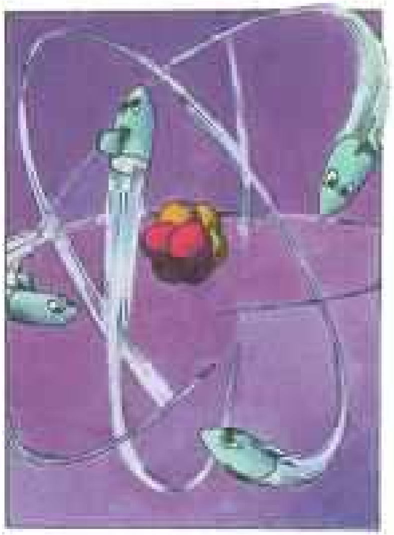
Where are the atoms?



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Locating the global minimum of a potential energy surface

Locating the global minimum of a potential energy surface belongs to the class of problems known in complexity theory as “NP-hard”
(Non-deterministic Polynomial-time hard)

An algorithm which solves an NP-hard problem exactly is expected to scale very badly with the number of variables

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The law of future employment prospects for many-particle physicists:
Most really interesting models in physics involve many interacting particles and almost all such models cannot be solved exactly

Counting the number of degrees of freedom

Consider a crystal with N atoms in a unit cell of arbitrary size and shape

Number of degrees of freedom:

$$N_d = 3N - 3 + 6$$

Guess the number of minima in the potential energy surface:

$$N_{\text{minima}} \sim e^{N_d} = e^{3N+3}$$

Suppose we have 10 atoms in the unit cell:

$$N_{\text{minima}} \sim e^{33} \simeq 10^{14}$$

Searching for the global minimum

Simple search algorithm: choose random points in the configuration space and relax to a local minimum

The above analysis suggests that this is not a useful algorithm for N=10 (about 10^{14} minima), or even for N=5 (about 10^7 minima)

But maybe it is not so bad!

If there were only $N_{\mathrm{minima}} \sim e^{0.1 N_d}$ minima then:

$$\begin{aligned} N_{\mathrm{minima}} &\sim e^{3.3} \simeq 27 \qquad \text{for } 10 \text{ atoms} \\ &\sim e^{1.8} \simeq 6 \qquad \text{for } \ 5 \text{ atoms} \end{aligned}$$

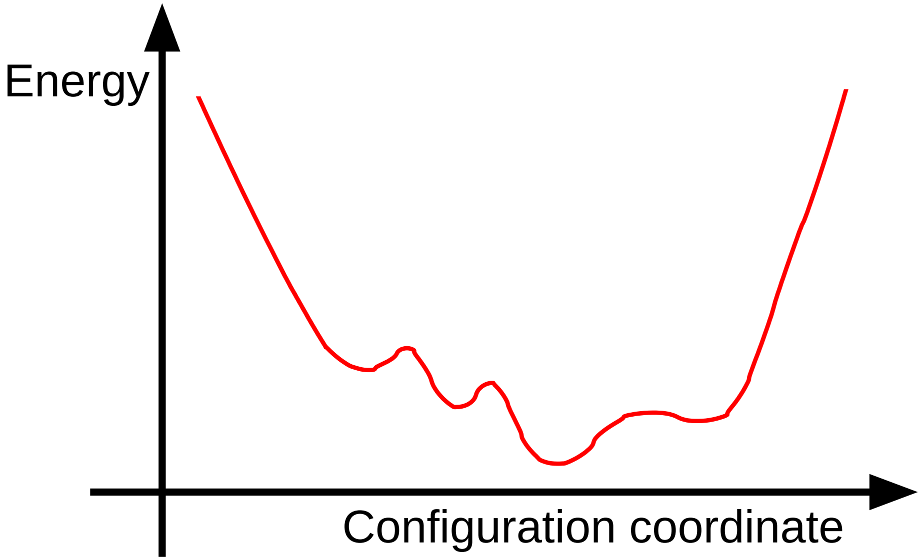
Random searching might work quite well for a small number of atoms

Is random searching useful for finding crystal structures?

