An infinite family of $bc8$-like metastable phases in silicon

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We show that new silicon crystalline phases, observed in the experiment with the laser-induced microexplosions in silicon crystals (Rapp et al. Nat. Commun. 6, 7555 (2015)), are all superstructures of a disordered high-symmetry phase with $F\bar{4}3d$ cubic space group, as well as known for many years phases $bc8$ (Si-III) and $r8$ (Si-XII). The physics of this phenomenon is rather nontrivial: The $bc8$-like superstructures appear as regularly ordered patterns of switchable atomic strings, preserving everywhere the energetically favorable tetrahedral coordination of silicon atoms. The variety of superstructures arises because each string can be switched between two states independently of the others. An infinite family of different phases can be obtained this way and a number of them are considered here in detail. In addition to the known $bc8$, $b8$, and $r8$ crystals, 128 tetrahedral structures with 16 (6 phases), 24 (22 phases), and 32 (100 phases) atoms per primitive cell are generated and studied, most of them are new ones. For the coarse-grain description of the structures with two possible states of switchable strings, the black/white (switched/nonswitched) Shubnikov symmetry groups has been used. An ab initio relaxation of the atomic positions and lattice parameters shows that all the considered phases are metastable and have higher density and energy relative to the $bc8$ phase at the ambient pressure. A possible scenario for appearance of those phases from the high-temperature amorphous phase is discussed.

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I. INTRODUCTION

Despite the fact that our contemporary civilization is now based on one type of silicon crystals with the diamond structure, the diversity of crystal forms of this chemical element is not much inferior to that of carbon. There are numerous exotic structures with tetrahedral and more complicated atomic arrangements, including a big family of high-pressure silicon phases with higher coordinations. The silicon phases are interesting first of all owing to their electronic properties and the latter are determined by details of the atomic structures and impurities. Another promising application is related to micro-electromechanical systems (MEMS) where the elastic properties of silicon are used. For all these purposes, one needs to look for new silicon-based crystals with the hope to find new unusual properties and applications.

One of the exotic tetrahedral structures, the $bc8$ phase, was discovered in 1963: its name means body-centered cubic with 8 atoms per primitive cell (that is 16 atoms per the body-centered cubic (bcc) unit cell, the lattice parameter $a = 6.64$ Å, and the space group is $Ia\bar{3}$). It is also called Si-III because it has been found after Si-I (diamond-like) and Si-II ($\beta$-Sn-like) silicon phases. All the atoms in $bc8$ are crystallographically equivalent, they are located at the three-fold axes, 16c positions $(x, x, x)$ of group $Ia\bar{3}$ ($x \approx 0.1$), and have non-ideal tetrahedral coordination with one interatomic bond directed along a three-fold cubic axis ($A$-bond) and three longer bonds ($B$-bonds) in non-symmetric directions. Structurally, the $bc8$ phase can be considered as the cubic arrangement of atomic strings directed along four ⟨111⟩ axes (this point is discussed in detail below). This phase was first obtained from the high-pressure $\beta$-Sn-like phase after pressure release and was found to be metastable at the ambient conditions. Its structural, thermodynamical, and electronic properties have been studied in detail for many years. In the $bc8$ phase, like in diamond, there are only even-membered rings of interatomic bonds and the shortest rings are six-membered.

The first $bc8$-like structure, $r8$ or Si-XII, was discovered in 1999. $r8$ means rhombohedral with 8 atoms per unit cell, its space group is $R3$, a subgroup of $Ia\bar{3}$. The structure of $r8$ appears from $bc8$ during a first-order pressure-induced structural transition as a result of breaking and rebonding of all the $A$-bonds directed along cubic direction [111]. Indeed, according to the rebonding can be understood as motion of the atom at $(x, x, x)$ along direction [111] of the $bc8$ unit cell until the $A$-bond to the atom at $(\bar{x}, \bar{x}, \bar{x})$ is broken and a new $A$-bond to the atom at $(\frac{1}{2} - x, \frac{1}{2} - x, \frac{1}{2} - x)$ is formed (Fig. 1). As a result of the rebonding, all the [111] atomic strings are switched into another sequence of bonds preserving nevertheless the energetically favorable tetrahedral atomic arrangement. The phase transition is of the first order because the rebonding is accompanied by small but finite atomic displacements changing the topology of rings; in particular, five-membered rings appear in the $r8$ phase.

Both phases $bc8$ and $r8$ can also appear as a result of mechanical microindentation and their thermal relaxation back to the diamond silicon has been studied in numerous research works. The electronic and optical properties of $bc8$ and $r8$ may have interesting practical applications everywhere the energetically favorable tetrahedral coordination of silicon atoms.

