Electronic Supporting Information

Dispersion Interactions in Silicon Allotropes

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Contents of the Supporting Information:

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1. LMP2/TZVPP potential energy scan for the lattice constant of *α*-Si (*cF*8)

We carried out a potential energy scan for the lattice constant of *α*-Si (*cF*8) at the LMP2/TZVPP level of theory. Since the lattice constant *a* of the cubic *α*-Si is the only degree of freedom in the structure, the potential energy scan can also be considered as a structural optimization at the LMP2/TZVPP level of theory. The results of the scan are shown in Figure S1. The relative energy Δ*E* of the minimum energy structure 5.43 has been set to 0.0 kJ/mol. The data in Figure S1 illustrates that the potential energy behaves smoothly enough so that a minimum energy structure can be found. The energy differences close to the minimum are very small, only about 0.01 kJ/mol for 5.42 and 5.43 Å.

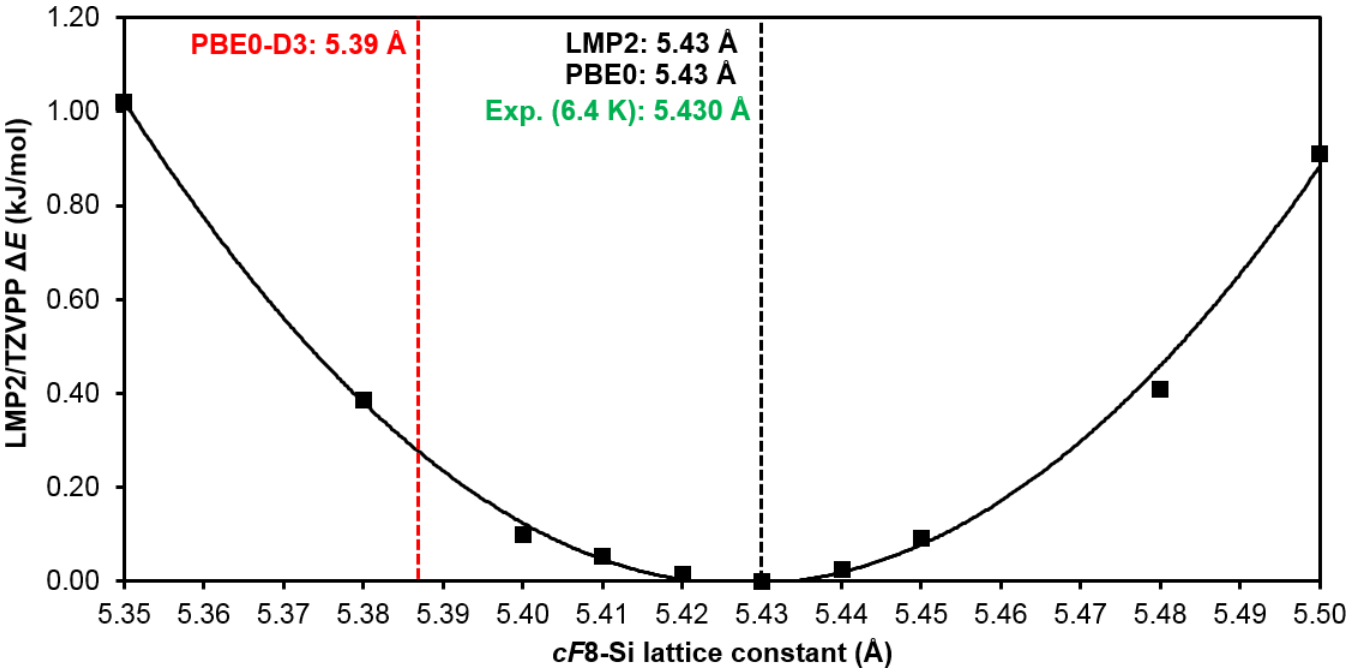

Figure S1. LMP2/TZVPP potential energy scan for the lattice constant of *α*-Si (*cF*8). The minimum energy structure (Δ*E* = 0.0 kJ/mol) was found for *a* = 5.43 Å. The squares are the calculated data points and the black line is a second order polynomial fit to the data (to serve as a guide to the eye). The experimental value at 6.4 K is from D. N. Batchelder and R. O Simmons *J. Chem. Phys.* **1964**, *41*, 2324.

