\simeq 4.0$ states/eV, respectively. The density of electron states at E_F of the $P4/mmm$ structure at 20 GPa and 30 GPa is lower, roughly 0.5 states/eV. Due to the large primitive cells (12 atoms) and low symmetries (monoclinic) of the $P2_1/m$ and $C2/m$ structures, calculations for their T_c are substantially heavy, and for this reason, we have not done this work. However, it is possible that these phases are superconducting at 0 and 10 GPa with relatively high critical temperatures, possibly about 5 K.

IV. CONCLUSIONS

The family of Mg-Si binary compounds is rich with energetically competing phases, which are easily reordered by external pressure. This paper provides some insights into the experimental observations of MgSi_2 , MgSi , Mg_9Si_5 , Mg_5Si_6 , and Mg_4Si_7 , whose proposed structures were found (computationally) to be thermodynamically unstable at ambient

conditions. We find that at some finite pressures, the low-energy structures of MgSi_2 , MgSi , and Mg_9Si_5 become stable. This result suggests that these binary compounds may likely be pressure-stabilized materials. The other two binary compounds considered, i.e., Mg_5Si_6 and Mg_4Si_7 are found to be unstable at pressure up to 30 GPa. This paper supports previous experimental and computational studies [19–23], claiming that the β'' phase of the Al-Mg-Si alloys is not Mg_5Si_6 as initially proposed. Similarly, the conjectured presence of Mg_4Si_7 [6,7] remains an open question. On the other hand, some other compounds, including Mg_2Si_3 and Mg_3Si_2 , are “nearly” stable at some ranges of pressure, and thus they may exist. Apparently, pressure should be considered for any computational studies of the formation of Mg-Si based solids,

especially those found in their metastable phases. Finally, we find that MgSi_2 is a potential superconductor within a wide range of pressure with the critical temperature of the order of 5 K.

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