

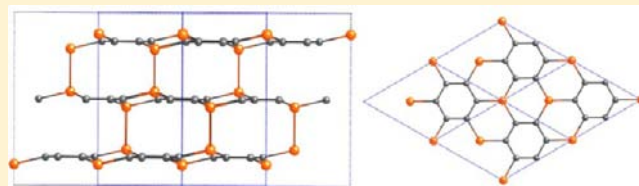
The Unusual and the Expected in the Si/C Phase Diagram

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S Supporting Information

ABSTRACT: In the Si/C phase diagram, the only stable phases at $P = 1$ atm are the numerous polytypes of the simplest 1:1 stoichiometry, SiC. However, many metastable yet likely to be kinetically persistent phases can be found for almost any composition. Given the instability of simple graphite-type structures with considerable Si content, we thought these metastables would be only of the diamondoid class. Indeed they are for Si_3C , a stoichiometry we studied on the silicon-rich side of the phase diagram. Yet on the carbon-rich side, which we chose to explore computationally with SiC_3 , there was a surprise in store, a series of unusual metastable structures. The most striking of these had the appearance of a collapsed graphite structure, with benzenoid C_6 units and SiSi bridges between layers. This SiC_3 structure is related to known *meta*-(1,3,5)cyclophanes. Three other metastable structures featured layers with all carbon polyene and polyphenylene arrays. Some of these can be metallic, as we have found.



INTRODUCTION

On the way to a study of the Ca/Si/C phase diagram, we had to look at the Si/C binary system. The 1:1 phase, SiC, has been experimentally well-known since the time of its synthesis by Berzelius in 1824. It occurs in a mineral, moissanite, and is, in fact, the only known stable composition (other than the elements) in the Si/C phase diagram.¹ We expected to reproduce the sparsely populated phase diagram, but, given that Si and C atoms favor tetrahedral coordination, we also anticipated many metastable diamondoid structures, for every composition, and this was indeed so.

We could, on paper, just as well substitute Si for C in a graphite lattice. Yet all-Si graphite-like structures have real troubles. Multiple bonding at Si leads to both kinetic and thermodynamic instability;² molecules containing Si=Si double bonds are very reactive and need to be sterically protected, if they are to be isolated in bulk. There is mounting literature on silicene, all on supported sheets of this graphene analogue.³ Going on to a 3D solid built out of such reactive silicene sheets, in a study of group 14 elemental structures we examined AA, AB, and ABC stacked graphitic silicon structures.⁴ The ABC stacking collapsed to the Si diamond-type structure. The AA and AB silicene stackings also collapsed, but now to leave some or all of the silicons as 5-fold coordinated. The energies of these were 0.38 and 0.55 eV/Si, respectively, above the diamond Si structure. A single silicon sheet is 0.68 eV/Si above α -Si. This is quite a contrast to what we know for graphite.

We thus expected that if we plotted the relative enthalpies of graphitic and diamondoid Si_xC_y phases at $P = 1$ atm (and included in that sketch metastable as well as stable structures) that we would get Figure 1. We were in for a surprise, and perhaps this should have been anticipated.

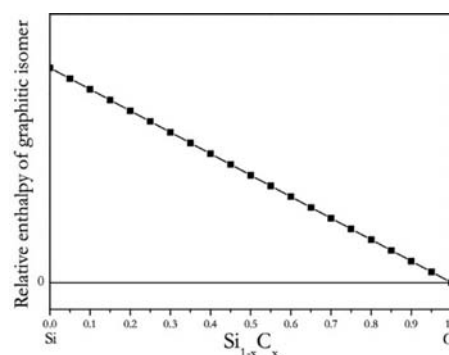


Figure 1. Schematic diagram of the expected enthalpy per formula unit of graphene-type $\text{Si}_{1-x}\text{C}_x$ phases as a function of the mole fraction of C, x . The zero of enthalpy is assumed to be the enthalpy of a diamond-type allotrope.