2. Additional computational details

Both LMP2 and DFT calculations were carried out using a localized Gaussian-type basis set of triple-zeta-valence + double polarization (TZVPP) quality (Table S2). The basis set was originally derived from the molecular def2-TZVPP Karlsruhe basis set for LMP2 studies on noble-gas-filled group 14 clathrates (see main paper for the references). Here we further improved the basis set by decreasing the exponent of the outermost d-function from 0.318 to 0.276 (the geometric mean of the two outermost d-functions with exponents of 0.470 and 0.160 in def2-TZVPP). The TZVPP basis set used for *cF8*-Ge and *hP*8-Ge reference calculations is listed in Table S2 (also derived from the molecular def2-TZVPP basis set).

For the evaluation of the Coulomb and exchange integrals (TOLINTEG), tight tolerances of 8, 8, 8, 8, and 16 were used in the DFT calculations. The geometries of the structures were fully optimized with both the PBE0 and the PBE0-D3 functionals using the default optimization convergence criteria and DFT integration grids of CRYSTAL14. The calculation of the Hartree-Fock reference wavefunction for LMP2 was carried out using a tight SCF convergence criterion (TOLDEE 9). In the HF and LMP2 calculations, the Coulomb and exchange integrals were evaluated using very tight tolerances of 10, 10, 10, 20, and 50.

Table S1. TZVPP-Si basis set in CRYSTAL14 input format

```
14 11
0 0 7 2.0 1.0
  44773.358078      0.55914765868E-03
  6717.1992104      0.43206040189E-02
  1528.8960325      0.22187096460E-01
  432.54746585      0.86489249116E-01
  140.61505226      0.24939889716
  49.857636724      0.46017197366
  18.434974885      0.34250236575
0 0 3 2.0 1.0
  86.533886111      0.21300063007E-01
  26.624606846      0.94676139318E-01
  4.4953057159     -0.32616264859
0 0 2 2.0 1.0
  2.1035045710       1.3980803850
  1.0106094922       0.63865786699
0 0 1 0.0 1.0
 0.28251158837       1.0000000000
0 1 1 0.0 1.0
 0.11000000000       1.0 1.0
0 2 6 6.0 1.0
  394.47503628      0.26285693959E-02
  93.137683104      0.20556257749E-01
  29.519608742      0.92070262801E-01
  10.781663791      0.25565889739
  4.1626574778      0.42111707185
  1.6247972989      0.34401746318
0 2 1 2.0 1.0
 0.81239864945       1.0000000000
0 2 1 0.0 1.0
 0.36808947649       1.0000000000
0 3 1 0.0 1.0
 2.30300000          1.00000000
0 3 1 0.0 1.0
 0.276               1.00000000
0 4 1 0.0 1.0
 0.336000000         1.00000000
```

Table S2. TZVPP-Ge basis set used for *cF8*-Ge and *hP*8-Ge reference calculations.

```
32 15
0 0 8 2.0 1.0
  466115.00592      0.22487264660E-03
  69875.420762      0.17435426729E-02
  15903.276716      0.90691482206E-02
  4501.8233453      0.36906174685E-01
  1466.0570924      0.12050167907
  527.07841728      0.28748641703
  205.00395074      0.41622321885
  81.251596065      0.22397845695
0 0 4 2.0 1.0
  505.74661282     -0.25184609291E-01
  156.96593744     -0.11898929721
  25.761448176      0.54930135870
  11.106654687      0.52939309129
0 0 2 2.0 1.0
  17.272059104     -0.22854595728
  2.9438289048      0.68377930317
0 0 1 2.0 1.0
  1.2852272293       1.0000000000
0 0 1 0.0 1.0
 0.30110831584       1.0000000000
0 1 1 0.0 1.0
 0.11000000000       1.0 1.0
0 2 6 6.0 1.0
  2633.9346241      0.22143925310E-02
  624.00161628      0.18140899141E-01
  200.58528404      0.86632184922E-01
  75.097081525      0.25649020592
  30.214388474      0.42658611262
  12.440087567      0.26200527313
0 2 3 6.0 1.0
  45.981316002     -0.20321767678E-01
  6.9945654416      0.32013744527
  2.9686001327      0.59051014555
0 2 1 2.0 1.0
 1.2452540491        1.0000000000
0 2 1 0.0 1.0
 0.36766682938       1.0000000000
0 3 5 10.0 1.0
  122.93850231      0.10586544521E-01
  36.242755203      0.69601280945E-01
  13.191062921      0.22807035287
  5.2163136729      0.40301067220
  2.0927838749      0.41304847015
0 3 1 0.0 1.0
 0.81259117944       1.0000000000
0 3 1 0.0 1.0
 0.40                1.0000000000
0 3 1 0.0 1.0
 0.20                1.0000000000
0 4 1 0.0 1.0
 0.36210645          1.0
```

