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Exploring the structure of solids through magic strains: prediction of a new metallic phase of Si

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Abstract. A new approach that allows thorough exploration of low-energy structures with arbitrary symmetry for any material is presented, along with an application to silicon. This approach, coupled with first-principles total-energy calculations, has led us to discover a previously unknown metastable structure of Si. The physical properties of this structure and the insight they afford to metallic versus covalent bonding and the nature of the amorphous and liquid phases are discussed.

The structure of condensed phases of matter in terms of a regular (crystalline) or an irregular (amorphous or liquid) distribution of atoms is the cornerstone of our understanding of their electrical, chemical and mechanical properties. Despite the variety of composition in solids, the vast majority of stable crystal phases fall in a few, well established and widely studied categories, which have usually very high symmetry [1]. Among these, lattices with close packed sites are preferred by metals, whereas lattices with more open site distribution (diamond, cubic) are favoured by covalent or ionic materials (semiconductors and insulators). Structural changes in solids are induced either by increasing the temperature or the pressure. The resulting structures can be hard to identify or fundamentally different from the original equilibrium structure (as in the case of melting).

From the theoretical standpoint, first-principles calculations based on the local density approximation to density functional theory [2] (LDF for short) provide an accurate and reliable framework for comparing total energies of crystal structures [3]. Based on such energy (or enthalpy) comparisons, the thermodynamic stability of different phases as a function of volume (or pressure) can be assessed [4]. In this sense, theory can make predictions about crystal structure as a function of pressure. These predictions have been limited, however, to comparisons between the few well established crystal structures of high symmetry, or structures suggested directly by experiment. Temperature effects are much harder to describe from first-principles calculations, which are limited to simulation of relatively small systems and involve very large computational effort [5]. Empirical laws for atom–atom interactions have been developed to simulate the finite-temperature behaviour of very large systems [6].

One method of obtaining information on the structure of complicated phases without resorting to large scale simulations, is to identify all the *local* atomic

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configurations that are relevant. The relevance of a configuration is determined by its energy and its physical properties (equilibrium volume, nature of bonding, coordination, electronic states, etc). Here we discuss a method that allows one to describe and compare the energetically relevant crystal structures of arbitrary symmetry for any material. Using this method in conjunction with LDF total-energy calculations it is possible to identify, *strictly* from first-principles theoretical analysis, stable and metastable phases, as well as the pathways in configuration-space that connect them. Indeed, following this approach, we have recently identified a previously unknown metastable structure for one of the most widely studied materials, namely silicon [7]. This approach also makes feasible thorough searches for structures that may be relevant to the liquid and amorphous phases.

The exploration of the relevant crystal structures of a given material is based on the concept of magic strains [8]. These are lattice distortions that bring the crystal back to itself by 'scrambling' the atoms in the solid in many different ways. They are defined to be symmetric tensors, i.e. the distortion has no rotational component and thus could be produced by a torque-free stress. Take for example a lattice defined by the matrix $\mathbf{A}$, with each column representing the Cartesian coordinates of a primitive lattice vector. Suppose that this lattice is transformed through a strain tensor $\mathbf{S}$ so that $\mathbf{B} = \mathbf{SA}$. The matrix $\mathbf{B}$ defines the same Bravais lattice as $\mathbf{A}$, but the two matrices are distinguished by the choice of primitive vectors. A symmetric strain matrix $\mathbf{S}_\mathrm{m}$ is built by taking the square root of the product $\mathbf{S}^\mathrm{T}\mathbf{S}$, which involves putting $\mathbf{S}^\mathrm{T}\mathbf{S}$ in diagonal form through multiplication by the matrix of its eigenvectors ($\mathbf{U}$), followed by a transformation back to the original basis: $\mathbf{S}_\mathrm{m} = \mathbf{U}[\mathbf{U}^\mathrm{T}\mathbf{S}^\mathrm{T}\mathbf{S}\mathbf{U}]^{1/2}\mathbf{U}^\mathrm{T}$. The transformed lattice can be put in the same orientation as the original one by a rotation $R = \mathbf{S}_\mathrm{m}\mathbf{S}^{-1}$. Notice that $\mathbf{S}_\mathrm{m}$ is determined by the choice of $\mathbf{A}$ and $\mathbf{B}$ since $\mathbf{S} = \mathbf{BA}^{-1}$. Several combinations of $\mathbf{A}$ and $\mathbf{B}$ give equivalent $\mathbf{S}_\mathrm{m}$s (equivalence of two magic strain matrices means that their eigenvalues are identical). To illustrate these points, consider a 2D hexagonal lattice defined by