RESULTS AND DISCUSSION

Exploring the Si/C Phase Diagram. We began with 25, 50, and 75 atom % C, corresponding to possible macroscopic phases Si_3C , SiC, and SiC_3 . Initial structures were constructed by simple substitution in the diamond and graphite lattices. Even for these specific stoichiometries, there are, of course, many distinct ways to effect the substitutions; we will show below the choices we made. The C–C separation in cubic C diamond is 1.54 Å, in diamond-structured Si is 2.35 Å.⁵ So for any given stoichiometry, the Si_xC_y structure is going to have to readjust in its interatomic separations substantially to

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substitution, even if the general structural type is retained. To be certain to reach any possible minima, we used as starting points both elemental C and Si structures (with their respective metrics) for all stoichiometries considered, and then allowed the programs to optimize the structures. We also carried out independent structure searches with CALYPSO.⁶ The underlying structural relaxations were carried out with density functional theory using the Perdew–Burke–Ernzerhof exchange–correlation functional⁷ as implemented in the VASP code.⁸ The phonon calculations were carried out by using a supercell approach⁹ within the PHONOPY code.¹⁰ Details of the calculations (density functional theory, Vienna Ab-initio Simulation Package) are given in the Supporting Information.

Throughout this Article, the structures computed are all ground state and static, at $P = 1$ atm.

SiC: Just as Expected. SiC exists in experiment in a great variety of polymorphs, based on various stacking patterns in the parent cubic and hexagonal diamond structures. These include zinc blende (3C, ABC stacking, see Figure 2) and wurtzite

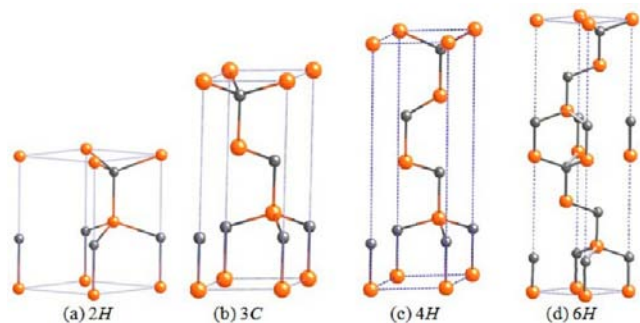


Figure 2. Three-dimensional view of the primitive hexagonal unit cells of the 2H-(wurtzite), 3C- (zinc blende), 4H-, and 6H-SiC polytypes of SiC. The orange (large) and gray (small) spheres represent Si and C, respectively. The 3C structure is shown in a hexagonal representation of the cubic cell.

stackings (2H, 4H, 6H, respectively, AB, ABCB, and ABCACB stacking variants).^{1,11} So far as we know, in all polymorphs Si–Si and C–C bonds are avoided; each Si is surrounded by 4 carbons, and vice versa. We calculated several of these structures (Figure 2); the enthalpies of the various polymorphs are all quite similar. The Si–C separation in all is 1.89 Å, of course intermediate between the CC and SiSi separations in diamond and α -Si.

Graphitic SiC is not known. Our calculations explored different stacking of “alternating” sheets, in each sheet each C surrounded by 3 Si, each Si by 3 C. All of such graphitic SiC structures are, as expected, very unstable relative to the diamond form. The most stable one is shown in Figure 3; it is

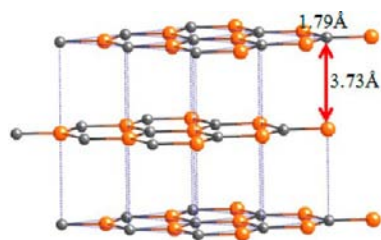


Figure 3. A graphitic $P\bar{6}m2$ structure for SiC. The orange (large) and gray (small) spheres represent Si and C, respectively.

0.99 eV/formula unit (f.u.) above diamondoid SiC. Note that the SiC separation within a graphitic layer shows signs of multiple bonding; it is 0.10 Å shorter than that in diamondoid SiC.