3. Structural data for the studied structures

Lattice parameters (Å) and fractional atomic coordinates for the studied structures are listed below (DFT-PBE0/TZVPP level of theory). These structures were used for the LMP2/TZVPP calculations. The coordinates are given in the CRYSTAL input format:

```
Space group number
Minimal set of lattice parameters a,b,c,α,β,γ
Number of non-equivalent atoms in the asymmetric unit
<atomic number> <fractional x> < fractional y> < fractional z>
```

*cF*8

```
227
5.43392972
1
14  .125  .125   .125
```

*hP*8

```
194
3.83265593 12.59438754
2
14    0.000000000000E+00   0.000000000000E+00   9.323893118227E-02
14    3.333333333333E-01  -3.333333333333E-01   1.559641060512E-01
```

*hP*4

```
194
3.82526733 6.32449168
1
14    3.333333333333E-01  -3.333333333333E-01   6.301048731404E-02
```

*tP*12

```
138
5.18522875 9.23727465
2
14   -2.500000000000E-01   2.500000000000E-01  -2.500000000000E-01
14    8.660305175483E-02   8.660305175483E-02  -3.925188933671E-01
```

*oP*32

```
57
7.85308703 11.29409273 7.44910429
6
14    3.311386206546E-01   2.773307600738E-01  -2.500000000000E-01
14   -1.535783700487E-01  -2.500000000000E-01   0.000000000000E+00
14    4.361954941718E-01  -4.148506366166E-01   2.500000000000E-01
14    4.846201730297E-01  -3.878271895172E-01  -2.500000000000E-01
14    3.011704678895E-01  -3.528675134542E-01  -1.168610807291E-02
14    2.482169023920E-02  -4.130600406730E-01  -8.559106903431E-02
```

*hP*6

```
178
5.44213208 5.08499513
1
14   -2.323498855317E-01   2.323498855317E-01   4.166666666667E-01
```

*tP*24

```
137
7.42426541 9.15180722
3
14   -1.992567818184E-02   1.992567818184E-02   2.500000000000E-01
14    2.500000000000E-01  -8.720693971958E-02  -4.161281383954E-01
14    2.500000000000E-01   4.140722708798E-01   3.682504788249E-01
```

*oC*24

```
63
3.82041998 10.68425836 12.66445622
3
14   -3.049695997126E-17   2.571897737875E-01  -5.496998958790E-02
14   -7.624239992815E-18   7.151650708920E-02  -1.573714960879E-01
14   -5.000000000000E-01  -2.873865097232E-02  -9.057902423745E-02
```

*cF*136

```
227
14.64746602
3
14   -1.250000000000E-01  -1.250000000000E-01  -1.250000000000E-01
14   -2.170340838999E-01  -2.170340838999E-01  -2.170340838999E-01
14    3.174949191829E-01  -1.825050808171E-01   1.295418958975E-01
```

*cI*46

```
217
10.03878229
4
14    2.500000000000E-01   5.000000000000E-01   4.659155379568E-17
14   -1.321413835696E-21   0.000000000000E+00  -1.321413835696E-21
14   -8.457923550544E-02  -8.457923550544E-02  -3.567273342191E-01
14   -1.356590274752E-01  -1.356590274752E-01  -1.356590274752E-01
```

*cP*46

```
223
10.16331819
3
14   -2.301073837868E-39   3.080174033799E-01   1.170620795402E-01
14    1.836471962445E-01   1.836471962445E-01   1.836471962445E-01
14    2.500000000000E-01  -6.137875492535E-17  -5.000000000000E-01
```