$$\mathbf{A} = \begin{pmatrix} 1 & \frac{1}{2} \\ 0 & \frac{\sqrt{3}}{2} \end{pmatrix}$$

which is transformed to the hexagonal lattice

$$\mathbf{B} = \begin{pmatrix} 1 & -\frac{1}{2} \\ 0 & \frac{\sqrt{3}}{2} \end{pmatrix}$$

through the magic strain

$$\mathbf{S}_\mathrm{m} = \begin{pmatrix} \frac{\sqrt{3}}{2} & -\frac{1}{2} \\ -\frac{1}{2} & \frac{5}{2\sqrt{3}} \end{pmatrix}$$

with eigenvalues $s_1 = \sqrt{3}$ and $s_2 = 1/\sqrt{3}$. There are three equivalent magic strains of this type, the other two arising from the transformation of $\mathbf{A}$ into the matrices

$$\mathbf{B}' = \begin{pmatrix} 1 & \frac{3}{2} \\ 0 & \frac{\sqrt{3}}{2} \end{pmatrix}$$

and

$$\mathbf{B}'' = \begin{pmatrix} \frac{3}{2} & 1 \\ \frac{\sqrt{3}}{2} & 0 \end{pmatrix}.$$

The idea of exploring the possible low-energy distortions of a lattice is now straightforward. One needs to identify the magic strains through pairs of matrices **A** and **B** that define the stable lattice. A parametrized equation can then be written, that brings the crystal back to itself through gradual application of the magic strain. The intermediate lattices obtained through the gradual transformation are given by the matrix

$$\mathbf{C}(\lambda) = [(1-\lambda)\mathbf{I} + \lambda \mathbf{S}_{\mathrm{m}}]\mathbf{A} \tag{1}$$

(where **I** is the identity matrix), with λ ranging from 0 to 1. In the example considered here, $\lambda = \frac{1}{2}$ corresponds to a square lattice, whereas $\lambda = 0$ and 1, both give a 2D hexagonal lattice (the matrices **A** and **B** defined above). The two hexagonal lattices, however, involve a non-trivial rearrangement of the relative positions of the sites. This is shown in figure 1, where the three sublattices of the original hexagonal lattice are coloured black, white and cross. The three sublattices are interpenetrating (every site is surrounded by three neighbours of each of the other two colours) in the original lattice (figure 1(*a*)). The neighbours have been 'scrambled' in the final hexagonal lattice (figure 1(*c*)). Now consider that the sites in the above example represent atoms interacting through some potential that gives the hexagonal lattice as the ground state. It is plausible that there exist other metastable structures of low energy. These structures could be 'hidden', in the sense that non-trivial transformations may be needed to reach them. The concept of magic strains would allow a thorough search for such possibilities. Indeed, it is possible to construct potentials that have the 2D hexagonal lattice as the ground state and the square lattice (figure 1(*b*)) as a 'hidden' metastable structure.

The method outlined above can be very powerful in uncovering unknown low-energy structures in real materials. By exploring the configuration-space generated from magic strains, we have found a new structure for Si [7] which is quite unusual. As will be evident from the discussion below, this structure could not have been surmised by heuristic arguments based on the known tendency of Si atoms to form tetrahedral covalent bonds. Furthermore, its properties reveal interesting aspects of bonding in Si which may be relevant to the liquid and amorphous phases. We describe briefly how the structure was obtained. It derives from parametric application of the magic strain that connects two equivalent definitions **D** and **E** of the FCC lattice

$$\mathbf{D} = \begin{pmatrix} 1 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 1 \end{pmatrix}$$

$$\mathbf{E} = \begin{pmatrix} 1 & 1 & -1 \\ 1 & 0 & 0 \\ 0 & 1 & 1 \end{pmatrix}$$