Si₃C. There are many ways to substitute three of four atoms in a carbon diamond or graphite structure by Si. Now it is impossible to avoid SiSi bonds. Also, as we mentioned, in the graphite structure these are a source of kinetic and thermodynamic instability. Yet in a diamond structure, they cause no particular problem, although they certainly cause local stress, as a SiSi separation of ~ 2.35 Å is so much longer than a CC one. The two most stable diamond-type structures that we found by systematic substitution (see the Supporting Information for their geometries) were, however, higher in enthalpy than two structures found by the CALYPSO method, $\bar{I}42d$ (also a diamondoid structure) and $C222_1$ (Figure 4).

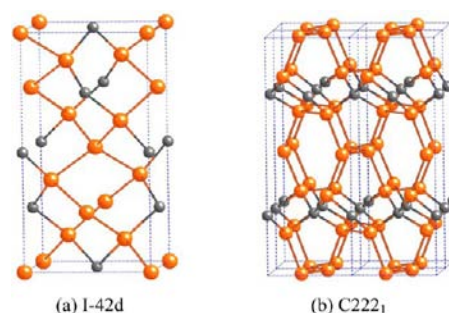


Figure 4. Predicted $\bar{I}42d$ and $C222_1$ structures for Si₃C at 1 atm. Orange, large spheres are Si; gray, small spheres are carbon.

In both $\bar{I}42d$ and $C222_1$ structures, the Si and C atoms are all four-coordinate; the major difference between the two structures is that there are only six-membered rings in $\bar{I}42d$, while there are five- and six-membered rings in $C222_1$. The Si–C bond length is nearly the same in the two, 1.95 Å in $\bar{I}42d$ and 1.91–1.93 Å in $C222_1$ (the Si–C in SiC is 1.89 Å), while the Si–Si bond lengths are a little different, 2.33 and 2.32–2.46 Å in $\bar{I}42d$ and $C222_1$, respectively.

Both of these structures are dynamically stable, with no imaginary phonons. They are calculated to be 0.91 and 0.90 eV unstable, respectively, to reaction to SiC and 2Si. The 1:1 stoichiometry, with all equal Si–C separations, is really a point of ground-state stability in the Si/C system. Importantly, other quite different structures for Si₃C also emerge as the pressure is raised; these we will explore in a separate contribution.

SiC₃: Surprises. One cubic-diamond substitution structure we found for SiC₃ is $P\bar{4}m2$ shown in Figure 5. The optimized C–C bond lengths, there must be some for this stoichiometry, are 1.65 Å in this structure. These are a little long¹² (the CC bond length in diamond is 1.54 Å), indicating strain in the structure. Also, the nonbonded Si–Si separation is 2.80 Å, which is on the short side for a nonbonded separation. The structure is dynamically stable, but enthalpically quite unstable with respect to SiC and graphite, by over 2 eV per SiC₃.

Now comes the surprise: another structure is substantially more stable (by 0.8 eV/SiC₃) than any diamond-substituted structure, and in particular the structure just described. This $R\bar{3}m$ structure is shown in Figure 6. Although we obtained it initially from optimization of a high energy diamondoid net, the structure may also be derived from a graphitic stacking, and is easiest visualized from the latter starting point.

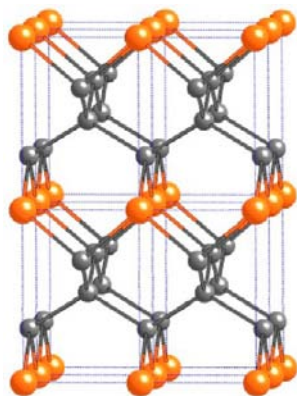


Figure 5. The $P\bar{4}m2$ structure of SiC_3 at 1 atm. Orange, large spheres are Si; gray, small ones are C.