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expected to be rather different from those of $bc$, $bt$ space symmetry of $bt$ axes, relating switched and non-switched strings. The of was predicted, where all the strings of nation. In particular, a new tetragonal silicon phase ($bc$) is rather universal: in the ambient pressure $bt$ is more dense than $bc$ and $r8$ and it becomes energetically more favorable than $bc$ and $r8$ at pressures above 13 GPa where the $\beta$-tin silicon structure is, in fact, more favorable than all the $bc8$-like phases. Later on, in 2013, the $bt8$ phase was independently reinvented and studied $ab\ initio$ for silicon and germanium$^{27}$ and for carbon as well$^{26}$ (in the latter case the symmetry was claimed to be $I4_1$ whereas the calculated atomic coordinates corresponded in fact to the more symmetric $I4_1/a$ space group). The $bc8$-like structures were also studied by algebraic geometry$^{24}$ and by the high-dimensional projection methods used for quasicrystals and their approximants$^{30}$.

The real breakthrough happened in 2015 when Rapp et al. found evidence for several metastable silicon phases after ultrashort laser-induced confined microexplosions$^{32}$ at the interface between a transparent amorphous silicon dioxide layer (SiO$_2$) and an opaque single-crystal Si substrate. They determined the lattice parameters and possible atomic structures of the following phases: $bt8$, $st12$ (analog of $st12$ in germanium), two tetragonal phases with 32 atoms per unit cells, and some others. For description of the structures they used an $ab\ initio$ random structure search$^{31}$. It should be noted that one of the 32-atoms tetragonal phases was found independently$^{33}$ using the ideas of metadynamics and evolutionary algorithms. The exotic silicon phases like $bc8$, $r8$, and those new discovered by Rapp et al. have provided a novel insight into the local structure and properties of the amorphous phase of silicon$^{9,10,24,35}$.

In the present paper we suggest a unified description of all new silicon crystalline phases (except $st12$) observed by Rapp et al. and numerous similar phases. Those complicated phases are shown to be the $bc8$-like structures with periodically switched strings, like in the simple case of $r8$. As a result, the lattice vectors of those phases are some periods of $bc8$. In addition to known $bc8$, $r8$, and $bt8$, we generate a complete set of $bc8$-like phases with 16, 24, and 32 atoms per primitive cells and relax their structures $ab\ initio$.

**II. BC8 STRUCTURE AND STRING SWITCHING**

As mentioned in the introduction, the atomic structure of the $bc8$ phase can be considered as a set of atomic strings parallel to the threefold axes of the cubic space group $Ia3$, no. 206. Here the string structure is described in detail (Fig. 1). All atoms are located in the position of $16c$ $(x, x, x)$, $x = x_w \approx 0.1$, with threefold point symmetry, and each string possesses two nonequivalent inversion centers in the positions of $8a$ $(0, 0, 0)$ and $8b$ $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. In $bc8$ all strings are equivalent to each other. Let us consider one of them, say, that parallel to axis $[111]$ and passing through the origin $(0, 0, 0)$. Then its atoms have applications (see$^{22,23}$ and references therein).

In 1999, it was shown$^{24,25}$ that the rebonding mechanism found by Crain et al.$^{27}$ is rather universal: in the $bc8$ structure, any set of the atomic strings can be independently switched without violation of tetrahedral coordination. In particular, a new tetragonal silicon phase ($bt8$) was predicted, where all the strings of $bc8$ parallel to two cubic diagonals (say $[111]$ and $[\overline{1}1\overline{1}]$) were switched and those parallel to $[111]$ and $[\overline{1}1\overline{1}]$ were not (Fig. 1). The space symmetry of $bt8$ is $I4_1/a$ and it is not a subgroup of $Ia3$: there are new symmetry elements, fourfold screw axes, relating switched and non-switched strings. The $bt8$ structure demonstrates the maximum density of five-membered bond ring$^{26}$ and its electronic properties are expected to be rather different from those of $bc8$, $r8$, and $bc8$ diamond phases. Energetics and structural relaxation of $bt8$ have been studied $ab\ initio$ both for silicon$^{28}$ and carbon$^{26}$. It has been shown that at the ambient pressure $bt8$ is more dense than $bc$ and $r8$ and it becomes energetically more favorable than $bc$ and $r8$ at pressures above 13 GPa where the $\beta$-tin silicon structure is, in fact, more favorable than all the $bc8$-like phases. Later on, in 2013, the $bt8$ phase was independently reinvented and studied $ab\ initio$ for silicon and germanium$^{27}$ and for carbon as well$^{26}$ (in the latter case the symmetry was claimed to be $I4_1$ whereas the calculated atomic coordinates corresponded in fact to the more symmetric $I4_1/a$ space group). The $bc8$-like structures were also studied by algebraic geometry$^{24}$ and by the high-dimensional projection methods used for quasicrystals and their approximants$^{30}$.

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In the present paper we suggest a unified description of all new silicon crystalline phases (except $st12$) observed by Rapp et al. and numerous similar phases. Those complicated phases are shown to be the $bc8$-like structures with periodically switched strings, like in the simple case of $r8$. As a result, the lattice vectors of those phases are some periods of $bc8$. In addition to known $bc8$, $r8$, and $bt8$, we generate a complete set of $bc8$-like phases with 16, 24, and 32 atoms per primitive cells and relax their structures $ab\ initio$. 

