Helium incorporation induced direct-gap silicides

Shicong Ding\textsuperscript{1}, Jingming Shi\textsuperscript{1}*, Jiahao Xie\textsuperscript{1}, Wenwen Cui\textsuperscript{2}, Pan Zhang\textsuperscript{1}, Kang Yang\textsuperscript{1}, Jian Hao\textsuperscript{1}, Lijun Zhang\textsuperscript{2} and Yinwei Li\textsuperscript{1,\textsuperscript{3}}

The search of direct-gap Si-based semiconductors is of great interest due to the potential application in many technologically relevant fields. This work examines the incorporation of He as a possible route to form a direct band gap in Si. Structure predictions and first-principles calculations show that He and Si, at high pressure, form four dynamically stable phases of Si\textsubscript{2}He (oP\textsubscript{36}-Si\textsubscript{2}He, tP\textsubscript{9}-Si\textsubscript{2}He, mC\textsubscript{18}-Si\textsubscript{2}He, and mC\textsubscript{12}-Si\textsubscript{2}He). All phases adopt host–guest structures consisting of a channel-like Si host framework filled with He guest atoms. The Si frameworks in oP\textsubscript{36}-Si\textsubscript{2}He, tP\textsubscript{9}-Si\textsubscript{2}He, and mC\textsubscript{12}-Si\textsubscript{2}He could be retained to ambient pressure after removal of He, forming three pure Si allotropes. Among them, oP\textsubscript{36}-Si\textsubscript{2}He and mC\textsubscript{12}-Si\textsubscript{2}He exhibit direct band gaps of 1.24 and 1.34 eV, respectively, close to the optimal value (~1.3 eV) for solar cell applications. Analysis shows that mC\textsubscript{12}-Si\textsubscript{2}He with an electric dipole transition allowed band gap possesses higher absorption capacity than cubic diamond Si, which makes it to be a promising candidate material for thin-film solar cell.

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INTRODUCTION

With the growth of population and the development of science and economy, human beings need more energy to create a better living environment. However, burning traditional fossil fuels is causing climate change, global warming, air pollution, acid rain, and a serious of other environmental problems\textsuperscript{5–8}. Thus, energy becomes one of the most important issues on the international environment and development agenda. Photovoltaic modules provide a clean, reliable, and abundant way to convert solar energy into electricity to meet the growing demand for energy\textsuperscript{5}. Conformational space annealing calculations have uncovered two new Si allotropes, Q\textsubscript{135} and D\textsubscript{135}, with direct band gaps of 0.98 and 1.33 eV, respectively, both of which were proposed to be good photovoltaic materials with estimated photovoltaic efficiency of ~30%\textsuperscript{23}. Ab initio random structure searching has also revealed a new Si structure with space group \textit{Pbam} and a direct band gap of 1.4 eV\textsuperscript{24}. By substituting C or Ge atoms in their structures with Si atoms, at least 17 candidate structures were predicted\textsuperscript{25–30}, of which nine\textsuperscript{27–29} (M\textsubscript{8}58, P\textsubscript{bam}-32, P\textsubscript{6}/mmm, I\textsubscript{m}3\textsubscript{m}, C\textsubscript{2}c, I\textsubscript{4}/mmc, I\textsubscript{4}/mmm, P\textsubscript{2}1\textsubscript{1}/m, and P\textsubscript{4}/nmm) have direct band gaps of 0.65–1.51 eV. Ab initio minima hopping structure predictions have also predicted more than 44 Si structures, of which eleven (R\textsubscript{3}m-1, R\textsubscript{3}m-2, C\textsubscript{2}i, I\textsubscript{4}mm, I\textsubscript{4}2\textsubscript{2}d, I\textsubscript{2}1\textsubscript{1}2, and P\textsubscript{4}2\textsubscript{1}2\textsubscript{1}2\textsubscript{1}) exhibit direct band gaps of 1.0–1.8 eV\textsuperscript{21,32}. All these direct or quasi-direct Si structures are metastable, possessing a high energy relative to CD-Si, and thus are difficult to synthesize directly.