Many known crystal structures have only a few atoms per primitive unit cell, so perhaps many of the unknown ones also do

Structures at high pressures tend to be simple and have a small number of atoms per primitive unit cell

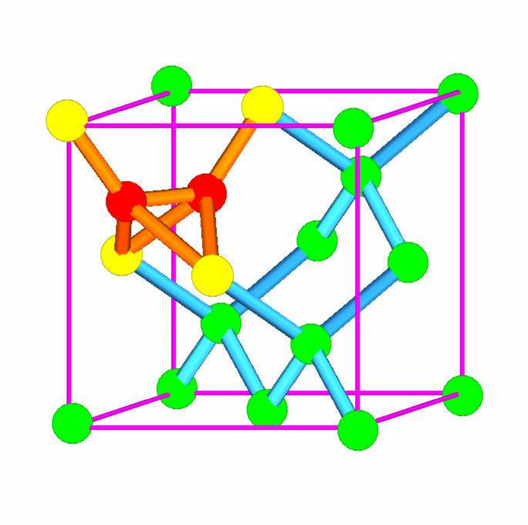
What does the potential energy surface look like?



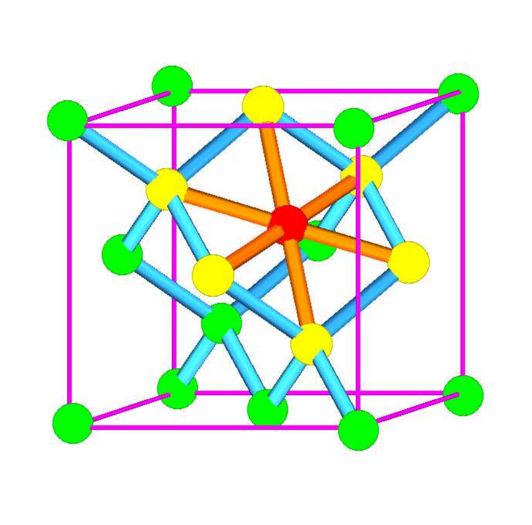
Note: almost no minima at high energies

Self-interstitial defects in silicon

(i) Start with 32-atom body-centred-cubic cell of silicon
(ii) Take out an atom and its four nearest neighbours
(iii) Put six atoms at random in a sphere of radius 1.5 bonds lengths centred on the first atom removed



split-$\langle 110 \rangle$ interstitial



hexagonal interstitial

All other self-interstitial energy minima at least 0.3 eV higher in energy

Performance of random searching algorithm

Tests

Silicon at zero pressure: 100 randomly chosen 2-atom cell configurations gave the diamond structure (15 times), β-tin (2 times), Imma (14 times), and simple hexagonal (15 times)

Carbon at 300 GPa: 8-atom cells gave the diamond structure and other phases including BC8

Hydrogen at 250 GPa: found, among others, the $Cmca$ "molecular" phase

A number of other applications... SECRET !

Comments

Results are not very sensitive to the details of how the "random" initial configurations are generated

Results can be sensitive to the accuracy of calculations

Have we found the global minimum?

Continue generating configurations until the low energy/enthalpy relaxed structures are generated several times

