# Refined phase diagram and kagome-lattice superconductivity in Mg-Si system

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In this work, by employing a variable-composition evolutionary algorithm combined with first-principles calculations, we have performed a comprehensive structural search for the magnesium silicide (Mg-Si) system and determined a hyperfine pressure-composition phase diagram. Three new pressure-stabilized structures, namely, P6/mmm-MgSi<sub>3</sub>, Cmmm-MgSi, and  $Pm\overline{3}m$ -Mg<sub>3</sub>Si, are found. Of particular interest is that P6/mmm-MgSi<sub>3</sub> with silicon kagome-lattice characteristic is a single-gap superconductor with a superconducting transition temperature ( $T_c$ ) about 13.7 K (higher than those of the experimental reported kagome superconductors), which is closely associated with strong electron-phonon coupling mainly determined by silicon kagome lattice. Moreover,  $Pm\overline{3}m$ -Mg<sub>3</sub>Si exhibits a zero-dimensional (0D) electride characteristic with the excess electrons trapped in the Mg-based octahedral cavity. Our findings not only refine the phase diagram of the Mg-Si system, but also expend an in-depth comprehension of the structural diversity and unique electronic states in the alkaline-earth metal silicides under high pressure, which also provide insights into exploring the formation and evolution of the structure of the rocky planets.

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# I. INTRODUCTION

The metal-containing carbides or silicides have attracted extensive attention owing to their unique structural phases and rich physical properties, such as covalently metallic feature [1,2], superconductivity [3–7], and electride state [8]. Among these materials, a notable example is the calcium carbide (Ca-C) system. On the one hand, the discovery of the carbonrich compounds provides a unique degree of freedom to design novel carbon allotropes, which can be obtained by removing guest metal atoms due to the covalent framework formed by the carbon sublattice [5–7]. Subsequently, this similar idea called "two-step" method is successfully applied to design and synthesis silicon allotropes [9-11]. On the other hand, the existence of the covalent bonding causes large phonon frequencies and a large electron-phonon coupling (EPC), leading to a high  $T_c$  superconductivity [2]. Pressure, as an important thermodynamic parameter, has become a powerful tool to obtain unconventional stoichiometric compounds with unexpected properties or structural feature [12-14]. For instance, the pressure-induced recurrence of superconductivity in the CaC<sub>6</sub> compound is unexpectedly observed due to the carbon atomic rearrangement under compression [6]. More diverse rearrangement features of carbon atoms from zero-dimensional (0D) dumbbell to one-dimensional chain to two-dimensional layer can also be found in the CaC<sub>2</sub> compound under pressure [7]. Additionally, high pressure paves an effective route to enable novel stoichiometries with the remarkable structure. LiSi3 and NaSi6 formed by silicon kagome networks can be stabilized and exhibit intrinsic superconductivity at high pressures [10,15]. However, the structure-property relationships between kagome lattice and superconductivity have not been well revealed. These studies motivate us to further think about an interesting question: do other metal silicides inherit this similar structure and exhibit more richer physical properties?