The magic strain was parametrized by first transforming to the coordinate system that diagonalizes $\mathbf{S}_{\mathrm{m}}$, and in this coordinate frame, expressing the diagonal elements of the strain (s) in a volume conserving form

$$s_{11} = (1+f)^{-1/3}(1+g)^{2/3}$$
$$s_{22} = (1+g)^{-1/3}(1+f)^{2/3}$$
$$s_{33} = (1+f)^{-1/3}(1+g)^{-1/3}.$$

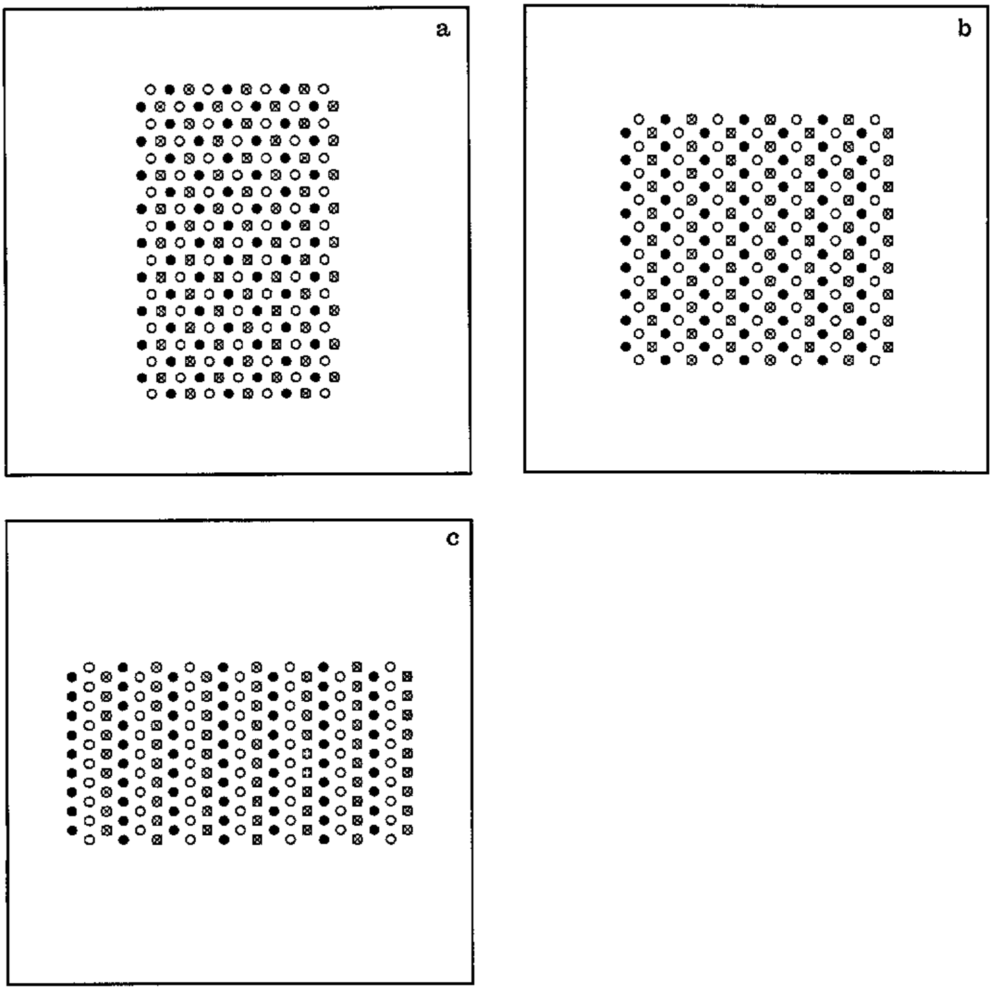


Figure 1. 2D example of a magic strain transformation: (*a*) initial hexagonal lattice, with the three interpenetrating sublattices coloured black, white and cross; (*b*) the square lattice, at the midpoint of the magic strain transformation ($\lambda = \frac{1}{2}$ in equation (1)); and (*c*) the final hexagonal lattice ($\lambda = 1$), with the sites 'scrambled'.