Look for the occurrence of previously-known "marker" structures

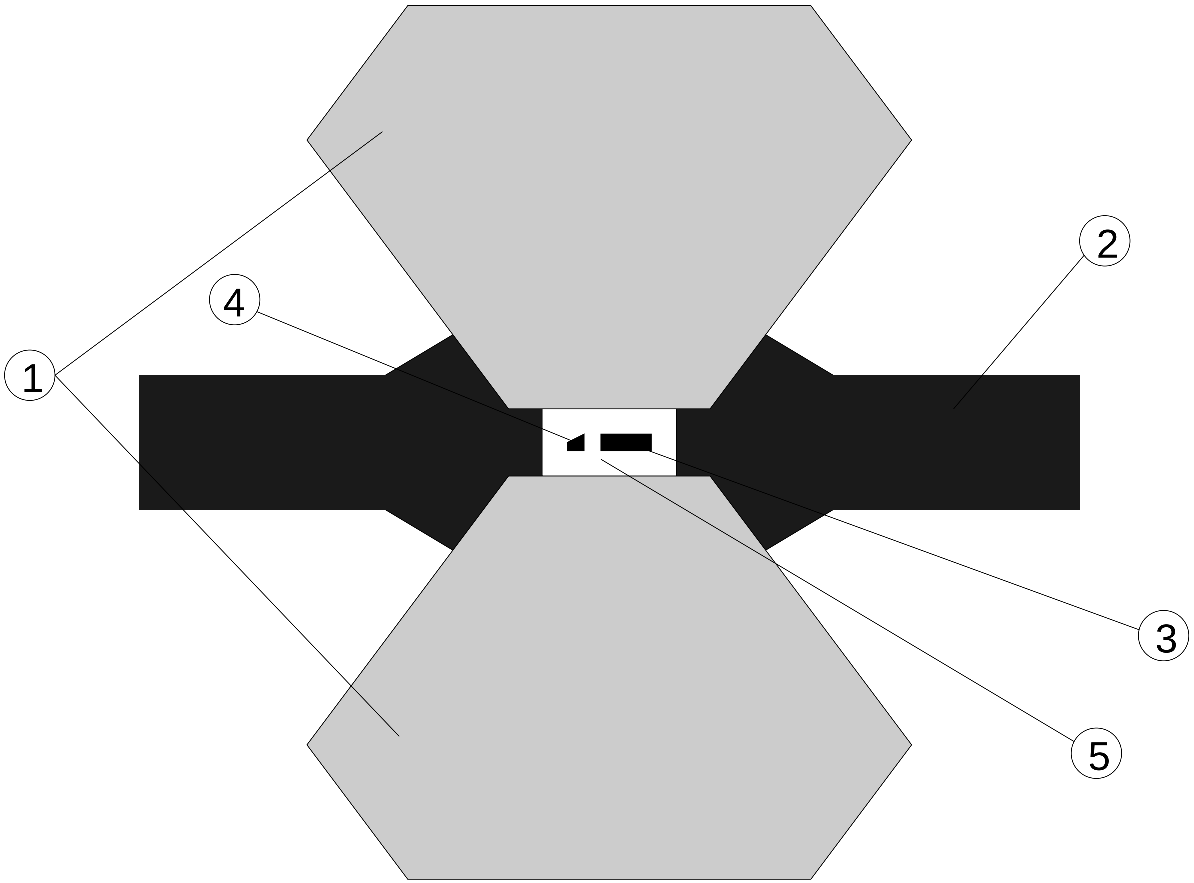
Other search strategies used with DFT

Intelligent design
Select initial configurations using experimental knowledge about the system, the known structures of similar materials, chemical intuition, and results from simpler computational methods

Genetic algorithms (solids)
Oganov and Glass, J Chem Phys 124, 244704 (2006)
Abraham and Probert, Phys Rev B 73, 224104 (2006)

Minimum/basin hopping (clusters)
Yoo and Zeng, Angewandte Chemie International Edition 44, 1491 (2005)
Goedecker, Hellmann, and Lenosky, Phys Rev Lett 95, 055501 (2005)

Diamond anvil cell



Schematic depiction of a DAC. 1: diamonds, 2: gasket, 3: sample, 4: reference material such as ruby, 5: pressurising medium

Metallic hydrogen in a terrestrial laboratory?

In 1935 Wigner and Huntingdon suggested that hydrogen would become metallic under sufficient compression

Attempts to produce metallic hydrogen in diamond-anvil-cells at pressures up to 342 GPa have not been successful

Pressure limit for DAC has probably been (nearly) reached

Ashcroft, Phys Rev Lett 92, 187002 (2004): Hydrogen in CH_4, SiH_4, GeH_4 is "chemically precompressed" and these hydrides might become metallic at pressures achievable in a DAC

Feng, Grochala, Jaron, Hoffmann, Bergara, and Ashcroft, Phys Rev Lett 96, 017006 (2006) predicted metallisation of SiH_4 at 91 GPa

Experiments on silane underway......