As one of alkaline-earth metal adjacent to Na and Li, Mg has one more electron than the above alkali metals, which shows higher reaction activity. Meanwhile, high pressure can change the chemical reactivity of the element by affecting the electronic configuration. Thus, compared to Li-Si and Na-Si systems [10,15], it is expected the Mg-Si system have more diverse structures under high pressure. As is well known, Mg<sub>2</sub>Si is the only energetically stable structure at ambient pressure [16,17]. It is theoretically demonstrated that pressurized Mg<sub>2</sub>Si undergoes a phase transition sequence  $Fm\overline{3}m \rightarrow$  $Pnma \rightarrow P6_3/mmc \rightarrow C2/m$  with pressure transition points of 6, 24, and 38 GPa, respectively [18]. However, experimental work has demonstrated that Fm3m-Mg<sub>2</sub>Si can be decomposed to Mg<sub>9</sub>Si<sub>5</sub> and Mg above 3 GPa at high temperature condition [19]. In addition, other binary Mg-Si compounds, such as Mg<sub>9</sub>Si<sub>5</sub> [20], MgSi [21,22], Mg<sub>5</sub>Si<sub>6</sub> [23],  $Mg_4Si_7$  [24], and  $MgSi_2$  [25] have subsequently been reported or suggested in the experiment of the precipitation-hardened Al-Mg-Si alloys. However, the experimental observation of the Mg-Si structures seems to contradict the theoretical prediction [18,26], which is likely related to the unusual thermodynamic phase diagram. In order to settle this inconsistency in the Mg-Si system and considering the fact that Mg-Si compounds are common minerals in the earth and rocky planets [27], and its research on high-pressure properties is crucial for understanding the formation and evolution of the planetary internal structure, we need to resort to a more effective structural prediction method, such as the variable-composition

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FIG. 1. (a) Convex hull diagram for the Mg-Si system at selected pressures. At a given pressure, the compounds located on the convex hull are thermodynamically stable. (b) Pressure-composition phase diagram of the Mg-Si system. Solid and dashed lines represent thermodynamically stable and metastable phases, respectively. Blue and red lines denote metallic and semiconducting characteristic, respectively.

structural search method, which exhibits its strong predictable ability [28,29].

To this end, we here performed a comprehensive structural search on the Mg-Si system at pressures up to 60 GPa by *ab initio* evolutionary algorithm. Three new Mg-Si compounds are found to be stable under pressure, namely, *P6/mmm*-Mg<sub>3</sub>Si, *Cmmm*-MgSi, and *Pm*3*m*-MgSi<sub>3</sub>, and all of them exhibit metallic characteristic. Especially, *P6/mmm*-MgSi<sub>3</sub> is found to be a single-gap superconductor with the  $T_c$  of about 13.7 K and superconducting gap of about 2.1 meV, which stems from the strong EPC between the in-plane vibrational phonons and Si-*p* electronic states in the silicon kagome layer. Moreover, Mg<sub>3</sub>Si with *Pm*3*m* space group is identified as a 0D electride and its chemical formula can be expressed as  $[Mg_3Si]^{2+} \cdot 2e^{-}$ .

### **II. COMPUTATIONAL DETAILS**

The structural searches for the Mg-Si system under high pressure are carried out using the evolutionary algorithm USPEX code [28,29] coupled with the Vienna ab initio simulation package (VASP) program [30] based on densityfunctional theory (DFT) within the generalized gradient approximation with the exchange-correlation functional of Perdew-Burke-Ernzerhof (PBE) [31]. We adopted projectoraugmented wave (PAW) method with  $3s^2$  for Mg and  $3s^23p^2$ for Si represented as the valence electrons [32]. The cutoff energy is set to 500 eV and appropriate Monkhorst-Pack k meshes are used in the calculations. The electron localization function (ELF) [33] is used to analyze the interatomic bonding. The phonon spectra and electron-phonon coupling calculations are carried out with the density-functional perturbation theory as implemented in the QUANTUM ESPRESSO package [34]. The cutoff energies of wave function and charge density are 80 Ry and 480 Ry, respectively. The k mesh (q mesh) were chosen to be  $8 \times 8 \times 16$  ( $8 \times 8 \times 16$ ) for the MgSi<sub>3</sub>. The superconducting gap is estimated by solving the anisotropic Migdal-Eliashberg equation as implemented in electron-phonon Wannier (EPW) code [35,36], in which the interpolated k point and q grid of  $20 \times 20 \times 40$  and  $20 \times 20 \times 40$  are used.