Si-rich compounds with open framework structures formed at high pressures are good precursors to obtain new Si allotropes. A two-step synthesis method has made two metastable allotropes (a clathrate S\textsubscript{i}3\textsubscript{α3},\textsuperscript{33} and a channel-like S\textsubscript{i}24\textsuperscript{34}) by removing Na from high-pressure Na–Si compounds. Channel-like S\textsubscript{i}24 was prepared by first synthesizing at high pressure a Na\textsubscript{2}S\textsubscript{i}24 precursor that contained a channel-like sp\textsuperscript{3} Si host structure filled with linear Na chains. Na atoms were removed along the open channels via thermal degassing, leaving the pure S\textsubscript{i}24 allotrope. Electrical conductivity and optical absorption measurements confirmed a...
quasi-direct band gap of 1.3 eV, making $\text{Si}_{24}$ a potential photovoltaic material.

The noble gas He becomes reactive at high pressure, leading to several new compounds, including some materials which are synthesized on experiment, such as Na$_4$He$_4$ and NeHe$_2$, and some predicted materials, such as $\text{He}_4$, $\text{He}$–alkali oxides (sulfides) $^{53}$, $\text{He}$–Fe $^{44}$, $\text{Fe}$–O–He $^{45}$, $\text{Mg}$($\text{Ca}$)F$_2$He $^{46}$, $\text{He}$–$\text{H}_2\text{O}$, $^{47,48}$, $\text{He}$–$\text{CH}_4$, $^{49}$, and $\text{He}$–$\text{NH}_3$. $^{50-52}$ Although most of these materials are predicted under extreme condition, the results provide a clear indication that He can break through the chemical inert barrier and react with other substances. The incorporation of inert He tends to form open framework structures with weak interactions between He and the host sublattice. For example, our previous calculations predicted a $\text{HeN}_4$ compound formed at high pressure $^{42}$, which consists of open channels of $\text{N}$ atoms holding He. Their weak interactions allow the removal of the He from the structure, leading to a pure $\text{N}$ framework.

**RESULTS**

Crystal structure searches

Structure predictions are first performed for $\text{Si}_2\text{He}$ at 10 GPa with a maximum of eight formula units (f.u.) in a simulation cell. The previously proposed $\text{hP6-Si}_2\text{He}^{53}$ is successfully predicted, but with much higher enthalpy, as shown in Fig. 1. Instead, the four structures we predicted are energetically favorable than $\text{hP6-Si}_2\text{He}^{53}$. Crystal structures of four phases are shown in Fig. 2 and the lattice parameters of these structures are listed in the Supplementary Table 1. The four structures with increasing energy are $\text{oP36-Si}_2\text{He}$, $\text{tP9-Si}_2\text{He}$, $\text{mC18-Si}_2\text{He}$, and $\text{mC12-Si}_2\text{He}$ in addition to $\text{hP6-Si}_2\text{He}^{53}$. The He atoms trapped inside the channels are easily removed from $\text{oP36-Si}_2\text{He}$, $\text{tP9-Si}_2\text{He}$, and $\text{mC12-Si}_2\text{He}$ to form $\text{oC24-Si}$, $\text{tP6-Si}$, and $\text{mC8-Si}$, respectively. Interestingly, $\text{oP36-Si}_2\text{He}$ and $\text{mC12-Si}_2\text{He}$ are direct-gap semiconductors with band gaps of 1.24 and 1.34 eV, respectively, proximately to the Shockley–Queisser limit (1.34 eV). In particular, $\text{mC12-Si}_2\text{He}$ has an electric dipole transition allowed direct band gap, making it a good candidate photovoltaic material.