Searching for high-pressure phases of silane

Test runs: with 1, 2, 4, SiH_4 formula units per cell at 250 GPa

1 formula unit: no very low enthalpy phases; system is too constrained

2 formula units: low enthalpy structures generated several times

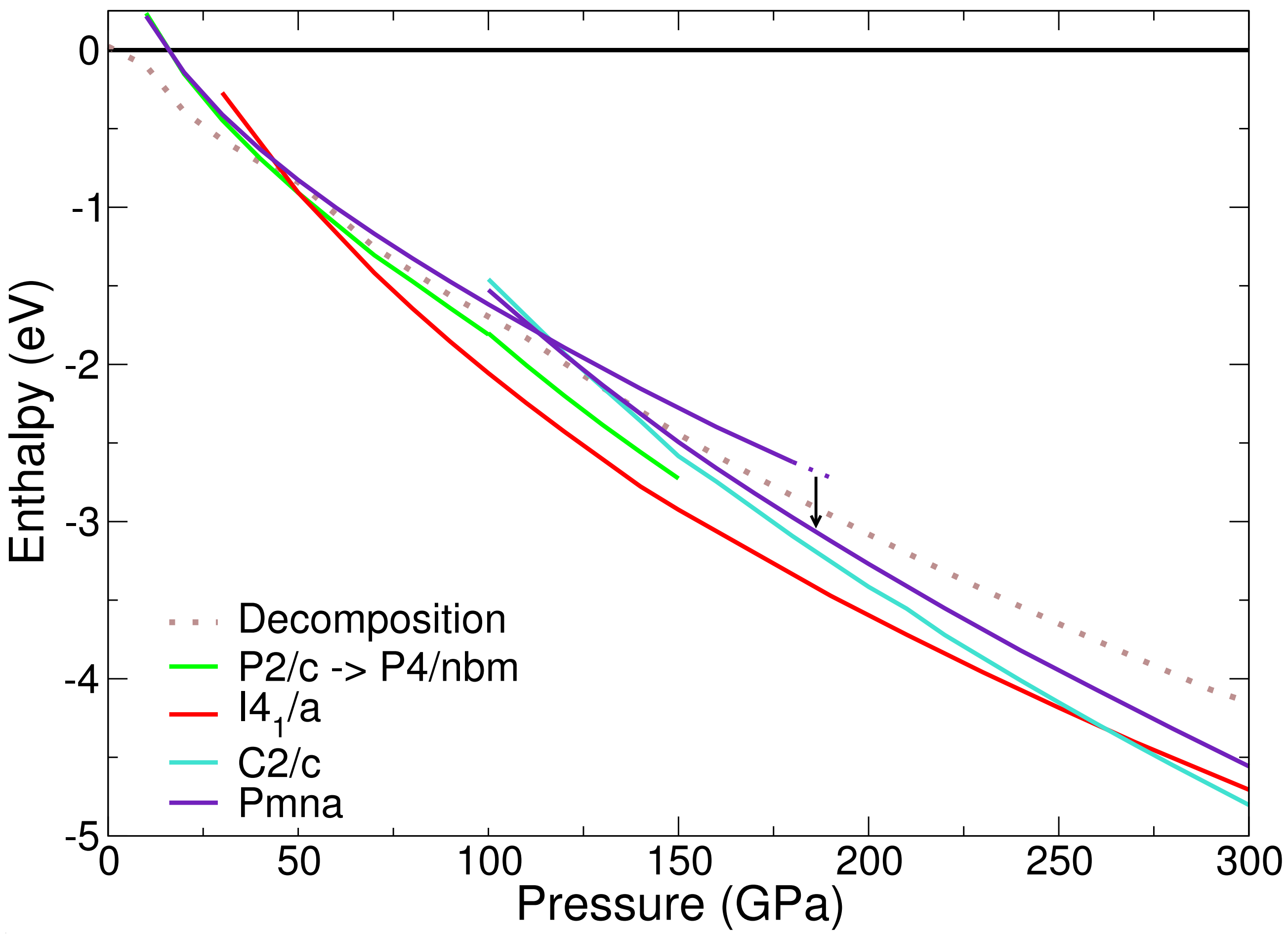
4 formula units: no very low enthalpy phases; system has too many degrees of freedom for search algorithm to be successful

Production runs:
2 formula units for runs at 0, 50, 100, 150, 200, and 250 GPa

Our structures have considerably lower enthalpies than those of Feng *et al.*

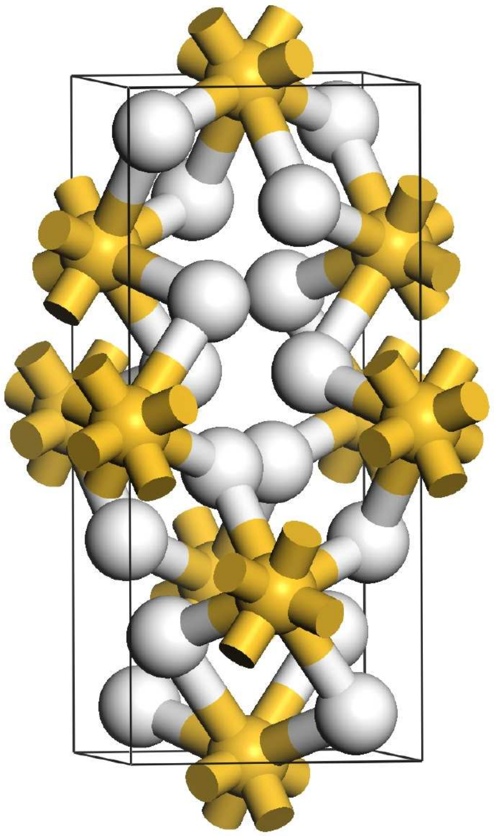
Have neglected zero-point motion of the nuclei, which could be important