## **III. RESULTS AND DISCUSSION**

### A. Phase stability and structural characteristics of Mg-Si compounds

In order to obtain stable structures of Mg-Si systems, extensive structural searches are performed by using the variable-composition scheme at selected pressures of 0, 15, 45, and 60 GPa. The relative thermodynamic stabilities of the Mg-Si compounds at different pressures are shown in the convex hull in Fig. 1(a). Here, the formation enthalpy  $(\Delta H)$  relative to elemental Mg and Si solids for all predicted Mg-Si structures in each chosen stoichiometry are evaluated, according to  $\Delta H(Mg_rSi_v) = [H(Mg_rSi_v) - Mg_rSi_v)$ xH(Mg) - yH(Si)]/(x + y). All thermodynamically stable phases represented with filled circles lie on the global stability line, whereas compositions represented with hollow circles are metastable or unstable. Consequently, three new highpressure structures with various stoichiometries or structural phases, namely, Pm3m-Mg<sub>3</sub>Si, P6/mmm-MgSi<sub>3</sub>, and Cmmm-MgSi, emerge with the increasing pressure. As shown in Fig. S1 of the Supplemental Material (SM) [37], we have also calculated the phonon spectra of all thermodynamically stable phases and no imaginary frequency modes are observed, indicating their dynamical stability.

Next, we construct the pressure-composition phase diagram to determine the stable pressure range of the three new found compounds, and the results are shown in Fig. 1(b). Consistent with the previous studies [18,26], only the known Mg<sub>2</sub>Si composition with  $Fm\overline{3}m$  phase is thermodynamically stable at 0 GPa. Under pressure, the ambient phase  $Fm\overline{3}m$  of Mg<sub>2</sub>Si transforms at 6 GPa into *Pnma* phase, then into the *P*6<sub>3</sub>/*mmc* phase at 20 GPa, and finally becomes metastable when pressure is larger than 30 GPa. For Mg<sub>9</sub>Si<sub>5</sub>, only one energetically favored *P*6<sub>3</sub>/*m* phase is found and is stable from

Structure	Space group	Pressure (GPa)	Lattice parameters	Wyckoff sites
Mg <sub>3</sub> Si	Pm3m	15	a = b = c = 4.258  Å $\alpha = \beta = \gamma = 90.00^{\circ}$	Mg 3 <i>d</i> (0.00 0.00 0.50) Si 1 <i>b</i> (0.50 0.50 0.50)
MgSi	Cmmm	58	a = 5.594 b = 7.845 c = 2.791 Å	Mg 4 <i>j</i> (0.00 0.78 0.50) Si 4 <i>g</i> (0.21 0.50 0.00)
MgSi <sub>3</sub>	P6/mmm	10	$a = \beta = \gamma = 90.00$ $a = b = 5.045 \text{ Å}$ $c = 2.601 \text{ Å}$ $\alpha = \beta = 90.00^{\circ} \gamma = 120.00^{\circ}$	Mg 1 <i>b</i> (0.00 0.00 0.50) Si 3 <i>f</i> (0.50 0.50 0.00)

TABLE I. Space groups, lattice parameters, and Wyckoff sites of  $Pm\bar{3}m$ -Mg<sub>3</sub>Si, P6/mmm-MgSi<sub>3</sub>, and Cmmm-MgSi at the selected pressures.

4 to 21 GPa, which are in accordance with Ref. [26]. Starting from 12 GPa, the previously known MgSi<sub>2</sub> composition is stable in P6/mmm phase. We also note that the formation enthalpy of P6/mmm-MgSi2 is very close to those of the other two competing phases *Imma* and  $P6_3/mmc$ , as shown in Fig. 1(a). This is because the above three phases tend to be similar with the increasing pressure. In addition, the known  $P\overline{1}$ -MgSi is stable from 9 to 15 GPa, and P4/mmm-MgSi becomes stable in the pressure ranges of 26–58 GPa. Besides  $P\overline{1}$  and P4/mmm phases for MgSi composition, there is a new Cmmm phase, and the predicted Cmmm phase is more stable than P4/mmm phase above 58 GPa. Following Refs. [20,25], the reported C2/m phase of Mg<sub>5</sub>Si<sub>6</sub> and Mg<sub>4</sub>Si<sub>7</sub> always remain thermodynamically metastable in the studied pressure range (see Fig. S2 [37]), consistent with the recently reported results [26]. More interestingly, it can be seen that both of the two new predicted *Pm3m*-Mg<sub>3</sub>Si and *P6/mmm*-MgSi<sub>3</sub> compositions have only one high-pressure phase and are energetically stable in the pressure ranges of 11-60 GPa and 10-59 GPa, respectively.