As we can see, Si–Si bonds have formed between the Si atoms of the otherwise graphene-like layers. These layers are perforce slightly buckled, but nevertheless retain nearly planar benzenoid six-membered rings of carbon, with a separation (1.42 Å) not that different from benzene (1.40 Å). The interlayer Si–Si bonds are 2.45 Å, a little long as compared to the single bond length in α -silicon of 2.35 Å. The vertical separation between planes of two benzene rings in different layers is 3.32 Å, similar to the dispersion-force dictated graphite spacing of 3.4 Å.

In paracyclophanes¹³ (Figure 7 left, molecule 1), well-known molecules where benzene rings are forced to be near each other, the separation between two ring carbons is as low as 2.6 Å. (1,3,5)Cyclophanes¹⁴ (2), superphane¹⁵ (3), and Si-bridged paracyclophanes¹⁶ (4) are known, as are multilayered cyclophanes.¹⁷ These are models for the bonding arrangement in the $R\bar{3}m$ structure. For comparison, the Si–Si separation in 4 is 2.38 Å, and the ring–ring separation is 3.35–3.46 Å, which is not very different from our SiC_3 structure.

The ground state of the remarkable $R\bar{3}m$ structure is, however, also unstable relative to $\text{SiC}+2\text{C}$. Yet it is dynamically stable, and we expect the activation energy for transforming it to SiC and graphite or diamond to be very large. We have, however, not faced up to calculating this barrier.

Our initial expectation of the instability of graphitic substitutions in this phase diagram (Figure 1) then has to be revised. We should have known, given our studies of elemental Si and interlayer collapse there, that for some stoichiometry and geometry, Si–Si interlayer bonding in a hypothetical graphitic Si_xC_y would lead to a comfortable “collapsed” structure. The

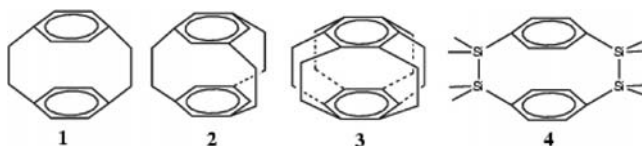
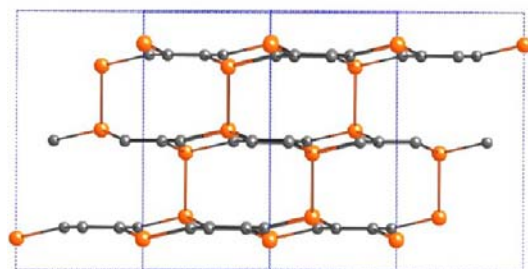


Figure 7. A (2,2)*para*-cyclophane (1); a (1,3,5)cyclophane (2); superphane (3); and a sila-(2,2)*para*-cyclophane (4).

$R\bar{3}m$ structure is just such. Yet there are still more stable structures for SiC_3 .

In a further structure search with CALYPSO, we found the same $P\bar{4}m2$ and $R\bar{3}m$ structures that we just discussed. We also found a number of more stable structures. Four of these are shown in Figure 8; the most stable, Cm , is 0.5 eV/ SiC_3 in enthalpy below the $R\bar{3}m$ structure.