For $f_m = -0.4398$ and $g_m = 0.7580$ the above expressions give the eigenvalues of $\mathbf{S}_m$. Stepping f and g from 0 to their magic values f_m, g_m, and allowing the remaining structure parameters to relax gives a minimum energy path. For convenience, the remaining structure parameters can be limited to the volume and the relative position of the two atoms in the unit cell. By allowing just three parameters (f, g and the volume) to describe a strain path from **D** to **E**, we have restricted the region of strain space to be explored. Calculations using this parametrization scheme were sufficient to establish the existence of a metastable structure of silicon. A more complete optimization was performed, which included off-diagonal elements of the strain tensor s to determine the precise metastable structure [9].

In the new structure for Si identified in this way all atoms are five-fold coordinated

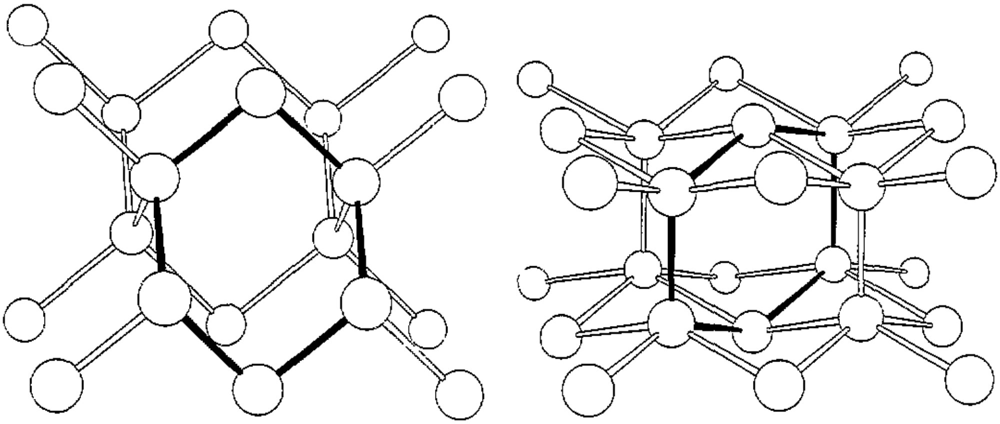


Figure 2. The diamond (left) and BCT5 (right) structures. Six-fold rings are highlighted.

in a body-centered tetragonal lattice (space group $I4mmm$). This structure (named BCT5) is not a familiar one for Si, which under normal conditions forms predominantly tetrahedrally coordinated structures. Figure 2 gives perspective views of the diamond lattice (the ground state of Si under normal conditions) and the BCT5 structure. In diamond, atoms form the familiar six-fold rings, which are not planar. In BCT5, atoms form six-fold rings which lie exactly on the (110) planes of the BCT lattice. In addition, there are four-fold rings in BCT5, which lie almost on the (001) plane. The unusual coordination of atoms in BCT5 prompted us to calculate its elastic constants, and thus determine its stability. The stability conditions are

$$\begin{array}{lll} C_{11} > 0 & C_{33} > 0 & C_{44} > 0 \\ C_{66} > 0 & C_{11} - C_{12} > 0 & C_{33}(C_{11} + C_{12}) - 2C_{13}^2 > 0. \end{array}$$

The calculated values of the elastic constants (in Mbar) of BCT5 are

$$\begin{array}{lll} C_{11} = 1.44 & C_{33} = 1.60 & C_{44} = 0.35 \\ C_{66} = 0.63 & C_{12} = 1.24 & C_{13} = 0.45 \end{array}$$

which satisfy all of the stability conditions.

Although several structures of Si have been identified at higher pressure [10, 11], to our knowledge, a structure similar to BCT5 has not yet been observed. We consider here the conditions under which this might be possible. The calculated total energy of the diamond and BCT5 structures as a function of volume are shown in figure 3. This figure also includes the energy versus volume curve for the β-tin structure, which is known to be the stable structure of Si above 11 GPa [11]. This structure can be obtained by compressing the diamond lattice along a (100) crystallographic direction while expanding in the orthogonal directions. Theoretical estimates for the pressure at which the transition from the diamond to the β-tin structure takes place, range from 7.0–9.9 GPa [12, 4] (our calculations give 8.3 GPa). This pressure is determined by the common tangent construction (see figure 3). For the diamond–BCT5 transition pressure, we calculate a value of 12.6 GPa. Theoretical values typically underestimate