![](image.png)

**FIG. 1:** (Color online) Comparison of the crystalline silicon structures $bc8$, $r8$, and $bt8$. An atomic layer is chosen to be parallel to plane $(100)$ of $bc8$. In the phases $r8$ and $bt8$, the bonds coinciding with those of $bc8$ are shown in blue, and the new switched bonds along the $(111)$ directions are yellow. The most dissimilar phases $bc8$ and $bt8$ differ by switching one eighth of the total number of bonds.
coordinates \((\frac{1}{2}, \frac{1}{2}, \frac{1}{2}) \pm (x_w, x_w, x_w)\), where \(n\) is an arbitrary integer. The \(A\)-bonds between neighboring atoms of the string are \((2x_w, 2x_w, 2x_w)\) and they alternate with next-neighbor distances \(A' (\frac{1}{2} - 2x_w, \frac{1}{2} - 2x_w, \frac{1}{2} - 2x_w)\). Therefore, the string of atoms looks like a sequence of alternating \(A\)-bonds centered at inversion centers \((\frac{1}{2}, \frac{1}{2}, \frac{1}{2})\), and approximately 1.5 times longer stretches \(A'\) centered at inversion centers \((\frac{1}{2} + n, n + \frac{1}{2}, n + \frac{1}{2})\), \((\frac{1}{2} + n, \frac{1}{2} + n, \frac{1}{2} + n)\), (Fig. 2b). The string of this type will be called white, hence the subindex \(w\).

However, there is another value of \(x\), \(x = x_b = \frac{1}{4} - x_w\), which gives an identical \(bc8\) structure rotated relative to the former by \(\frac{\pi}{2}\) around a twofold axis (the subindex \(b\) means black). The black and white \(bc8\) structures can be also transformed one to another by small local shifts of atoms along threefold directions resulting in breaking/switching of \(A\)-bonds, as suggested by Crain et al. for the \(r8\) phase and described above in the introduction. In the string picture, the rebonding means simply that \(A'\) and \(A\)-bonds are locally permuted (switched), Fig. 2c. Thus, for the black \(bc8\), in the considered above string \([111]\) the \(A\)-bonds are centered at \((\frac{1}{2} + i, \frac{1}{2} + n, \frac{1}{2} + n)\), whereas \(A'\) at \((\frac{1}{2}, \frac{1}{2}, \frac{1}{2})\).

An important observation is that any set of strings can be independently switched between black and white states without violation of energetically favorable tetrahedral coordination. The tetrahedral coordination means that each atom has four neighbors, the lengths of bonds are not very different, and all interbond angles exceed \(\pi\). An example of bond length and angle statistics can be found below in Section V. The switching of a single isolated string in the perfect \(bc8\) structure has been simulated \(ab initio\) and it has been found that it costs less than 0.02 eV per atom.

Since every string is allowed to be switched independently of the others, there exist \(2^N\) different combinations of switching, where the total number of strings \(N\) is proportional to the surface area of a crystal. This huge number of possible structures arises from the purely combinatorial consideration, without taking into account their physical properties. Note that all members of the infinite family of \(bc8\)-like crystals have a similar topological structure. Indeed, the string switching affects only the bonds lying along the four axes of type \((111)\). Any \(bc8\)-like phase can be obtained from \(bc8\) by switching at most one half of \(A\)-bonds, i.e. one eighth of the total number of bonds (Fig. 1).

As mentioned above, the rotation of \(bc8\) by \(\frac{\pi}{2}\) changes the color of all atomic strings. This means that different combinations of switching can define the same structure. For example, the two cases when all atomic strings have the same color, \((w, w, w, w)\) or \((b, b, b, b)\), correspond to a single structure, namely \(bc8\). Further, if the strings parallel to any two threefold axes are white, and those parallel to remaining two axes are black (the cases \((w, w, b, b)\), \((w, b, w, b)\), etc.), then the crystal symmetry becomes tetragonal, and identical \(bt8\) phases with different orientations of the tetragonal axis are obtained. Finally, if the sign of the strings parallel to any threefold axis is opposite to the sign of other strings (the cases \((w, w, w, b)\), \((w, b, b, b)\), etc.) then identical \(r8\) phases arise with different orientations of the rhombohedral axis. The three phases, \(bc8\), \(bt8\), and \(r8\), exhaust the list of \(bc8\)-like structures with the minimal primitive cell containing 8 atoms. Their common feature is that parallel strings have the same color.

In spite of the obvious connection of the phases \(bc8\) and \(bt8\), there is no group-subgroup relation between them. We can assume the existence of a supersymmetric phase with space group \(Ia3d\), which is a subgroup for both \(Ia3\) and \(Ia41/a\). An evident way to construct the superphase is to turn all the strings into the half-switched state. In this case, all atoms are located in the position of \(16b\) of group \(Ia3d\) with three-coordinated graphene-like environment (Fig. 2a). However, this environment is not favorable for the silicon atoms. Another, more physical way to obtain a supersymmetric phase is to switch every string randomly to one of two possible states, white or black (Figs. 2b, 2c). In this case, the \(Ia3d\) symmetry is a result of disorder, and the phase transition to \(bc8\), \(r8\), \(bt8\), or a more complicated structure is of disorder-order type.

