Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

sp^3-bonded silicon allotropes based on the Kelvin problem

Hui-Yan Zhao,[1,2] Jing Wang,[1,2] Qing-Min Ma,[1,2] and Ying Liu[1,2,*]

[1]*Department of Physics and Hebei Advanced Thin Film Laboratory, Hebei Normal University, Shijiazhuang 050024, Hebei, China*

[2]*National Key Laboratory for Materials Simulation and Design, Beijing 100083, China.*

1. Structural information for Kelvin Silicons

Table S1 Crystallographic data for Kelvin Silicons at 0 GPa.

K^{I} Space group $Im\bar{3}m$ $a = b = c =$ 6.7348 Å				
Atomic coordinates				
Si	12*d*	0.25000	0.00000	0.50000
K^{II} Space group $Pm\bar{3}n$ $a = b = c =$ 10.2350 Å				
Atomic coordinates				
Si1	16*i*	0.18370	0.18370	0.18370
Si2	24*k*	0.50000	0.80767	0.61714
Si3	6*d*	0.25000	0.50000	0.00000
K^{III} Space group $C2/c$ $a =$ 25.4751 Å, $b =$ 15.2199 Å, $c =$ 9.8931 Å				
Atomic coordinates				
Si1	8*f*	0.05400	0.59918	0.60088
Si2	8*f*	0.13876	0.53982	0.60624
Si3	8*f*	0.13356	0.40954	0.73362
Si4	8*f*	0.16893	0.28447	0.61924
Si5	8*f*	0.94914	0.39437	0.64040
Si6	8*f*	0.06563	0.11076	0.49278
Si7	8*f*	0.10566	0.17538	0.67808
Si8	8*f*	0.97505	0.15188	0.49502
Si9	8*f*	0.03689	0.24295	0.81261
Si10	8*f*	0.73340	0.38206	0.59602
Si11	8*f*	0.81136	0.46341	0.60383
Si12	8*f*	0.19369	0.59274	0.76670
Si13	8*f*	0.17645	0.72646	0.87847
Si14	8*f*	0.75572	0.26910	0.75327
Si15	8*f*	0.27309	0.63291	0.64193
Si16	8*f*	0.04053	0.74752	0.68228
Si17	8*f*	0.10809	0.81609	0.80305
Si18	8*f*	0.59132	0.45966	0.49777
Si19	8*f*	0.64846	0.43387	0.67450
Si20	8*f*	0.64715	0.56654	0.80097
Si21	4*e*	0.00000	0.50187	0.75000

K^{IV} Space group $I\bar{4}3m$ $a = b = c = 12.4874$ Å

Atomic coordinates				
Si1	48*h*	0.63106	0.76376	0.02279
Si2	8*c*	0.39135	0.60865	0.39135
Si3	2*a*	0.00000	0.00000	0.00000
Si4	24*g*	0.70878	0.93204	0.06796

K^{V} Space group $Cmmm$ $a = 17.6979$ Å, $b = 10.2316$ Å $c = 10.3782$ Å

Atomic coordinates				
Si1	16*r*	0.10476	0.81429	0.68774
Si2	16*r*	0.80974	0.69027	0.81308
Si3	8*n*	0.00000	0.88065	0.81309
Si4	4*h*	0.86770	0.50000	0.50000
Si5	8*o*	0.79075	0.50000	0.68778
Si6	8*o*	0.66677	0.50000	0.61237
Si7	8*q*	0.06628	0.69894	0.50000
Si8	4*i*	0.00000	0.74243	0.00000
Si9	8*p*	0.87888	0.62114	0.00000

K^{VI} Space group $Fd\bar{3}m$ $a = b = c = 25.9753$ Å

Atomic coordinates				
Si1	192*i*	0.82200	0.38630	0.50908
Si2	192*i*	0.81466	0.74944	0.62069
Si3	192*i*	0.30632	0.49257	0.37073
Si4	192*i*	0.85952	0.53257	0.46743
Si5	96*g*	0.30267	0.30267	0.19733
Si6	32*e*	0.25000	0.25000	0.25000