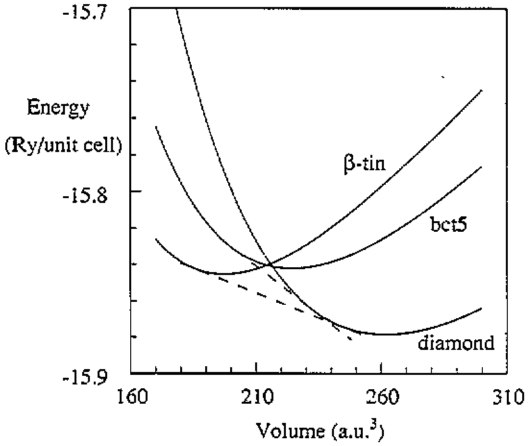


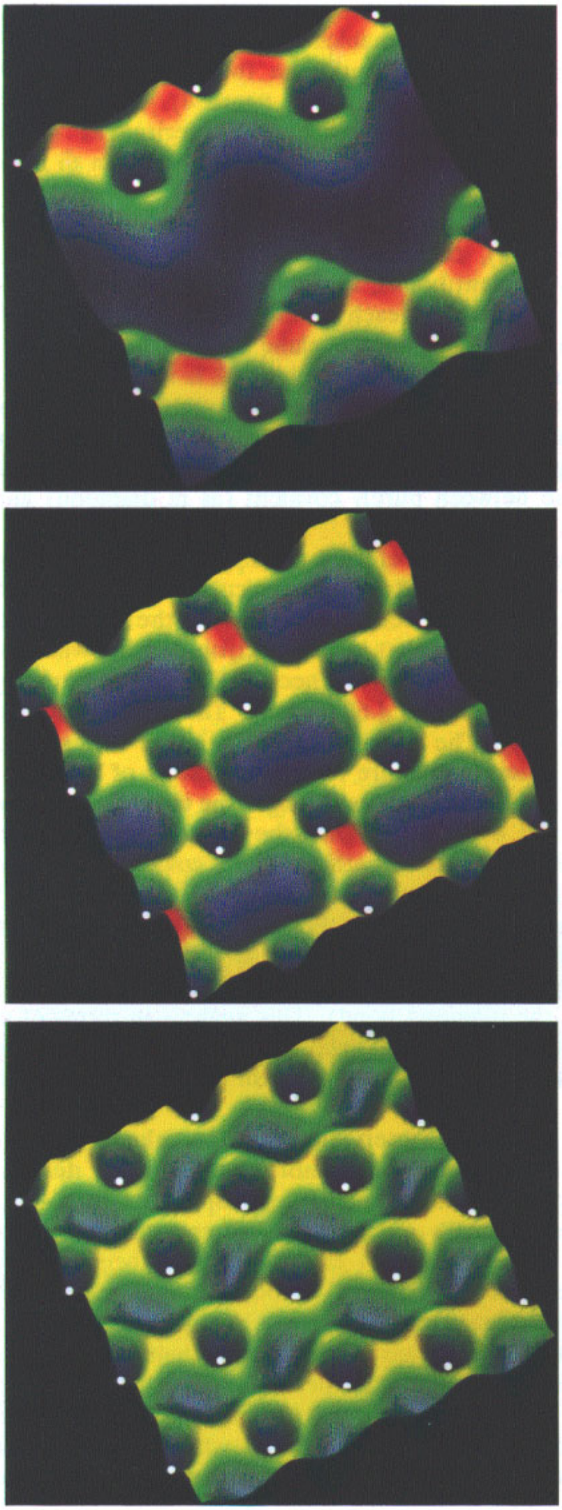
Figure 3. Total energy versus volume for the three structures of Si. Common tangent constructions give the transition pressures.

the transition pressure due to neglect of thermal effects. From the comparison of figure 3, and the fact that the equilibrium volume of BCT5 ($V_{\mathrm{BCT5}}/V_{\mathrm{diamond}} = 0.85$) is larger than the equilibrium volume of β-tin ($V_{\beta\text{-tin}}/V_{\mathrm{diamond}} = 0.75$) we conclude that BCT5 could be obtained under uniaxial stress in a crystallographic direction determined by the eigenvectors of the magic strain matrix. Shock experiments may be the most promising way of inducing such uniaxial stress.