**FIG. 2:** (Color online) An atomic string in the structure of \(bc8\)-like silicon. Each atom has one \(A\)-bond along the string and three \(B\)-bonds with atoms of other strings. The string can be switched from the mean position (a), corresponding to the structure with space group \(Ia3d\), to one of two extreme states, white (b) and black (c). Switching from white to black permutes the \(A\)-bonds with \(A'\)-distances, preserving tetrahedral atomic arrangement. In addition, the string can be split into white and black parts, separated by defects (d). The switching process may consist in moving such a defect along the string.
III. BC8-LIKE SUPERSTRUCTURES WITH ENLARGED PRIMITIVE CELLS

A more complicated bc8-like phase with larger primitive cell can occur if the structure contains parallel atomic strings of different colors. The primitive cell of the phase is a multiple in volume and number of atoms to the primitive cell of bc8, and its Bravais lattice is a subset of the bc8 Bravais lattice of bc8. In addition, each Bravais lattice corresponds to several different phases due to multiple ways to color the strings passing through its primitive cell. In order to enumerate and classify the structures with the same Bravais lattice, we need to calculate the number of independent, i.e. not connected by periodicity, strings in each of the four directions (111). This number is proportional to the volume of the primitive cell and inversely proportional to the smallest lattice period along the direction. For example, the number \( N_{111} \) of independent strings parallel to axis [111] is equal to the greatest common divisor of three triple products

\[
\begin{align*}
    n_a &= (1, 1, 1) \cdot [b \times c], \\
    n_b &= (1, 1, 1) \cdot [c \times a], \\
    n_c &= (1, 1, 1) \cdot [a \times b],
\end{align*}
\]  

where \( a, b, \) and \( c \) are the Bravais lattice periods, expressed in the parameters of the initial bc8 lattice.

The numbers \( N_{111}, N_{111}, \) and \( N_{111} \) can be calculated in the same way. Further, the combinatorial number of possible two-colorings of strings is equal to \( 2^{N_{111}+N_{111}+N_{111}} \), however, the actual number of different phases is significantly less. For example, in the case of the smallest primitive cell \( (N_{111} = N_{111} = N_{111} = 1) \), sixteen possible combinations of switching define only three different phases, bc8, bt8, and r8. This significant reduction in the number of different structures is due to two reasons. First, some structures can be connected by the elements of group \( Pa3d \) not included in the own space group of the structures. Second, some combinations of switching can define structures with smaller primitive cells.

Table 1 shows the currently known bc8-like phases of silicon. Recently, several new structures were experimentally observed, with primitive cells two and four times larger than that of bc8. They are listed in the bottom part of the table, with the names being written according to Ref. 31 as well as in our own notation (in parentheses). Along with conventional space groups of the crystals, we also indicate the black and white (Shubnikov) groups, the meaning of which will be explained later in Section IV. The last column shows the unit cell periods expressed in the parameters of the initial bc8 lattice. The phases listed in Table 1 unlike some others (diamond, st12, etc.), belong to the same family and can be described in the language of string switching. Figs. 3-4

The list from Table 1 is far from being exhaustive. As a first goal, we would like to find all the similar structures with double, triple, and quadrupole cells, containing 16, 24, and 32 silicon atoms, respectively. First we find all the Bravais lattices with the specified cell volumes, which are subsets of the initial bc8 lattice. Then, all possible structures are obtained by the enumeration of two-colorings of the independent strings.

In order to avoid double counting, we discard the structures with smaller primitive cells. For example, all the structures with basis vectors (100), (010), and (001) (lattice 16-2 in Table 1) actually have a two times smaller primitive cell, and therefore they coincide with the phases bc8, bt8, and r8. Thus, it turns out that some lattices

![FIG. 3: Atomic strings in phase m32 (m32-8) in projections onto the planes \{111\} perpendicular to them. For each projection its 2D generating cell is shown. White and black circles indicate the switching of strings. For projections (111) and (111) the string switching alternates along the perpendicular directions [011] and [211], correspondingly.](Image 340x263 to 539x451)

![FIG. 4: Atomic strings in phase m32* (sm16-2). For projections (111) and (111) the string switching alternates along the same direction [011].](Image 340x552 to 539x740)
from a symmetric graphene-like position of group Ia\(\overline{3}d\) to its real position with tetrahedral coordination. This vector is always parallel to the threefold axis (string) passing through the atom, whereas its direction alternates along the string. The situation resembles the ordering of magnetic moments arranged in the nodes of the original Ia\(\overline{3}d\) phase, provided that they are involved in two strong magnetic interactions: (i) a spin-orbit interaction, forcing the moments to align along the easy magnetization axes coinciding with strings; (ii) an antiferromagnetic exchange between neighboring atoms on the strings. It is obvious that in this analogy the conjugation plays the role of the time reversal operation, which in turn is independent of spatial symmetry. Therefore, it does not change the space group of the structure.