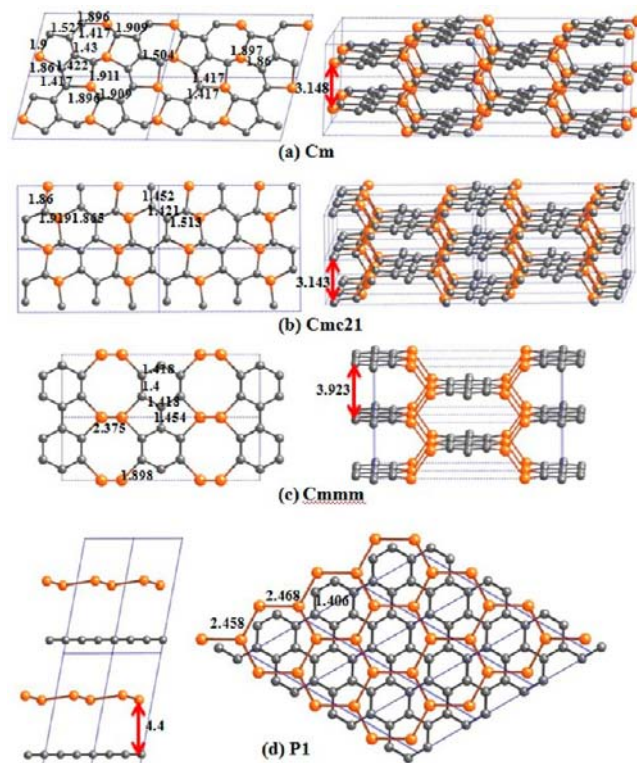


Figure 8. Four hypothetical SiC_3 structures at 1 atm: (a) Cm , (b) $Cmc2_1$, (c) $Cmmm$, and (d) $P1$. Orange, large spheres are Si; gray, small ones are C. The interlayer bonds are Si–Si and/or Si–C. The separations are given in angstroms.

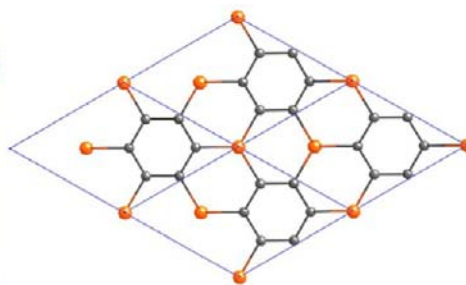


Figure 6. Different views of the $R\bar{3}m$ structure (on the right is just the top view of one layer of the structure at left). Orange, large spheres are Si; gray, small ones are C. The interlayer bonds shown are Si–Si.

Two of the structures are 3,4-connected, in the sense that some atoms have three neighbors, some four. The *Cm* and *Cmc*₂₁ structures shown in Figure 6a and b contain carbon polyene (polyacetylene) chains in trans and cis configurations.¹⁸ Interestingly, there is almost no bond alternation along the polyene chain in the trans form, whereas some is expected on theoretical grounds and also experimentally observed in the archetype polymer of prototype polyacetylene. There is a small degree of bond alternation along the *cis*-polyene chain in the *Cmc*₂₁ structure. The separation between polyene planes is 3.15 Å, which is shorter than the graphite spacing of 3.4 Å.

In the *Cmmm* structure (Figure 8c), we find that all of the carbon atoms are 3-connected, all Si 4-connected. The carbons form polyphenylene chains (a chain of benzene rings *meta*-bonded to each other) most clearly seen in the top view at left; the separation between layers of these is 3.92 Å. Some time ago, we suggested a variety of 3,4-connected structures for carbon.^{19,20} The three structures mentioned here were not among them; for all-C structures of this kind (i.e., analogous to those illustrated in Figure 8a–c), the interlayer spacing between the polyene chains would be substantially smaller at ~2.6 Å, with some instability as a consequence. The structures found by us now also have resemblance to some other 3,4-connected networks suggested for carbon.²¹

The fourth structure, close in enthalpy to the others, brings another surprise. The *P1* structure of Figure 8d is a layered structure composed of alternating silicene and graphene sheets separated by a large vertical separation of 4.4 Å. That such a network might exist makes sense if one thinks of typical CC and SiSi separations in graphitic lattices. For a CC separation of 1.42 Å in idealized graphite (in the *P1* net the separation is 1.41 Å), the separation between centers of two neighboring rings is 2.46 Å. That is not very much longer than a Si–Si separation in an isolated silicene sheet (2.29 Å). The low symmetry *P1* structure accommodates to this near registry, by small distortions of the silicon atoms off the carbon ring centers, as well as stretching to 2.6 and 2.7 Å. Unfortunately, this structure has associated imaginary frequencies in a supercell computation, and we have not yet been able to determine a geometry to which it transforms.