The structural characteristic is the most fundamental factor that determines the physical properties of the materials. In this regard, space group, lattice parameters, and Wyckoff sites of the predicted compounds at the selected pressures are given in Table I. For *Pm3m*-Mg<sub>3</sub>Si, each Si atom is 12-fold coordinated by Mg atoms, forming a [SiMg<sub>12</sub>] cuboctahedron with eight triangular faces and six square faces, as shown in Fig. 2(a). The similar structural feature can be found in Mg<sub>3</sub>Ge compound [38]. Moreover, the crystal structure of Pm3m-Mg<sub>3</sub>Si also contains a [Mg<sub>6</sub>] octahedra with the Mg-Mg bond length of 3.01 Å at 15 GPa. The existence of the [Mg<sub>6</sub>] octahedral cavity provides a great possibility to accommodate interstitial quasiatoms that behave as anions (discussed later). Figure 2(b) gives the crystal structure of the high-pressure phase Cmmm for MgSi compound (Cmmm-MgSi) at 58 GPa, wherein eight Si atoms surround each Mg atom to form a distorted [MgSi<sub>8</sub>] hexahedron with two inequal Mg-Si bond lengths of 2.57 and 2.51 Å. As shown in Fig. 2(c), MgSi<sub>3</sub> stabilizes into a hexagonal structure with P6/mmm space group, in which the intralayer and interlayer Si-Si bond lengths are about 2.52 Å and 2.60 Å at 10 GPa, respectively. More interestingly, the interlayer Si atoms form a kagome lattice, and Mg atom is located in the center of  $[Si_{12}]$ octahedron formed by the kagome bilayer of Si lattice. This similar kagome structure is commonly found in alkali-metal silicides, such as P6/mmm-LiSi<sub>3</sub> [15],  $Fd\overline{3}m$ -KSi<sub>2</sub> [39], and P2/m-NaSi<sub>4</sub> [40]. However, the high-pressure superconductive behaviors of these systems with unique structure have not received much attention. It is worth noting that the unique kagome structure often exhibits wealthy physical properties, such as flat band, superconductivity, and nontrivial topology [41]. This signals that it is necessary to study the relationship between these structures and their unexplored physical properties.

#### B. Electronic properties of Mg-Si compounds

To further understand the electronic properties of the new predicted Mg-Si compounds, their band structures and the corresponding projected density of states (PDOS) are investigated, as presented in Figs. 3(a), 3(c) and Fig. S3 [37]. The calculated results show that three predicted stable phases exhibit metallic feature. In detail, it is found that the electronic states near the Fermi level of  $Pm\overline{3}m$ -Mg<sub>3</sub>Si mainly come from Si-*p* and Mg-*s*/*p* electrons, and these states exhibit a strong hybridization from its PDOS result. Considering the formal valence states of Mg<sup>3+</sup> and Si<sup>4-</sup>, there should be two excess electrons that behave as anionic quasiatoms. This unique



FIG. 2. The atomic crystal structures of (a)  $Pm\overline{3}m - Mg_3Si$ , (b) Cmmm - MgSi, and (c)  $P6/mmm - MgSi_3$ . Mg and Si atoms are represented by orange and blue balls, respectively.