K^{VII} Space group $P6_3/mmc$ $a = b = 10.4154$ Å, $c = 17.0590$ Å

Atomic coordinates				
Si1	24*l*	0.04984	0.33042	0.06454
Si2	12*k*	0.08433	0.54216	0.36473
Si3	12*k*	0.12352	0.87648	0.86128
Si4	4*f*	0.33333	0.66667	0.31962
Si5	4*e*	0.00000	0.00000	0.31818
Si6	6*h*	0.06939	0.53469	0.75000
Si7	6*h*	0.20224	0.79776	0.75000

K^{VIII} Space group $P\bar{3}m1$ $a = b = 10.0979$ Å, $c = 16.0108$ Å

Atomic coordinates				
Si1	12*j*	0.00116	0.38093	0.29528
Si2	12*j*	0.75683	0.00078	0.17352
Si3	12*j*	0.91169	0.33349	0.05811
Si4	6*i*	0.86691	0.13309	0.49945
Si5	6*i*	0.79104	0.20896	0.62182
Si6	6*i*	0.79117	0.20883	0.37672
Si7	2*d*	0.66667	0.33333	0.42649
Si8	2*d*	0.66667	0.33333	0.57190

K^{IX} Space group $Cmcm$ $a = 16.7904$ Å, $b = 12.9014$ Å, $c = 10.0253$ Å

Atomic coordinates				
Si1	16*h*	0.38084	0.71275	0.44098
Si2	16*h*	0.32399	0.87541	0.37336
Si3	16*h*	0.19229	0.91851	0.44092
Si4	8*e*	0.39901	0.00000	0.50000
Si5	8*f*	0.00000	0.24825	0.56097
Si6	8*f*	0.00000	0.42098	0.63107
Si7	8*g*	0.11579	0.04402	0.75000
Si8	8*g*	0.42917	0.37152	0.75000
Si9	4*c*	0.00000	0.14370	0.75000

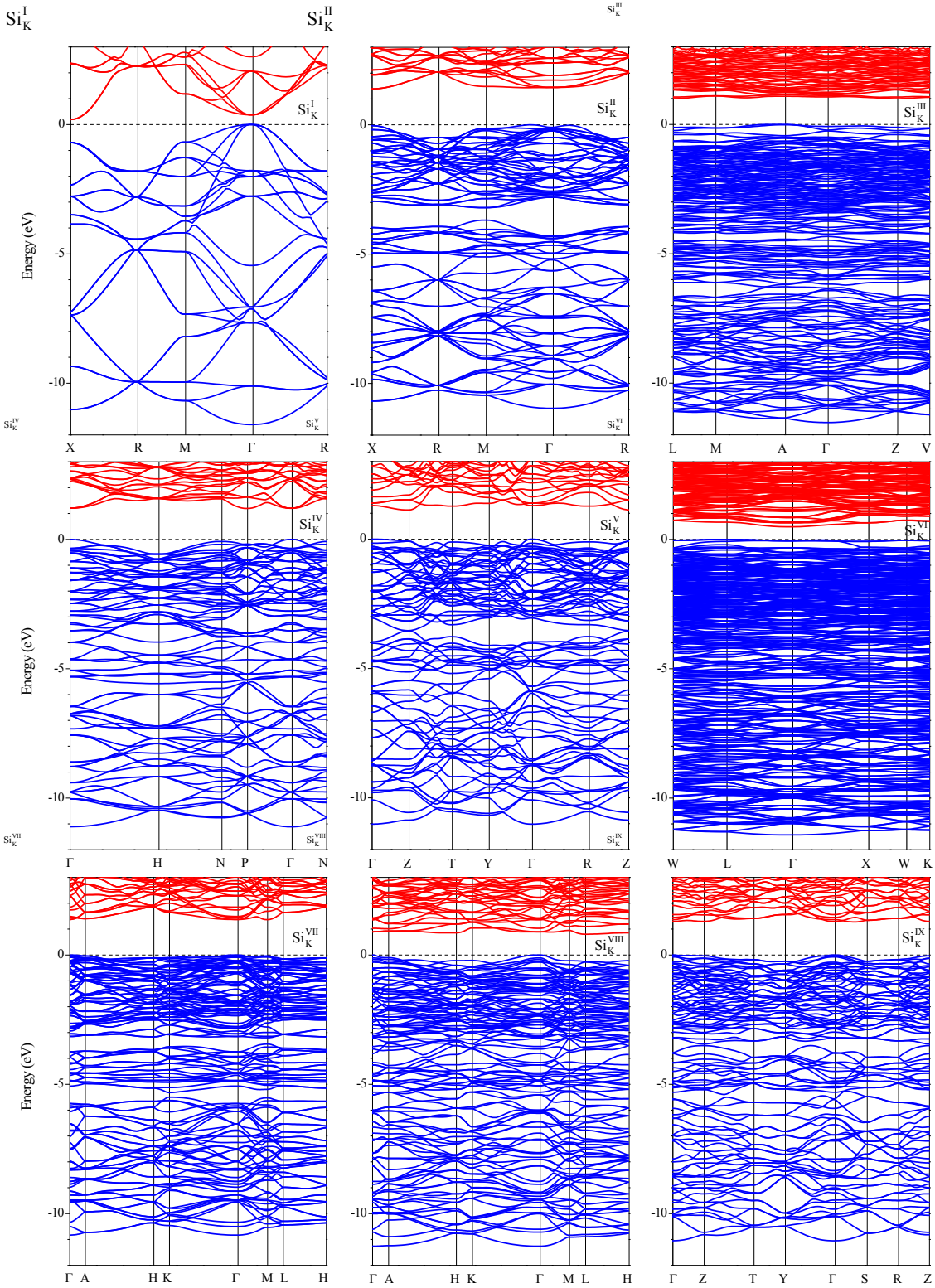
K^{X} Space group $P4_2/nmc$ $a = b = 10.2614$ Å, $c = 24.3468$ Å