Structural configurations of predicted phases

All structures are channel frameworks composed of four coordination Si atoms and filled with He atoms in the voids, as shown in Fig. 2. The energetically most stable structure $\text{oP36-Si}_2\text{He}$ is orthorhombic with space group $Pnnm$ (12 f.u. in a unit cell), as shown in Fig. 2a. The Si sublattice of $\text{oP36-Si}_2\text{He}$ along the $a$-axis shows a one-dimensional channel structure composed of ten-, six-, and five-membered rings. The Si–Si bond lengths are ranging from 2.28 to 2.33 Å, slightly shorter than that of $\text{hP6-Si}_2\text{He}$ (2.35 Å$^{53}$). Helium atoms are stacked in triangles in quasi-circular channels of ten membered rings (see Supplementary Fig. 2). The triclinic $\text{tP9-Si}_2\text{He}$ has a symmetry of $P3_12$ (3 f.u. in a unit cell), as shown in Fig. 2b. The silicon atoms form a spiral staircase configuration with a six-membered circular channel, and the helium atoms are distributed in three vertical columns in the channel with the He–He distance of 2.34 Å. The $\text{mC12-Si}_2\text{He}$ phase is monoclinic with the symmetry of $C2/m$ (6 f.u. in a unit cell). The Si atoms form six- and five-membered rings, and two six-membered rings are connected by two layers of five-membered rings dislocated and stacked along the $c$-axis, as shown in Fig. 2c. The Si–Si bond lengths are ranging from 2.30 to 2.37 Å. The He atoms form a tilted triangle arranged along the channel. The $\text{mC12-Si}_2\text{He}$ is monoclinic with space group $C2/m$ (4 f.u. in a unit cell), as shown in Fig. 2d. Two kinds of channels sharing edges are found along the $b$-axis formed by five- or seven-membered rings of Si atoms. A zigzag arrangement of He atoms is located inside the larger channels formed by the seven-membered rings. The shortest distances between He and the Si channel in structures of $\text{oP36-Si}_2\text{He}$, $\text{tP9-Si}_2\text{He}$, $\text{mC18-Si}_2\text{He}$, and $\text{mC12-Si}_2\text{He}$ are 2.73, 2.36, 2.64, and 2.49 Å, respectively, which are shorter than the Na–Si distance (3.01 Å) in $\text{Na}_4\text{Si}_2\text{He}^{54}$. Similar host–guest structures have been reported in several other compounds, such as $\text{Na}_5\text{Si}_{24}$ $^{34}$ and $\text{HeNa}_4$. $^{42}$ The previously proposed $\text{hP6-Si}_2\text{He}^{53}$ can also be regarded as a host–guest structure with a distorted diamond hexagonal host Si sublattice encapsulating guest He atoms inside the hexagonal channels. The lowest enthalpy of $\text{oP36-Si}_2\text{He}$ compared with $\text{hP6-Si}_2\text{He}$ suggests that Si can form larger channels for the incorporation of He. The dynamic stability of $\text{oP36-Si}_2\text{He}$, $\text{tP9-Si}_2\text{He}$, $\text{mC18-Si}_2\text{He}$, and $\text{mC12-Si}_2\text{He}$ at 10 and 0 GPa are confirmed by phonon dispersion calculations, as shown in Supplementary Figs. 4 and 5 (including the vdW interaction).
The MD simulation (with the vdW interaction) reveals that all structures exhibit thermodynamic stability at ambient pressure and temperature (300 K), suggesting that all of them could be quenched and recovered at ambient conditions once formed (see Supplementary Fig. 6).

### Charge transfer and CI-NEB energy barrier of silicides

Electron localization function calculations exclude the existence of Si–He covalent bonds in both compounds given the absence of electron localization between them (see Supplementary Fig. 3). Bader charge analysis suggests slight charge transfer from the Si framework to each He atom of (0.03 electrons in oP36-Si2He, 0.05 electrons in tP9-Si2He, 0.09 electrons in mC18-Si2He, and 0.05 electrons in mC12-Si2He), similar to those predicted in Na2He40 and FeO2He45. The weak interaction between the Si frameworks and He atoms provides a good a priori condition for removal of the He from the structures, but the process can also be influenced by different Si frameworks. Therefore, we examine the energy barriers of He diffusing along the channels, see Fig. 3a. CI-NEB calculates energy barriers of 0.08, 0.01, 1.51, and 0.37 eV for oP36-Si2He, tP9-Si2He, mC18-Si2He, and mC12-Si2He, respectively. We also checked the calculations with including vdW interaction, as shown in Supplementary Table 3. The vdW interaction has no effect on the energy barrier of all structures. The energy barriers of all structures except mC18-Si2He are much lower than that (0.74 eV) of Na2Si24 for removing Na4, see Fig. 3b and Supplementary Fig. 7 (with the vdW interaction), indicating comparatively easy removal of He atoms from oP36-Si2He, tP9-Si2He, and mC12-Si2He. For the mC18-Si2He, there exhibits a hexagonal channel structure both along a- and b-axes with a diameter of only about 3.9 Å and is much shorter than that of oP36-Si2He (6.4 Å), which induces a high energy barrier of 1.51 eV and indicates that He is difficult to be removed. This suggests that the structural configuration also plays a very important role in removing helium atoms.