FIG. 3. The orbital-projected band structure and DOS of (a)  $Pm\overline{3}m$ -Mg<sub>3</sub>Si at 15 GPa, (b) P6/mmm-MgSi<sub>3</sub> at 10 GPa. "X" denotes the interstitial electron. The corresponding ELF maps of  $Pm\overline{3}m$ -Mg<sub>3</sub>Si and P6/mmm-MgSi<sub>3</sub> with the isovalues of 0.69 and 0.65, respectively.

electronic behavior can be confirmed by the ELF map shown in Fig. 3(b). There are some localized electrons trapped in the interstitial spaces located on the center of [Mg<sub>6</sub>] octahedra, indicating that  $Pm\bar{3}m$ -Mg<sub>3</sub>Si is a zero-dimensional (0D) electride with the excess electrons confined in the [Mg<sub>6</sub>] cavity. For convenience, the anionic quasiatoms are denoted by X in Figs. 3(a) and 3(c). To identify the contributions from these interstitial electrons, we adopt the pseudoatom method where a pseudoatom with a Wigner-Seitz radius of 0.76 Å is placed in the center of [Mg<sub>6</sub>] octahedra to calculate X-projected band structure and DOS, as shown in Fig. 3(a). We find that the contribution of the interstitial electrons (X) is smaller than that of the Mg and Si atoms due to their localized characteristic. Moreover, we consider the effect of different Wigner-Seitz radius sizes, as shown in Fig. S4 [37]. One can conclude that our adopted value used for the analysis of the electronic distribution is reasonable, indicating the reliability of our results. To further estimate the number of the interstitial electrons, we have performed the Bader charge analysis, and found that the Bader charges of Mg, Si, and X atoms are 1.37 |e|, -2.20 |e|,and -2.21 |e|, respectively, which means that the interstitial electrons are actually derived from the exceeding electrons of Mg atoms. Combined with the above results,  $Pm\overline{3}m$ -Mg<sub>3</sub>Si is a metallic 0D electride and its chemical formula can be written as  $(Mg_{3}Si)^{2+} \cdot 2e^{-}$ .

Figure 3(c) presents the orbital-projected band structure and DOS of P6/mmm-MgSi<sub>3</sub> at 10 GPa. We can find that Si-*p* states mainly contribute to the electronic bands around the Fermi level, which implies that the main physics of P6/mmm-MgSi<sub>3</sub> is essentially related to the Si kagome lattice. From ELF map of P6/mmm-MgSi<sub>3</sub> shown in Fig. 3(d), one can see that MgSi<sub>3</sub> shows obvious ionic-like characteristics for Mg-Si bonding, which in nature attributes to the large difference in electronegativity between the Mg atom and Si atom. For *Cmmm*-MgSi compound, as shown in Fig. S3 [37], it is shown that the electronic states in the low-energy bands



FIG. 4. (a) Phonon dispersion, PHDOS, Eliashberg function  $\alpha^2 F(\omega)$ , the linewidths for phonon mode  $\gamma_{qv}$  are denoted by the size of red circle. The insert shows the  $B_{2u}$  phonon mode with strongest EPC at  $\Gamma$  point. (b) Temperature-dependent superconducting gap distribution of P6/mmm-MgSi<sub>3</sub> obtained by anisotropic Migdal-Eliashberg theory. Red dashed curve represents the superconducting gap. (c) Distribution of the electron-phonon coupling strength  $\lambda_k$ . (d) Normalized superconducting quasiparticle DOS of P6/mmm-MgSi<sub>3</sub> at 3 K and 11 K.

are mainly contributed by the Si-*p* electrons. This is closely associated with the unique Si-Si bonding feature, which can be demonstrated by the ELF. There is a dumbbell-like shape between the two adjacent Si atoms in the ELF map shown in Fig. S3 [37], indicating that they are strong covalently bound in the metallic Si-Si dimer.