Atomic coordinates				
Si1	16*h*	0.18346	0.31598	0.47133
Si2	16*h*	0.20578	0.12227	0.61131
Si3	16*h*	0.32019	0.24563	0.68328
Si4	16*h*	0.18019	0.38278	0.73473
Si5	16*h*	0.50000	0.31000	0.55372
Si6	16*h*	0.50000	0.36958	0.64783
Si7	16*h*	0.00000	0.38028	0.52430
Si8	16*h*	0.00000	0.23569	0.60339
Si9	16*h*	0.00000	0.38399	0.67690
Si10	8*e*	0.00000	0.00000	0.00000

K^{XI} Space group $R\bar{3}$ $a = b = \mathrm{c} = 17.6221$ Å

Atomic coordinates				
Si1	24*d*	0.34597	0.41824	0.23752
Si2	24*d*	0.31547	0.40412	0.60584
Si3	24*d*	0.30775	0.40162	0.10815
Si4	24*d*	0.30260	0.29669	0.52667
Si5	24*d*	0.28632	0.38982	0.73659
Si6	24*d*	0.27115	0.51309	0.54110
Si7	24*d*	0.26841	0.51848	0.91664
Si8	24*d*	0.10412	0.52669	0.41579
Si9	24*d*	0.10644	0.43729	0.04476
Si10	8*c*	0.31039	0.31039	0.31039
Si11	8*c*	0.26609	0.76609	0.73391