![Fig. 2 Structural configurations of the predicted Si2He phases.](image)

Crystal structures of a oP36-Si2He, b tP9-Si2He, c mC18-Si2He, and d mC12-Si2He at 10 GPa. Black and green spheres represent He and Si atoms, respectively.

![Fig. 3 Migration pathways and energy barriers.](image)

a Migration pathways of He atoms from site A to site B along the channels in oP36-Si2He, tP9-Si2He, mC18-Si2He, and mC12-Si2He. The shaded regions indicate the longitudinal section of the channels. b Energy barriers for He migration along the channels at zero pressure, as well as Na migration in Na2Si24.
**Fig. 4  Structural configurations of the Si allotropes.** Crystal structures of a oC24-Si, b tP6-Si, and c mC8-Si at 0 GPa.

**Fig. 5  Electronic properties of the Si2He compound.** Electronic band structures of a oP36-Si2He, b tP9-Si2He, c mC18-Si2He, and d mC12-Si2He at 0 GPa calculated based on the HSE06 functional. Red solid and blue hollow circles represent the valence band maximum and conduction band minimum, respectively. The lower panels in each figure are the square of the transition dipole moment.
denoted as oC24-Si, tP6-Si, and mC8-Si, respectively. Both Si allotropes retain Si frameworks nearly identical to those of the corresponding compounds. Phonon dispersion calculations confirm the stability of three allotropes (see Supplementary Fig. 4). A literature survey surprisingly found that these three Si structures have been previously predicted with much higher energies (~80 meV) than CD-Si\textsuperscript{21,58,59}. Metastable structures with higher energies are generally difficult to synthesize directly. Here, we provide a potential chemical pathway for the synthesis these metastable Si allotropes, namely removing He atoms from pressure-stabilized Si–He compounds by thermal degassing.

**Electronic and optical properties**

Photovoltaic materials require a suitable direct band gap to ensure a large overlap with the solar spectrum in the visible range, and thus strong solar absorption. Electronic band gaps of the compounds are calculated by using the HSE06 functional and the band structures are shown in Fig. 5. Although the HSE06 functional can well evaluate the band gaps, we still make a test of the Fock exchange percentage to check its accuracy with GW method\textsuperscript{60} and including vdW interaction. The comparisons are shown in Supplementary Tables 2 and 3. The results show that the original parameter of HSE06 (Fock exchange percentage in 0.25) can well evaluate the band gaps of our Si–He system. Take the cubic silicon as an example, the band gap of CD-Si is about 1.17 eV on experiment, our calculated value is about 1.18 eV (HSE06) and 1.14 eV (GW). While for mC12-Si2He, the band gap is about 1.34 eV in HSE06 and 1.26 eV in GW, respectively. So the band gap values obtained by using the HSE06 original parameter (Fock exchange percentage in 0.25) is reasonable. From Supplementary Fig. 3, we can see that when we include the vdW interaction, the electronic band gaps change a little. Take mC12-Si2He as an example, the band gap is about 1.35 eV (with the vdW interaction), while is 1.34 eV without considering vdW interaction. From our calculations (see Fig. 5), we can clearly find that tP9-Si2He and mC18-Si2He are indirect-gap semiconductors with indirect band gaps of 2.18 and 0.91 eV, respectively, which excludes the possibility of being good photovoltaic materials. Interestingly, oP36-Si2He and mC12-Si2He have direct band gaps of 1.24 and 1.34 eV, respectively, close to the Shockley–Queisser limit (1.34 eV), which indicate that they can be viewed as good potential photovoltaic materials. We also calculated the Si allotropes electronic band structure after the removal of He atoms in oP36-Si2He, tP9-Si2He, and mC12-Si2He (see Fig. 6). After removing the He atoms, the electronic band gaps of these Si allotropes decrease and degenerate from the direct band gaps to the indirect band gaps. As shown in Fig. 6, the band gap of oC24-Si can be viewed as a quasi-direct gap with a value of 0.95 eV, while for tP6-Si and mC8-Si are indirect with values of 2.12 and 0.84 eV, respectively. These results reveal that the incorporation of He benefits to forming the direct-gap semiconductor compounds for the Si–He system.