#### C. Electron-phonon coupling and superconductivity

The extensive explorations of superconductivity in the kagome materials provide a great platform to study potentially exotic superconducting behavior on the kagome lattice [41]. We will thus explore the possible superconductivity of P6/mmm-MgSi<sub>3</sub> compound. Although MgSi<sub>3</sub> is not thermodynamically stable at 0 GPa, it is dynamically stable shown in Fig. 4(a) because no imaginary frequencies are observed. Moreover, according to the statistics, about 20% of the fabricated materials are actually metastable and some of them even have the positive formation enthalpies [42–44]. This behavior is also observed in alkaline-earth metal-IVA compounds, such as  $CaC_6$  [5,6], in which the metastable feature is maintained in the whole pressure range and does not preclude its successful synthesis in experiment. As such it is expected that P6/mmm-MgSi3 compound can be synthesized experimentally. Therefore, we here take P6/mmm-MgSi<sub>3</sub> compound at 0 GPa as an example, and the corresponding phonon dispersion, atom-projected phonon DOS (PHDOS), Eliashberg spectral function  $\alpha^2 F(\omega)$ , and integrated  $\lambda(\omega)$  are calculated, as shown in Fig. 4(a). To further understand the nature of the EPC, the linewidths for phonon mode  $\gamma_{qv}$  are attached on phonon dispersion curves. It is clearly seen that the main contribution to the EPC strength is from the optical branches, and the largest  $\gamma_{qv}$  from the optical branch at  $\Gamma$  point is dominated by the Hyper-Raman active mode  $B_{2u}$ . Note that the Mexican-hat-like feature for the  $B_{2u}$  branch observed around  $\Gamma$  point gives rise to the  $\delta$ -like peaks around 8.0 THz in both the PHDOS and the spectral function  $\alpha^2 F(\omega)$ , thus leads to a large EPC constant  $\lambda$  of about 0.81. From the atom-projected PHDOS, the  $B_{2u}$  mode is dominated by Si atoms, which can also be demonstrated by the insert of Fig. 4. It is shown that  $B_{2\mu}$  mode only involves the relative vibration between Si atoms along the xy plane or the in-plane direction. From the PHDOS, Eliashberg spectral function  $\alpha^2 F(\omega)$ , and integrated  $\lambda(\omega)$ , the entire EPC can be divided into the contributions from three frequency regions: low frequencies below 3 THz, intermediate frequencies between 3 THz and 9 THz, and high frequencies above 9 THz. The calculated results show that low-frequency and high-frequency vibrations are dominated by Mg atoms and these only contribute 8.4% of the total value of  $\lambda$ , demonstrating that the main contributions to  $\lambda$  are from the intermediate-frequency vibrations dominated by Si atoms. Next, the contributions of the atomic vibrational directions are analyzed and the results are shown in Fig. S5 [37]. It is found that the intermediate-frequency vibrations stem from the inplane vibrations of Si atoms  $(Si_{x+y})$  and the contributions from the out-of plane ones  $(Si_z)$  are negligible, which is in accord with the fact that  $B_{2u}$  vibration mode contributes to the largest linewidth at  $\Gamma$  point. These results mean that kagome lattice constructed by silicon atomic layer plays a main role in the superconductivity of P6/mmm-MgSi<sub>3</sub>.