Even if BCT5 proves elusive in its pure crystalline form, its low energy and stability argue that it may be encountered as a local structure in other bulk phases. Thus, it is of interest to explore the physical properties of this metastable phase of Si. BCT5 can be viewed as an intermediate phase between the ground state (diamond lattice) and the high-pressure phase (β-tin lattice) of Si. This analogy is meaningful in several ways. The simplest comparison could be made in terms of coordination, which goes from 4 in diamond to 5 in BCT5 to 6 in β-tin (this is the conventional coordination assignment for β-tin, which will be examined critically below).

Another comparison is in terms of the electronic states in the three phases. Both the BCT5 and the β-tin structures have significant density of states at the Fermi level E_F (they are metallic phases), whereas the diamond structure has zero density of states at E_F (semiconducting phase). To gain insight on the nature of bonds, we display on a colour-coded topographic plot the valence electron density obtained from our LDF calculations. The charge density plots for the three structures (diamond, β-tin and BCT5) are shown in figure 4 on (110) planes. The scale of the electron density plots in figure 4 is exactly the same for the three structures, so visual comparison of

Figure 4. *Opposite.* Calculated valence electron charge density plots for the three structures of Si (top, diamond; middle, BCT5; bottom, β-tin). The colour scale reflects charge concentration (red = highest) and is the same for the three cases. The white dots represent atomic positions. The elimination of core electrons through the use of pseudopotentials results in a local minimum of the electron density (zero valence charge) at the positions of the ions.



the colour gives direct information about the electronic charge concentration. The use of a consistent colour scheme enables us to classify bonds in different categories. We shall refer to the charge distribution in the diamond structure as the typical 'covalent' bond (containing red regions, see figure 4). Distributions with somewhat lower charge density (up to yellow) will be characterized as 'metallic' bonds. Still lower density (blue to green) between two sites will be taken to indicate the absence of an interatomic bond.

In the diamond lattice, where each atom has four bonds (two of which are visible on the plane of figure 4), there are regions of very high electron density (red) corresponding to the covalent bonds, as well as regions where the electron density is zero (black). In the BCT5 lattice, each atom has one covalent bond and four other bonds (two of which are visible on the plane of figure 4) of more metallic nature (yellow). The six-atom ring highlighted in figure 2 is seen to consist of two covalent and four metallic bonds. The regions of zero charge density have been significantly reduced in BCT5. Finally, in the β-tin structure, there are no covalent bonds and the regions of zero charge density are entirely absent. The BCT5 structure is seen to be an intermediate phase between purely covalent (as in diamond) and predominantly metallic (as in β-tin) bonding.

The β-tin structure is usually referred to as a six-fold coordinated structure, with each atom having four short bonds (in our calculations they are 4.68 au long) and two longer bonds (4.98 au). As seen from figure 4, the short bonds correspond to a local flat maximum (yellow peaks) in the electron density, whereas the long bonds have much lower electron density (green necks). The two different types of bonds in the BCT5 structure are 4.37 au and 4.60 au long. The covalent bonds in the diamond structure are 4.44 au long. The short bonds in β-tin are very similar to the metallic bonds of BCT5. The emerging picture for the character of bonds is as follows. For distances within 2% of the diamond bond-length the covalent character of the bond is preserved. For distances 4–6% larger than the diamond bond-length (approximately 4.6–4.7 au) there is less charge density than in pure covalent bonds, but these can still be considered as well-defined bonds in the sense that there is a pile up of electronic charge between adjacent atomic sites. For distances larger than about 6% of the diamond bond-length, the charge distribution is relatively low and the term 'bond' may no longer be appropriate (as in the case of the long 'bonds' in β-tin, which are 12% longer than the diamond bond). This analysis in terms of coordination and bond-length, however, is incomplete since the *topology* of bonding is not taken into account. In particular, both in BCT5 and in β-tin the metallic bonds are very close to planar.