Enthalpies versus pressure

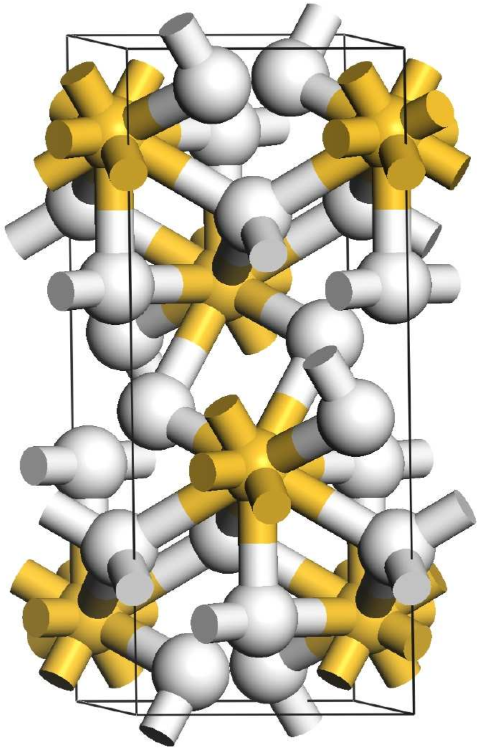


The enthalpies per SiH_4 unit of various structures as a function of pressure, referenced to the T1 phase of Feng *et al.*

The $I4_1/a$ and $C2/c$ structures



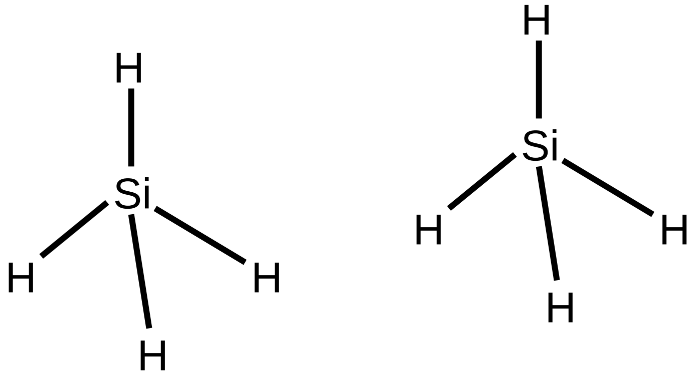
$I4_1/a$



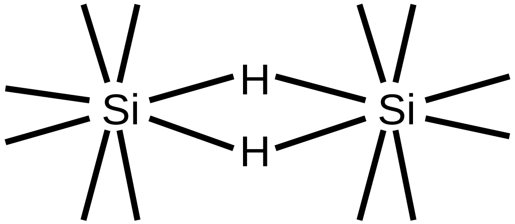
$C2/c$

Golden spheres: silicon atoms; white spheres hydrogen atoms
Note the Si_2H_2 planes made of electron-deficient three-centre-two-electron “banana bonds”, and the two, three and four-fold coordinated H atoms in the $C2/c$ structure

Why is $I4_1/a$ favoured at high pressures?