superconducting The transition temperature of P6/mmm-MgSi<sub>3</sub> is further estimated based on the McMillan-Allen-Dynes formula [45], namely,  $T_{\rm c} = \frac{\omega_{\rm log}}{1.2}$  $\exp[-\frac{1.04(1+\lambda)}{\lambda-\mu^*(1+0.62\lambda)}]$ . Here, we adopt a typical value of 0.11 for the effective Coulomb repulsion parameter  $\mu^*$  [46], along with the calculated logarithmic averaged frequency  $\omega_{log}$ of 254 cm<sup>-1</sup> and  $\lambda$  of 0.81, and the estimated  $T_c$  value of P6/mmm-MgSi<sub>3</sub> at zero pressure is about 11.4 K, which is higher than those of other superconducting kagome systems, such as  $C_{s}V_{3}Sb_{5}$ ,  $AV_{3}Sb_{5}$  (A = K, Rb, Cs), etc [47–49]. Next, we calculate band- and wave-vector-dependent EPC strength defined by  $\lambda_{\mathbf{k}} = \sum_{\mathbf{k}'} W_{\mathbf{k}'} \lambda(\mathbf{k}, \mathbf{k}', n = 0)$  to quantify the anisotropy of EPC, as shown in Fig. 4(b). It is shown that  $\lambda_k$  exhibits a wide spread between 0.6 and 1.1, signaling a strongly anisotropic EPC. To this end, the anisotropic Migdal-Eliashberg theory is employed to investigate the finte-temperature superconducting properties of P6/mmm-MgSi<sub>3</sub> at 0 GPa, as shown in Fig 4(c). The  $T_{\rm c}$  estimated by the anisotropic Eliashberg equation is around 13.7 K, which is higher than the  $T_c$  obtained by the McMillan-Allen-Dynes formula. In addition, the superconducting gap of P6/mmm-MgSi<sub>3</sub> at zero-temperature limit  $\Delta_0$  is about 2.1 meV, leading a large ratio  $2\Delta_0/k_{\rm B}T_{\rm c}$ of 3.56, which is close to the BCS value of 3.53. As shown in Fig 4(d), in addition, P6/mmm-MgSi<sub>3</sub> exhibits a distinct single-gap superconductivity and there is a peak in the normalized quasiparticle DOS.



FIG. 5. Pressure-dependent EPC constant  $\lambda(\omega)$ , the logarithmic averaged frequency  $\omega$ , and superconducting transition temperature  $T_c$  of P6/mmm-MgSi<sub>3</sub>.

Considering the fact that P6/mmm-MgSi<sub>3</sub> tends to be more stable in the thermodynamical behavior under high pressure, we thus study the pressure effect on superconducting properties of P6/mmm-MgSi<sub>3</sub>. Figure 5 presents the  $\lambda$ ,  $\omega_{log}$ , and  $T_c$  as a function of the external pressure. It is obvious that the  $\omega_{log}$  is enlarged with the increasing pressure but the  $T_c$  is almost linearly decreased. This theoretical behavior of  $T_c(P)$ stems from the significant suppression of  $\lambda$  with increasing pressure, which is ascribed to the decreasing of the electronic density of states at the Fermi level due to the widening of the band structure with pressure.

## **IV. CONCLUSION**

In summary, we have refined the phase diagram of the Mg-Si system by using the first-principles calculation coupled with the evolutionary crystal structure prediction method, three novel Mg-Si compounds (P6/mmm-Mg<sub>3</sub>Si, *Cmmm*-MgSi, *Pm3m*-MgSi<sub>3</sub>) are identified to be thermodynamically stable under high pressure. Moreover, the results of ELF and pseudoatomic projection analysis identify that the  $Pm\overline{3}m$ -Mg<sub>3</sub>Si is a 0D electride with the excess electrons confined in the [Mg<sub>6</sub>] octahedral cavity. Electron-phonon coupling calculation indicates that P6/mmm-MgSi<sub>3</sub> with kagome structure has intrinsic superconductivity, which is attributed to the strong coupling between in-plane vibrational phonons of silicon kagome layers and the Si-p electronic states. By solving the fully anisotropic Migdal-Eliashberg equations, we find that P6/mmm-MgSi<sub>3</sub> is a single-gap superconductor with the high  $T_c$  of 13.7 K and a superconducting gap  $\Delta_0$  of 2.1 meV. Our results not only enrich the phase diagram of the Mg-Si system, but also provide insights into structural diversity and exotic physical properties of the alkali-metal silicides under pressure.

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