The *Cm*, *Cmc*₂₁, and *Cmmm* structures, all dynamically stable, are all much lower in enthalpy than *P4̄m2* and *R3̄m*, obtained by substitution. However, they are also unstable with respect to SiC+2C; the lowest enthalpy *Cm* structure is 1.14 eV above SiC+2C.

Enthalpic Relationships in the Si/C System. The ground-state enthalpy relationships for the Si/C system at *P* = 1 atm are conveniently summarized in the form of a tie-line diagram, which gives the enthalpy of formation per atom (Figure 9). The reference line is pure silicon (diamond structure) and pure carbon (graphite). Only SiC has a negative formation enthalpy, in accord with experiment. The stoichiometries Si₃C and SiC₃ are not on the convex hull of this diagram; that is, they are unstable with respect to separation into the elements and also SiC+2Si, and SiC+2C, respectively. As mentioned above, such Si₃C and SiC₃ structures might still be capable of synthesis, as the barriers in the way of decomposition to SiC and Si or C are likely to be large.

Electronic Properties. In experiment, the band gaps in diamond, SiC, and α -Si are 5.48, 2.42, and 1.17 eV. They are calculated as 4.2, 1.4, and 0.6 eV, respectively; we know that our level of DFT usually underestimates band gaps.²² To get more reliable results, we also recalculated band gaps and band

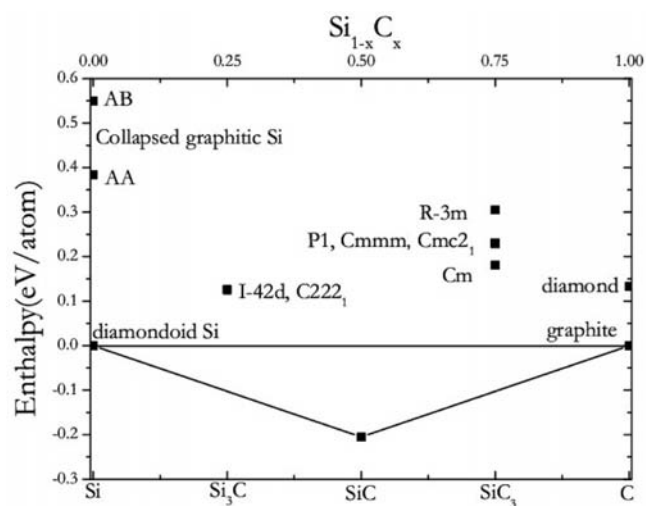


Figure 9. Ground-state and static enthalpy of formation per atom for the Si_{1-x}C_x phases with respect to their separated counterparts at 1 atm. Here, *x* = 0 corresponds to pure silicon (diamond-like structure), and *x* = 1 corresponds to pure carbon (graphite).

structures with the Heyd–Scuseria–Ernzerhof (HSE) hybrid functional,²³ which employs a screened Coulomb potential for the exchange interaction. The recalculated band gaps improve to 5.3, 2.2, and 1.0 eV for diamond, SiC, and α -Si, respectively. Graphite is a zero band gap semimetal. The two Si₃C structures discussed, *Cmmm* and *R3̄m*, and the diamondoid SiC₃ structure, *P4̄m2*, are calculated to have band gaps of 1.4, 1.1, and 2.4 eV, respectively.

For SiC₃, it is interesting to note that the *Cm* and *Cmc*₂₁ structures, the two most stable ones, are both calculated to be metallic with overlaps between conduction bands and valence bands, as shown in Figure 10. Presumably the overlap between conduction and valence bands derives from the close contact layering (~3.15 Å) along the *c* axis (see Figure 8). Consistent with this is the existence of the band gap for the *Cmmm* structure; here, the polyphenylenes are far apart (3.92 Å). The interesting *R3̄m* structure with its unstrained benzene rings stacked far apart also emerges as a semiconductor. The relatively well-isolated flat bands in the *R3̄m* structure also are consistent with the presence of molecular units (benzene rings, Si–Si bridges) in the structure.