Note that the analogy is not complete, because, in contrast to a magnetic moment, the atomic position shift changes sign upon inversion and remains the same upon time reversal. As for the strings, it is easy to see that they change their color upon rotations of 90° and keep it unchanged for all other rotations of point group \(m\overline{3}m\), as well as for inversion. For example, the \(xyz\)-component of a magnetic octupole moment behaves in a similar way. Using the magnetic analogy we can extend the space group of a \(bc8\)-like phase by adding symmetry elements conjugating its structure. Then, the symmetry of the phase will be described by a Shubnikov magnetic group\(\overline{bc8}\). Thus, the magnetic groups of the phases \(bc8\), \(bt8\), and \(r8\) are Ia\(\overline{3}d\)', I\(\overline{4}1/ac'd'\), and R\(\overline{3}c'\), correspondingly (Table I). In the supplemental material all \(bc8\)-like crystals are classified both by space and magnetic groups\(\overline{bc8}\).

V. MICROSCOPIC STRUCTURE AND PHYSICAL PROPERTIES

Let us now consider some structural features of the \(bc8\)-like phases and their correlation with physical properties such as energy and atomic density. As mentioned above, each atom has one \(A\)-bond along the string passing through it, and three \(B\)-bonds with atoms on other strings. Therefore, two kinds of angles between the bonds can be distinguished, the \(\alpha\) angle between bonds \(A\) and \(B\), and the \(\beta\) angle between two \(B\)-bonds. In the real structures, all the bonds tend to be of the same size. It is achieved when the \(A\)- and \(B\)-bonds have lengths of about \(\sqrt{2}/4 \approx 0.35\) lattice parameters of \(bc8\), and the \(A'\)-distances are about \((2\sqrt{3} - \sqrt{2})/4 \approx 0.51\) parameters of \(bc8\). In such ideal structure, the values of \(\alpha\) and \(\beta\) are determined by the colors of the neighboring strings. Thus, depending on switching, the angles \(\alpha\) are subdivided into \(\alpha' \approx 98.5^\circ\) and \(\alpha'' \approx 94.3^\circ\), and the angles \(\beta\) into \(\beta_1 \approx 107.0^\circ\), \(\beta_2 \approx 117.9^\circ\), \(\beta_2' \approx 119.5^\circ\), and \(\beta_3 \approx 130.6^\circ\) (Fig. 4). The statistical variation of the angles calculated from the structural data from Ref.\(\overline{37}\) is shown using Gaussian distributions. It is seen that the angles \(\alpha\), \(\beta_1\), \(\beta_2\), and \(\beta_3\) are well distinguished. Appar-
ently, the angles $\alpha$, which are close to $90^\circ$, have an excess energy, and the structure should undergo an additional distortion in order to increase them.

An important characteristic of tetrahedral structures is the statistics of atomic rings. All the considered $bc8$-like phases have a girth (i.e. the length of a shortest ring) equal to five, except for $bc8$ itself, which is made up exclusively of six-membered rings. For the first approximation, we can investigate the dependence of physical properties on the amount of five-membered rings per atom, which varies from $\nu_5 = 0$ for $bc8$ to $\nu_5 = 1$ for $bt8$. Fig. 7 shows dependencies of the energy and volume per atom on the value of $\nu_5$ for several $bc8$-like phases, calculated during ab initio simulations of the structural relaxation of the phases, performed with QUANTUM ESPRESSO package\textsuperscript{41,42} (see details of the DFT modeling in the supplemental material\textsuperscript{37}). It is seen that when the frequency of five-membered rings grows, both the energy and atomic density increase. The positive correlation between $\nu_5$ and energy per atom seems to be explained by the relation between five-membered rings and the “bad” angles $\alpha''$. Indeed, from geometrical considerations we can express the frequencies of different interbond angles through $\nu_5$: $\nu_{\alpha'} = 3 - 2\nu_5$, $\nu_{\alpha''} = 2\nu_5$, $\nu_{\beta_1} = \nu_{\beta_2} = \nu_{\beta_3} = \nu_5$, $\nu_{\beta_4} = 3 - 3\nu_5$.

All $bc8$-like phases are close to each other but differ from other silicon phases. For example, the belonging of a given structure to the family can easily be determined by comparing its periods to those of the $bcc$ lattice, and by the number of atoms in the unit cell multiple of eight. Furthermore, all these phases have similar energy and atomic density. It was recently found that the Raman spectra of some unidentified silicon phases obtained in the experiment with the laser-induced microexplosions resemble the spectra of the phases $bc8$, $r8$, and $bt8$, although the correspondence is not exact\textsuperscript{43}. Here, the existence of an infinite series of intermediate phases may be one of the possible explanations for the discrepancy.