2. Electronic band structures for Kelvin Silicons



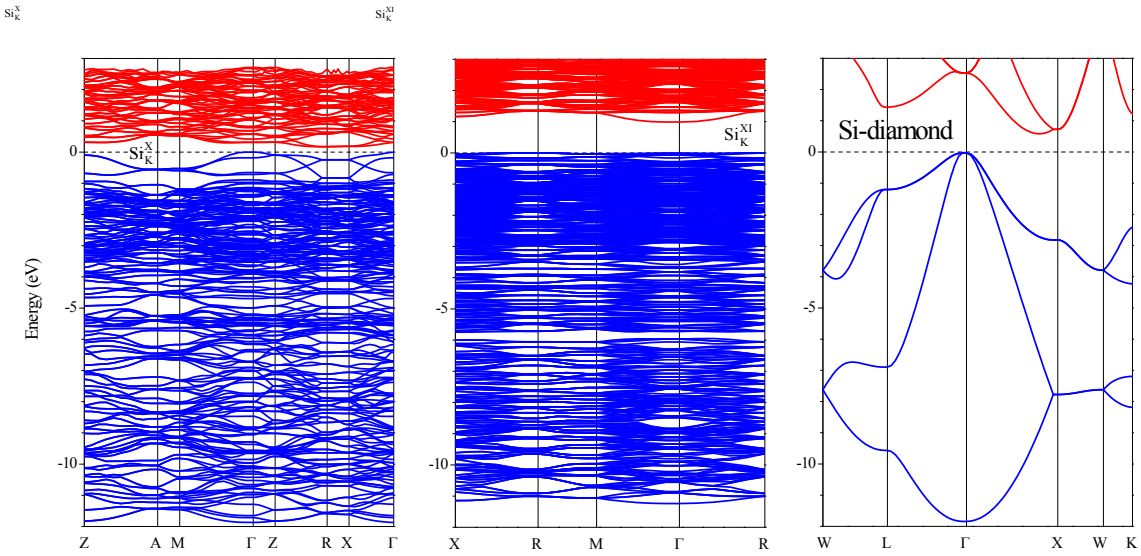


Figure S1 Electronic band structures of Kelvin Silicons and diamond phase of silicon.

3. X-ray diffraction spectra for Kelvin Silicons

To provide information and characters for possible experimental observation, the simulated XRD patterns at zero pressures are obtained by the REFLEX program implemented in Materials Studio 5.0 package.[S1]