CONCLUSIONS

Our computational exploration confirms that SiC is the most stable stoichiometry in the whole Si–C system in its ground state.²⁴ Interestingly, we find many metastable structures for both Si₃C and SiC₃. For Si₃C, the most stable structure is a diamond-like structure, 4-coordinate for both Si and C atoms. For SiC₃, we find several novel structural types, which incorporate isolated benzene rings, cross layer SiSi bonds, carbon trans and cis polyene chains, and polyphenylene chains. Although the structures now found for Si₃C and SiC₃ are all unstable relative to SiC and carbon or silicon, they are all dynamically stable, possessing local minima. The activation energies for transforming them to SiC and C or Si are likely to be very large; it appears that if they could be made they would persist.

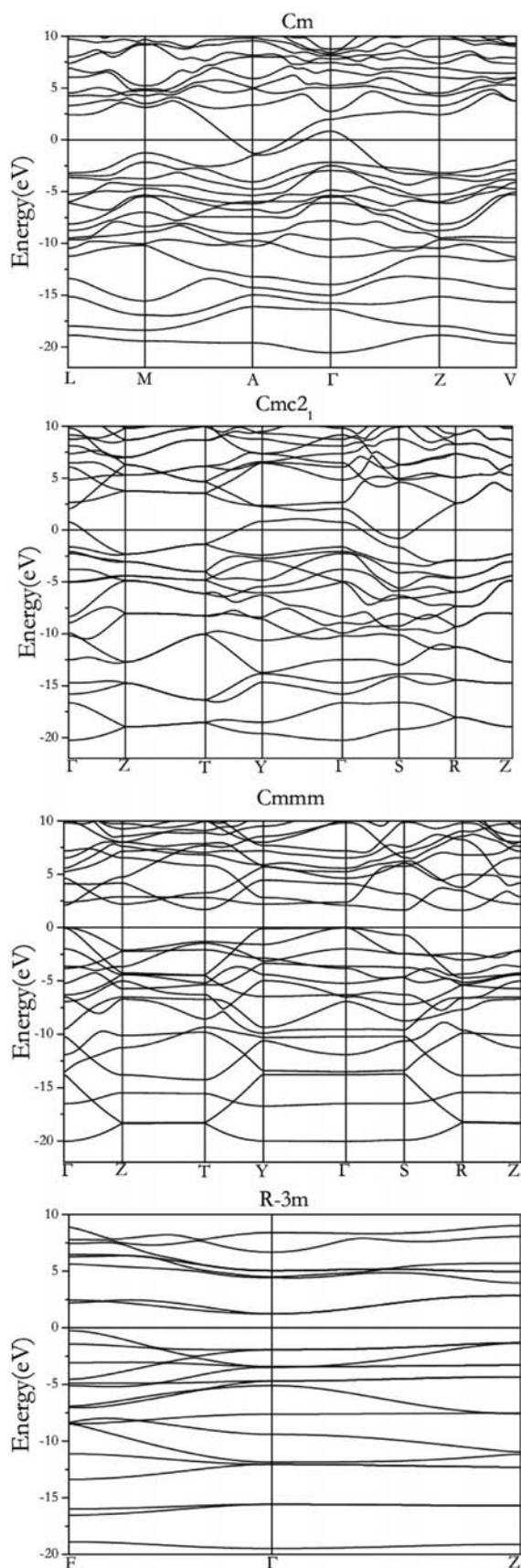


Figure 10. Electronic band structures for Cm , $Cmc2_1$, $Cmmm$, and $R\bar{3}m$ SiC_3 at 1 atm with HSE hybrid functional. Of these, Cm and $Cmc2_1$ are metallic.

■ ASSOCIATED CONTENT

📄 Supporting Information

Computational methods, other predicted structures for SiC_3 , phonon spectra, total density of states, and structural and energetic information for optimized structures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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