VI. DISCUSSION AND CONCLUSIONS

In summary, we described in detail the physical mechanism behind the complicated silicon structures observed by Rapp et al. after ultrashort laser microexplosions\textsuperscript{31}. Those silicon phases (except $s/12$) can be obtained from...
the phase \(bc8\) by switching the \((111)\) atomic strings in different regular (periodic) ways. The stochastic switching of the strings gives a disordered phase with \(Ia\overline{3}d\) cubic symmetry, and the space groups of the \(bc8\)-like phases are subgroups of \(Ia\overline{3}d\). All the possible phase transitions between different \(bc8\)-like phases should be of the first order (not continuous) because atoms of the switched strings jump over finite distances.

We have found possible rich polymorphism of \(bc8\)-like phases, and to distinguish between them it would be very important to study carefully any small differences in diffraction patterns and in other physical properties (e.g. in the Raman spectra). In addition, the considered family of \(bc8\)-like phases provides a good opportunity for studying the ability of existing empirical potentials to capture the structure and energetics of these phases and other complicated silicon materials (thanks to the Referee who attracted our attention to this option).

It would also be very interesting to use the technique of Rapp et al.\(^{24}\) for the \(bc8\) crystals instead of diamond silicon because in this case new \(bc8\)-like phases will grow on the parent \(bc8\) matrix. Reasonably large (several mm size) phase-pure \(bc8\) poly crystals have been grown recently by different methods.\(^{11}\)\(^{12}\)

Finally, we can propose a possible explanation for the observed polymorphism of \(bc8\)-like phases based on the ideas described above. It was shown in Ref.\(^{25}\) that the reduced intensity functions (the structure-dependent parts of the X-ray scattering pattern), are very similar for amorphous silicon and for disordered polycrystalline \(Ia\overline{3}d\) phase. Thus, we can suppose that the high-temperature/high-pressure amorphous phase first transforms into disordered \(Ia\overline{3}d\) phase and then, depending on local temperature, pressure, and shear, into different \(bc8\)-like phases for which \(Ia\overline{3}d\) is the parent phase. Therefore, quite probably, the \(bc8\)-like phases should also appear after the laser-induced microexplosions on the interface between \(SiO_2\) and amorphous silicon.

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See Supplemental Material at [URL] for the description of new bc8-like phases with enlarged primitive cells and corresponding crystallographic information files (CIF).

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TABLE I: The known bc8-like phases of silicon

| Phase | Fedorov group | Shubnikov group | Unit cell ideal periods |
|-------|---------------|-----------------|------------------------|
| bc8   | Ia3 (260)     | Ia3d' (230.148) | \{ (100), (010), (001) \} |
| bt8   | I4_1/a (88)   | I4_1/ac'd' (142.567) | \{ (11/2), (11/2), (11/2) \} |
| r8    | R3 (148)      | R3c' (167.107)   | \{ (11/2), (11/2), (11/2) \} |
| m32 (m32-8) | P21/c (14)  | P21/c (14.75)    | \{ (11/2), (11/2), (11/2) \} |
| m32* (sm16-2) | C2 (5)       | C2222' (14.75)   | \{ (11/2), (11/2), (11/2) \} |
| t32 (t32-1)  | P421c (114)  | P421c (114.281)  | \{ (11/2), (11/2), (11/2) \} |
| t32* (t32-3) | P4_12_12 (96)| P4_12_12 (96.149) | \{ (11/2), (11/2), (11/2) \} |

TABLE II: The supercells multiple to the primitive cell of bc8 and the number of possible bc8-like structures

| Cell name | Basis vectors | Multiplicity | Number of structures without/with enantiomorphs | The known structures |
|-----------|---------------|--------------|------------------------------------------------|---------------------|
| 8-1       | (1/2, 0, 0), (1/2, 0, 0), (1/2, 0, 0) | 1            | 3/3                                            | bc8, r8, bt8        |
| 16-1      | (1, 0, 0), (1, 0, 0), (1, 0, 0)        | 2            | 6/8                                            | m32*               |
| 24-1      | (1/2, 1/2, 1/2), (1/2, 1/2, 1/2), (1/2, 1/2, 1/2) | 3            | 18/23                                          |                     |
| 24-2      | (1/2, 1/2, 1/2), (1/2, 1/2, 1/2)       | 3            | 4/4                                            |                     |
| 24-3      | (0, 0, 0), (1, 0, 0), (1, 0, 0)         | 3            | -                                              |                     |
| 32-1      | (0, 0, 0), (0, 0, 0), (0, 0, 0)         | 4            | 6/8                                            | t32, t32*          |
| 32-2      | (1/2, 1/2, 1/2), (1/2, 1/2, 1/2), (1/2, 1/2, 1/2) | 4            | 46/68                                          |                     |
| 32-3      | (1/2, 1/2, 1/2), (1/2, 1/2, 1/2), (1/2, 1/2, 1/2) | 4            | 22/26                                          | m32                |
| 32-4      | (1/2, 1/2, 1/2), (1/2, 1/2, 1/2), (1/2, 1/2, 1/2) | 4            | 26/40                                          |                     |
| 32-5      | (0, 0, 0), (0, 0, 0), (0, 0, 0)         | 4            | -                                              |                     |
| 32-6      | (1, 0, 0), (0, 1, 0), (0, 1, 0)         | 4            | -                                              |                     |
| 32-7      | (1, 0, 0), (1, 0, 0), (1, 0, 0)         | 4            | -                                              |                     |
| 32-8      | (1, 0, 0), (1, 0, 0), (1, 0, 0)         | 4            | -                                              |                     |

Total: 131/180
SUPPLEMENTAL MATERIAL

Animated GIFs

Animation bondon.gif demonstrates a probable mechanism of the string switching from white to black and back. The process involves moving a dangling interatomic bond along a 3-fold axis, which can be associated with a quasi-particle called “bondon”. Note that the sign of switching does not correlate with the direction of bondon movement.