To evaluate the sunlight absorption abilities of a direct band gap material, the imaginary parts of the dielectric constant of oP36-Si2He, mC12-Si2He, and three silicon allotropes (oC24-Si, tP6-Si, and mC8-Si) were calculated by HSE06 functional, compared with that of CD-Si, as shown in Fig. 7. We also checked the results with the independent-quasiparticle approximation and solving the Bethe–Salpeter equation (BSE) to include excitonic and local-field effects\textsuperscript{61}. The HSE06 results are in good agreement with that was obtained by GW + BSE method. The GW + BSE results are shown in Supplementary Fig. 8. The calculation results show that the absorption spectra of oP36-Si2He is slightly higher than that of mC12-Si2He and both have much better solar absorption capacities than the other three silicon allotropes and the CD-Si, as indicated by their broader overlap with the AM1.5 solar spectrum\textsuperscript{62}. The optical absorption in oP36-Si2He and mC12-Si2He have an increasing trend at 1.2 and 1.4 eV, respectively. Another critical factor for a good

![Fig. 6 Electronic properties of the Si allotropes](image1)

**Fig. 6 Electronic properties of the Si allotropes.** Electronic band structures of a oC24-Si, b tP6-Si, and c mC8-Si at 0 GPa calculated based on the HSE06 functional. The lower panels in each figure are the square of the transition dipole moment.

![Fig. 7 Optical properties of the predicted Si2He and Si allotropes](image2)

**Fig. 7 Optical properties of the predicted Si2He and Si allotropes.** Imaginary part of the dielectric functions of oP36-Si2He, mC12-Si2He, and the three silicon allotropes (oC24-Si, tP6-Si, and mC8-Si) calculated with the HSE06 functional, as well as the reference air mass 1.5 (AM1.5) solar spectral irradiance\textsuperscript{62} and CD-Si.
photovoltaic material is a dipole-allowed direct transition. Therefore, further calculation of the square of the transition dipole moment ($P^2$) explores the transition permittibility between the direct band gaps (see the lower panels in Figs. 5 and 6). The direct band gap of op36-Si3He is located at Γ point in the first Brillouin zone, and the $P^2$ at Γ point is close to 0, which indicates that op36-Si3He is dipole-forbidden and same to the other three silicon allotropes (oC24-Si, tP6-Si, and mC8-Si). Instead, mc12-Si3He shows a dipole-allowed direct transition with large $P^2$ value at the Γ point, suggesting good potential as a photovoltaic material.

**Other predicted Si–He compounds**

To search for other possible Si–He compounds, structural predictions are also performed for Si3He and Si4He at 10 GPa using a maximum of 20 atoms in a simulation cell. Supplementary Fig. 9 summarizes the formation enthalpies of the stoichiometries with respect to decomposition into β-Sn Si and hcp He. Unfortunately, the formation enthalpy of all the Si–He compounds are positive. In fact, this does not completely rule out the possibility of experimental synthesis. A recent data mining study found that more than 60th percentile of the 0 K DFT-calculated possibility of experimental synthesis. A recent data mining study found that more than 60th percentile of the 0 K DFT-calculated metastability of all of the compounds within the inorganic Crystal Structure Database was 150 meV/atom above the convex hull.

Actually, some silicon-contained compounds with high formation enthalpy have been successfully experimentally synthesized. For example, the theoretical calculated formation enthalpy of clathrate (type-I) I$_2$S$_6$S$_{6}$S$_{6}$ is above convex hull 130 meV/atom, and SiB$_8$ has the formation enthalpy of 289 meV/atom, both of which have been synthesized. The crystal structures and electronic structures of Si$_3$He and Si$_4$He are shown in Supplementary Figs. 10–13. The formation enthalpies of Si$_3$He and Si$_4$He phases are both <130 meV/atom and they have direct band gap, which could be potential photovoltaic materials.