silane molecules

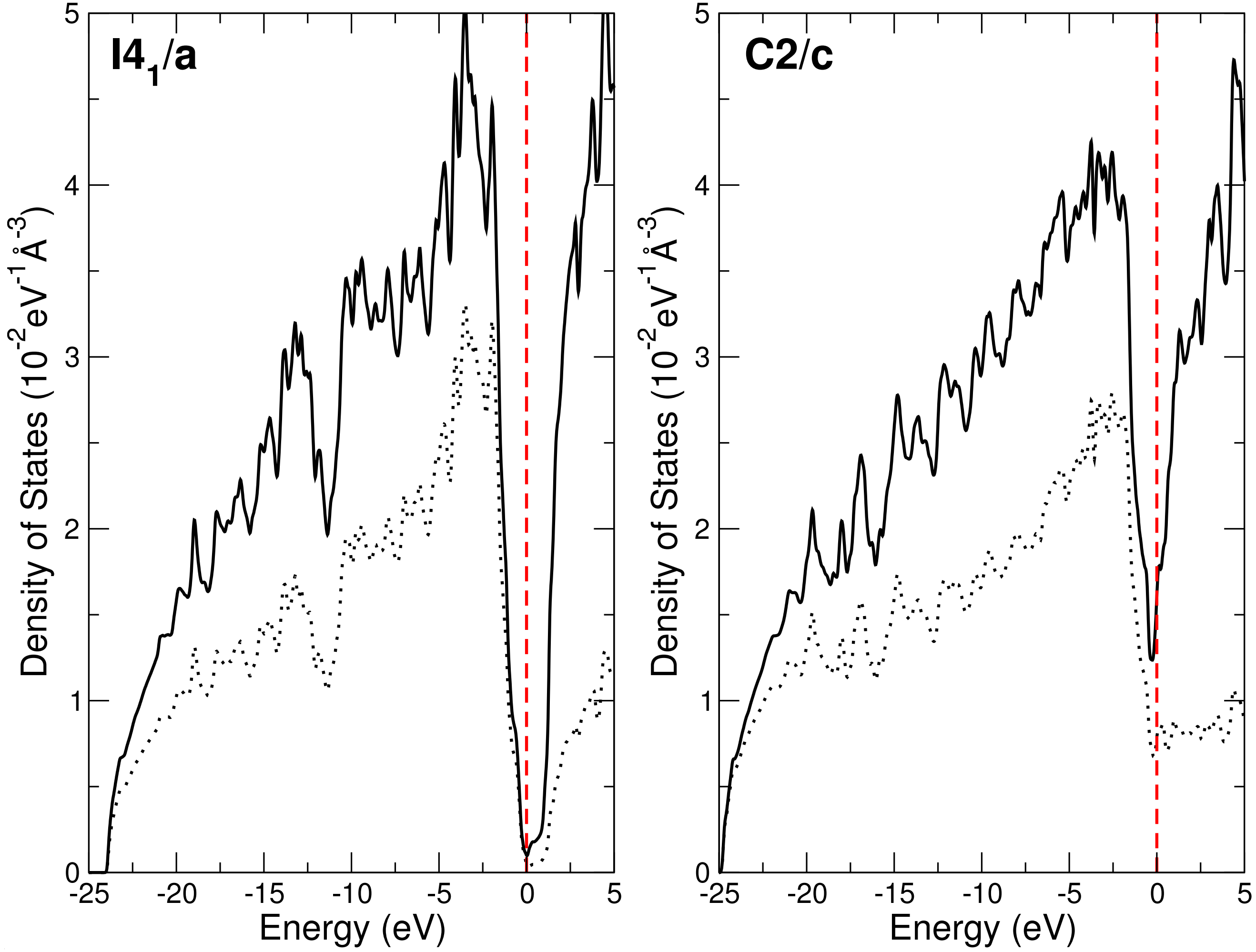


$I4_1/a$

Electron-deficient three-centre-two-electron “banana bonds” in $I4_1/a$ allow each Si atom to bond to 8 H atoms

This saves a lot of space!

Densities of states of the $I4_1/a$ and $C2/c$ phases



The densities of states of the $I4_1/a$ and $C2/c$ phases at their predicted coexistence pressure of 262.5 GPa. The partial density of states projected onto the H atoms is shown by dashed curves, and the Fermi energies are indicated by the vertical dashed lines.

Bardeen-Cooper-Schreiffer theory of superconductivity

Screening of the ionic motion can give a net attraction between electrons whose energies are close to the Fermi energy and whose separation in energy is less than a typical phonon energy

Leads to pairing of electrons and a BCS superconducting state

BCS formula for critical temperature, T_c:

$$k_B T_c = 1.13\,\hbar\omega_D\,e^{-1/(NV)}$$

ω = Debye frequency of phonons
N = density of states at the Fermi energy in normal state
V = effective electron-phonon interaction

Application of BCS theory to $C2/c$ silane at 262.5 GPa

Density of states at the Fermi energy has a large weight on the H atoms

Predict same density of states per unit volume at the Fermi energy as lead at zero pressure

If we assume the same effective electron-phonon interaction as lead at zero pressure then

$$T_c^{\mathrm{silane}} = T_c^{\mathrm{lead}} \frac{\omega_D^{\mathrm{silane}}}{\omega_D^{\mathrm{lead}}} = 7.2 \, \frac{2500}{62} = 290 \text{ K}$$

(Proper electron-phonon coupling calculations are underway at Berkeley)

Summary

- The "simplest possible" random searching algorithm is useful for finding crystal structures

- At high pressures, silane forms electron-deficient three-centre-two-electron "banana bonds"

- Silane is predicted to form a metallic $C2/c$ phase at 262.5 GPa, which is expected to be a high-temperature superconductor

- It would be interesting to use QMC to calculate the energies/enthalpies of structures obtained from DFT searches