Crystallographic information files

For generation and enumeration of possible bc8-like phases we use an approach based on the “ideal” atomic structure of the bc8 phase as a crystalline approximant of icosahedral quasicrystals where the switches of the string correspond to phasonic jumps of atoms. In this case, the A and B interatomic bonds are parallel, correspondingly, to three- and fivefold axes of an icosahedron, with the ratio of bonds $r_B/r_A = \sqrt{(7+2)/3} \approx 1.098$ ($\tau = (1 + \sqrt{5})/2$ is the golden mean). When the string is switched, the A bonds remain of the same length and the third type of bonds (C-bonds) appears, connecting atoms at switched and non-switched strings.

The folder cif\_zip contains Crystallographic Information Files (CIFs) with atomic coordinates in such ideal representation. The cell parameters are calculated based on the ideal bc8 crystal period $a = 6.658\text{Å}$. Note that the actual lattices of the idealized structures are characterized by the unit cell parameters (angles, ratio of periods) characteristic of the cubic lattice of the bc8 phase. A real structure may have slightly distorted cell parameters if phase symmetry allows it. The files from the folder cif\_zip describe the structures as having the least symmetrical group P1. All positions are listed for the primitive cell. Some of the structures have been relaxed using ab initio simulations. In these cases, the cif-file, tagged by an extra underscore symbol, also contains the refined crystallographic data. The cif\_zip file can be sent by request.

Details of ab initio simulation

For the ab initio DFT relaxation of the initial “ideal” bc8-like structures we used the QUANTUM ESPRESSO code. We selected the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional which seems to provide better agreement between experimental and theoretical lattice parameters than the local density approximation (LDA). We used the ultra-soft pseudopotential Si.pbe-nrkkus.psl.1.0.0.UPF, the plane-wave energy cutoff of 40 Ry, and the structural relaxations were supposed to be converged when all of the interatomic forces were less than $10^{-3}$ Ry/a.u. The bc8-like structures relaxed this way are presented in the cif-files tagged by an extra underscore symbol in the file names. This includes all bc8-like structures with the lattices 16-1, 24-1, 24-2, 32-1, the monoclinic phases m32-6,7,8 with the lattice 32-3, and the rhombohedral phases r32-3,4,5,6 with the lattice 32-4.

Lattices and structures

Below 131 bc8-like phases are listed and classified (180 with chiral enantiomorphs). The list exhausts all similar structures with 8, 16, 24, and 32 atoms in primitive cells, including previously known ones (bc8, b8, r8, m32-8 (m32\text{\tilde{m}}), sm16-2 (m32\text{\tilde{m}}), t32-1 (t32\text{\tilde{m}}), t32-3 (t32\text{\tilde{m}})), and 124 structures proposed for the first time.

The description of structures corresponds to the following scheme.

**Lattice type.** The phases described are divided into eight different lattices: one each with 8 and 16 atoms in primitive cell, two with 24 atoms, and four with 32 atoms. Every lattice is defined by periods, which coincides with some periods of the bcc lattice of the bc8 crystal. The type of Bravais lattice is indicated.

**Symmetry.** The structures of bc8-like phases are classified by their symmetry. Crystals with the same symmetry are combined together. Listed are the space groups, the Pearson symbols, and the black-white magnetic groups (in red) of the structures.

**Structures.** The name of each phase is constructed according to the csN-n scheme, where the optional symbol c means centering (b: body-centered, s: base-centered), s indicates crystal system (a: triclinic, m: monoclinic, t: tetragonal, r: rhombohedral, h: hexagonal, c: cubic), N is the number of atoms in the primitive cell, n is the sequence number. For a chiral structure, its enantiomorph is indicated in parentheses.