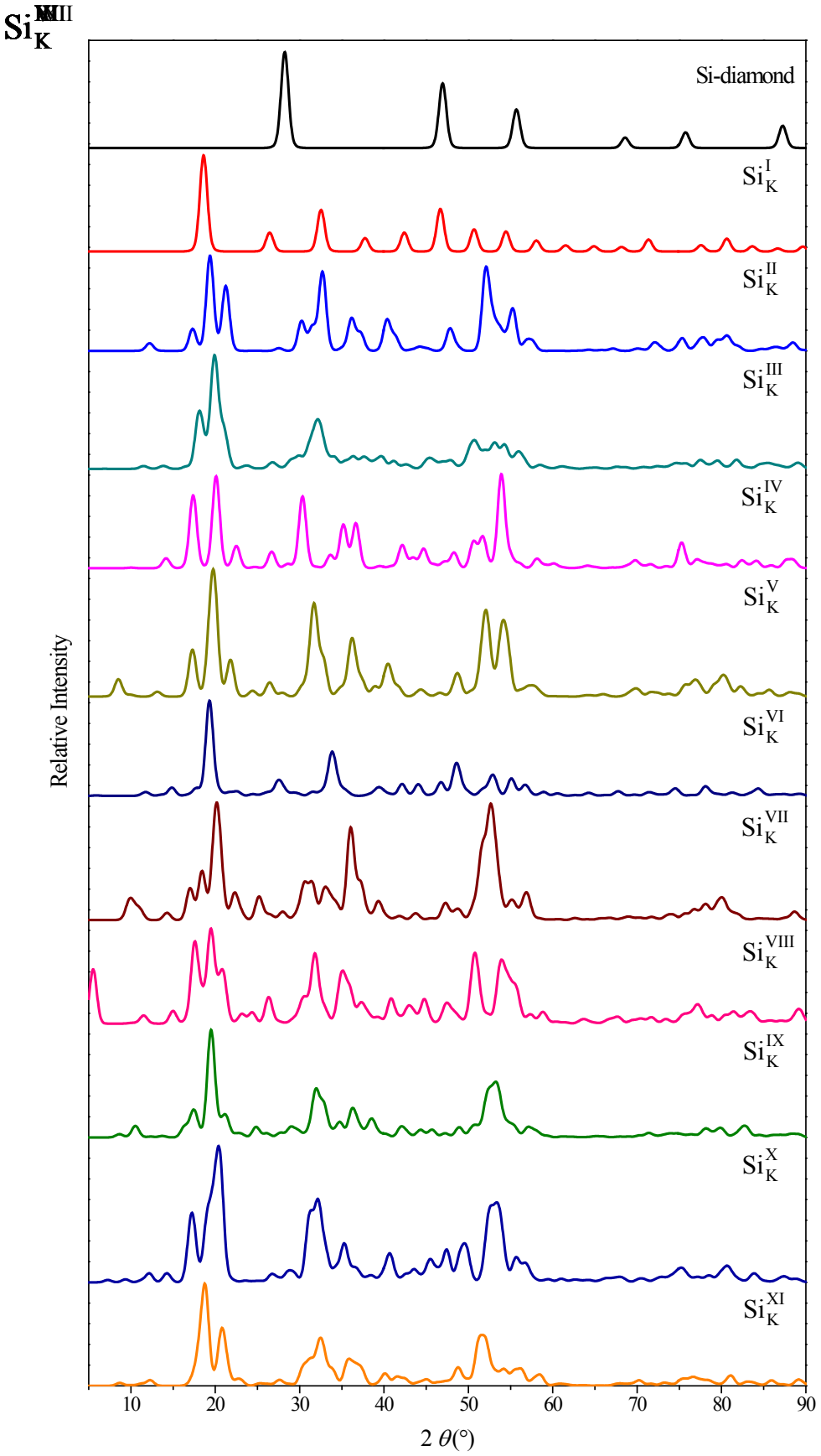


Figure S2 Simulated XRD patterns of diamond silicon and Kelvin Silicons at zero pressure. The X-ray wavelength is 1.5406 Å.

4. The calculated elastic constants for Kelvin Silicons

Table S2 The calculated elastic constants C_{ij} (GPa) for the Kelvin Silicons at 0 GPa.

Si_K^I			Si_K^{II}		
C_{11}	C_{44}	C_{12}	C_{11}	C_{44}	C_{12}
117	38	43	133	48	48

Si_K^{III}												
C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	C_{12}	C_{13}	C_{15}	C_{23}	C_{25}	C_{35}	C_{46}
133	120	130	43	43	39	47	45	-1	49	0	-1	-1

Si_K^{IV}			Si_K^{V}								
C_{11}	C_{44}	C_{12}	C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	C_{12}	C_{13}	C_{23}
132	43	45	135	135	126	48	48	45	44	42	42

Si_K^{VI}			Si_K^{VII}				
C_{11}	C_{44}	C_{12}	C_{11}	C_{33}	C_{44}	C_{12}	C_{13}
123	38	44	137	137	47	45	45

Si_K^{VIII}				
C_{11}	C_{33}	C_{44}	C_{12}	C_{13}
122	108	44	39	37

Si_K^{IX}								
C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	C_{12}	C_{13}	C_{23}
132	140	129	47	44	42	44	47	43

Si_K^{X}						Si_K^{XI}		
C_{11}	C_{33}	C_{44}	C_{66}	C_{12}	C_{13}	C_{11}	C_{44}	C_{12}
109	116	36	36	38	35	132	41	45

The mechanical stability of these Kelvin-Silicon structures studied in this work was also examined by calculations of the elastic constants using the CASTEP program implemented in Materials Studio 5.0 package.[S1] The corresponding values of the elastic constants for the Kelvin Silicons at 0 GPa were listed in Table S2. From Table S2, both structures are mechanically stable since their elastic constants satisfy the elastic stability criteria,[S2] i.e., the strain energy must be positive against any homogeneous elastic deformation. Remarkably, several elastic constants C_{15}, C_{35}, and C_{46} of the monoclinic Si_K^{III} are negative, while other Kelvin-Silicon structures have

no negative elastic constants. Based on the arguments given by Söderlind and Klepeis,[S3] these negative values do not mean an instability because the actual applied distortions all yield positive elastic coefficients.

References:

S1. M. Segall, P. Lindan, M. Probert, C. Pickard, P. Hasnip, S. Clark, and J. Payne, *J. Phys.: Condens. Matter*, 2002, **14**, 2717.

S2. J. F. Nye, Oxford University Press, Oxford, 1985.

S3. P. Söderlind, and J. E. Klepeis, *Phys. Rev. B*, 2009, **79**, 104110.