**DISCUSSION**

He, which has two electrons, is the most chemically inert natural element, although several recent works have predicted or synthesized He-containing compounds. Despite this, He can be regarded as chemically inert in Si–He, as the atoms are almost completely independent of the surrounding structure with negligible charge gained from Si. He appears to be chemically inert in all its known compounds (e.g., Na$_3$He and He$_4$), allowing it to be removed easily from the surrounding structure without changing the structure substantially. Interestingly, the incorporation of He in Si allotrope can form direct band gap semiconductors with the suitable band gaps, with the dipole-allowed direct band gap confirmed by mc12-Si3He. Therefore, He appears to be a good intermediate for designing potential functional materials.

In conclusion, through extensive structure searches of Si$_n$He systems, we predict four dynamically stable phases (op36-Si$_3$He, tp9-Si$_3$He, mc18-Si$_3$He, and mc12-Si$_3$He) with open framework structures comprising Si channels containing triangle or zigzag arrangements of He atoms. CI-NEB calculations reveal that the He atoms could be easily removed along the channels in them to leave the pure Si allotropes, oC24-Si, tP6-Si, and mC8-Si, respectively. op36-Si$_3$He and mc12-Si$_3$He exhibit direct-gap semiconductive property, while others possess indirect band gaps. The dipole-allowed direct band gap of 1.34 eV in mc12-Si$_3$He makes it a potential thin-film photovoltaic material. The current results demonstrate that He is an excellent element for regulating the properties of materials, as well as a good medium to synthesize functional materials.

**METHODS**

**Structural prediction and relaxation**

Structure predictions for the Si–He system were performed using CALYPSO$^{69}$, which has correctly predicted many stable compounds under high pressure$^{9,29}$. The structural optimization and electronic and optical properties were calculated using density functional theory as implemented in the Vienna ab initio simulation package$^{60}$, adopting the Perdew–Burke–Emzerhof exchange-correlation functional under the generalized gradient approximation$^{61,62}$.

**Electronic and optical properties calculations**

The Heyd–Scuseria–Emzerhof (HSE06) hybrid functional was employed to correct the electronic band structures$^{63}$ and calculate the optical properties. We also make a test of the Fock exchange percentage to check its accuracy with GW method$^{60}$ and the Fock exchange percentage is adopted the default value of 0.25. All electron projector augmented wave pseudopotentials with 1$^2$3$^2$3p$^2$ configurations were chosen for He and Si atoms, respectively$^{65}$. A plane wave cutoff energy of 800 eV and k-point mesh of 2×0.03 Å$^{-1}$ were set to ensure total energy and forces convergence better than 1 meV/atom and 1 meV/Å, respectively. VASPKIT$^{66}$ was used to resolve the results of the transition dipole moment and the optical absorption spectra (the imaginary part of the dielectric function, ε$_2$). Specially, we have checked our calculations (structural relaxation, band gap calculation, MD, and CI-NEB) with including the vDW interactions$^{67}$.

**Phonon and CI-NEB energy barrier calculations**

Phonon calculations were carried out using a supercell approach as implemented in PHONOPY code$^{68}$. First-principles MD simulations using N (number of particles), V (volume), and T (temperature) were performed at 0 GPa and 300 K. In total, 3 × 1 × 2 supercells for op36-Si3He (216 atoms), 3 × 3 × 2 supercells for tp9-Si3He (162 atoms), 2 × 1 × 2 supercells for mc18-Si3He (144 atoms), and 1 × 3 × 2 supercells for mc12-Si3He (144 atoms) were employed. The migration barriers were calculated using the climbing image nudged elastic band (CI-NEB) method$^{69}$ based on supercells containing one He atom and 48 host Si atoms for op36-Si3He, tp9-Si3He, mc18-Si3He, mc12-Si3He, and Na$_3$Si$^{34}$.

**DATA AVAILABILITY**

The authors declare that the main data supporting the findings of this study are contained within the paper and its associated Supplementary Information. All other relevant data are available from the corresponding author upon reasonable request.

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AUTHOR CONTRIBUTIONS

J.S. and Y.L. designed the project. S.D. and J.S. performed the calculations. S.D., J.S., J.X., W.C., P.Z., K.Y., J.H., L.Z. and Y.L. analyzed the data. S.D., J.S., W.C. and Y.L. wrote the paper. All the authors checked the manuscript.

COMPETING INTERESTS

The authors declare no competing interests.

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Correspondence and requests for materials should be addressed to J.S. or Y.L.

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