**LATTICE 8**

**PERIODS:** $a(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}), a(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}), a(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$

**BRAVAIS LATTICE:** body-centered cubic

**STRUCTURES:**

$Ia\overline{3}$ (206); $cI16$; $Ia\overline{3}d'$ (230.148) : bc8

$I4_1/a$ (88); $tI16$; $I4_1/acd'$ (142.567) : bt8

$R\overline{3}$ (148); $hR24$; $R3c'$ (167.107) : r8

**LATTICE 16-1**

**PERIODS:** $a(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}), a(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}), a(1,0,1)$

**BRAVAIS LATTICE:** base-centered orthorhombic
STRUCTURES:

C2 (5); mC32; C222' (21.41) : sm16-1(2)
P21 (4); mP16; C2'2'2'1 (20.33) : m16-1(2)
P1 (2); aP16:
    P2'/c' (13.69) : a16-1, a16-2
    P1 (2.4) : a16-3, a16-4

LATTICE 24-1

PERIODS: a(1, 1, 1), a(0, 1, 1), a(1, 0, 1)
BRAVAIS LATTICE: face-centered orthorhombic

STRUCTURES:

C2/c (15); mC48; Fd'd'd (70.530) : sm24-1, sm24-2
C2 (5); mC48; F2'2'2' (22.47) : sm24-3(5), sm24-4(6)
P1 (2); aP24:
    C2'/c' (15.89) : a24-1, a24-2, a24-3, a24-4, a24-5
    C2'/c' (15.89) : a24-6, a24-7
    P1 (2.4) : a24-8, a24-9, a24-10, a24-11
P1 (1); aP24; C2' (5.15) : a24-12(13), a24-14(15), a24-16(17)

LATTICE 24-2

PERIODS: a(1, 1, 1), a(0, 1, 1), a(1, 0, 1)
BRAVAIS LATTICE: hexagonal

STRUCTURES:

P3 (147); hP24; P3c'1 (165.95) : h24-1, h24-2
P1 (2); aP24; C2'/c' (15.89) : a24-18, a24-19

LATTICE 32-1

PERIODS: a(1, 0, 0), a(0, 1, 1), a(0, 1, 1)
BRAVAIS LATTICE: tetragonal

STRUCTURES:

P421c (114); tP32; P421c (114.281) : t32-1
P41212 (92); tP32; P41212 (92.117) : t32-2(3)
P4212 (96); tP32; P4212 (96.149) : t32-3(2)
C2/c (15); mC64; C2/c (15.85) : sm32-1, sm32-2
P1 (2); aP32; C2'/c' (15.89) : a32-1
P1 (1); aP32; P2' (3.3) : a32-2(3)

LATTICE 32-2

PERIODS: a(2, 2, 1), a(2, 2, 1), a(2, 0, 2)
BRAVAIS LATTICE: base-centered orthorhombic

STRUCTURES:

C2 (5); mC64; C222' (21.41) : sm32-3(9), sm32-4(10),
    sm32-5(11), sm32-6(12), sm32-7(13), sm32-8(14)
P21 (4); mP32; C2'2'2'1 (20.33) : m32-1(3), m32-2(4)
P1 (2); aP32:
    P2'/c' (13.69) : a32-4, a32-5, a32-6, a32-7, a32-8, a32-9,
    a32-10, a32-11, a32-12, a32-13, a32-14, a32-15
    P1 (2.4) : a32-16, a32-17, a32-18, a32-19, a32-20, a32-21,
    a32-22, a32-23, a32-24, a32-25, a32-26, a32-27
P1 (1); aP32;
    C2' (5.15) : a32-28(30), a32-29(31), a32-32(34), a32-33(35)
P2' (3.3) : a32-36(42), a32-37(43), a32-38(44), a32-39(45),
    a32-40(46), a32-41(47)
P1 (1.1) : a32-48(52), a32-49(53), a32-50(54), a32-51(55)

LATTICE 32-3

PERIODS: a(1, 0, 1), a(1, 0, 1), a(1, 0, 1)
BRAVAIS LATTICE: monoclinic

STRUCTURES:

P21/c (14); mP32; P21/c (14.75) : m32-5, m32-6, m32-7,
    m32-8
P1 (2); aP32:
    P2'/c' (13.69) : a32-56, a32-57, a32-58, a32-59
    P2'/c' (14.79) : a32-60, a32-61
    P1 (2.4) : a32-62, a32-63, a32-64, a32-65, a32-66, a32-67,
    a32-68, a32-69
P1 (1); aP32;
    P2' (3.3) : a32-70(72), a32-71(73)
P1 (1.1) : a32-74(76), a32-75(77)

LATTICE 32-4

PERIODS: a(2, 2, 1), a(2, 2, 1), a(2, 0, 2)
BRAVAIS LATTICE: rhombohedral

STRUCTURES:

R3 (148); hR96; R3c' (167.107) : r32-1, r32-2
R3 (146); hR96; R32' (155.47) : r32-3(5), r32-4(6)
P1 (2); aP32:
    C2'/c' (15.89) : a32-78, a32-79, a32-80, a32-81, a32-82,
    a32-83
    P1 (2.4) : a32-84, a32-85, a32-86, a32-87
$P1$ (1): $aP32$

$Cc' (9.39) : a_{32-88}(90), a_{32-89}(91)$

$C2' (5.15) : a_{32-92}(98), a_{32-93}(99), a_{32-94}(100), a_{32-95}(101), a_{32-96}(102), a_{32-97}(103)$

$P1$ (1.1): $a_{32-104}(108), a_{32-105}(109), a_{32-106}(110), a_{32-107}(111)$