We discuss next how these observations can be related to features of bonding and charge distribution in liquid and amorphous Si. The density of liquid Si is *higher* than that of the diamond structure corresponding to a ~ 10% decrease in volume [13]. The experimentally reported average coordination is ~ 6.4 [14]. Finally, liquid Si is metallic [13]. The most extensive first-principles molecular dynamics simulations of the structure of liquid Si (modelled by a periodically repeated unit of 64 atoms) have been performed by Stich, Car and Parrinello [5]. These authors found that the statistically averaged local order in their simulation exhibits features which are in excellent agreement with experiment (e.g., average coordination 6.5) [5]. Here we attempt to elucidate some details of the predominant local configurations by analysing structures such as BCT5 and β-tin which exhibit metallic-like bonding and have a lower equilibrium volume than diamond Si. From these structures it appears that a planar arrangement of nearest-neighbours is preferred when metallic bonding is prevalent. Interestingly, the metallic bonds in BCT5 and β-tin are 4.60 and 4.68 au long, both very close to the position of the first peak in the radial distribution function of the liquid (4.65 au) [5]. A configuration with coordination higher than five can be obtained by introducing additional atoms in the open spaces of the BCT5 structure (centres of hexagons) and allowing for some volume expansion in the (001) direction. The expansion would eliminate the bonds with covalent character in the BCT5 structure. Depending on the position of the extra atoms, this arrangement can lead to coordinations of up to eight.

For comparison, simulations based on an empirical potential that favours tetrahedral bonding (proposed by Stillinger and Weber (SW) [6]), also found high coordination (eight) in the liquid. SW report that by quenching the structure of the liquid periodically to the nearest potential-energy minimum, the coordination of atoms becomes four [6]. A more recent simulation using the SW potential [15] found that in the liquid there are more five-fold coordinated atoms than either four- or six-fold coordinated ones. We have calculated the relative energy of BCT5 and β-tin and found that the SW potential favours significantly the former (in our LDF calculations the two structures have almost equal energy, see figure 3). Thus, the predominance of five-fold coordination in the liquid structure of [15] and the four-fold coordination in the quenched structures of [6] are probably related to the properties of the SW potential. Five-fold coordination seems to be quite common in SW simulations of amorphous and glassy structures also [15]. In fact, the distribution of bond-angles around five-fold coordinated atoms in those structures is remarkably close to the bond-angles in the SW BCT5-structure (four 82.6°, four 109.3° and two 138° angles). Our first-principles results indicate that such geometries with a planar arrangement of bonds should be significant in *metallic* phases of Si. The pronounced peak in the bond-angle distribution at 90° found in the first-principles simulation of the liquid [5], also argues in favour of planar bond arrangements.

References

[1] See, e.g.,
Wyckoff R W G 1973 *Crystal Structures* (New York: Wiley)
[2] Kohn W and Sham L J 1965 *Phys. Rev.* **140** A1133
[3] For a recent review see
Pickett W E 1989 *Comput. Phys. Rep.* **9** 117
[4] Yin M T and Cohen M L 1982 *Phys. Rev.* B **26** 5668
[5] Stich I, Car R and Parrinello M 1989 *Phys. Rev. Lett.* **63** 2240; 1991 *Phys. Rev.* B **44** 4262
[6] Stillinger F H and Weber T A 1985 *Phys. Rev.* B **31** 5262
[7] Boyer L L, Kaxiras E, Feldman J L, Broughton J Q and Mehl M J 1991 *Phys. Rev. Lett.* **67** 715
[8] Boyer L L 1989 *Acta Crystallogr.* A **45** FC29
Van de Waal B W 1990 *Acta Crystallogr.* A **46** FC17
[9] For the LDF total-energy calculations we use the local-density parametrization of the exchange–correlation potential proposed by J Perdew and A Zunger (1984 *Phys. Rev.* B **23** 5048), a basis of plane waves including plane waves with kinetic energy up to 16 Ryd, and Brillouin zone summations involving sets of 512 to 1728 k-points in the full zone (these fold to different irreducible sets in the three structures considered, depending on the symmetry of the lattice). Atomic pseudopotentials from G B Bachelet *et al* (1982 *Phys. Rev.* B **26** 4199) were used to eliminate the core electrons.
[10] Olijnyk H, Sikka S K and Holzapfel W B 1984 *Phys. Lett.* **103A** 137
[11] Hu J Z, Merkle L D, Menoni C S and Spain I L 1986 *Phys. Rev.* B **34** 4679
[12] Needs R J and Martin R M 1984 *Phys. Rev.* B **30** 5390

[13] Glazov V M, Chizhevskaya S N and Glagoleva N N 1969 *Liquid Semiconductors* (New York: Plenum) ch 3
[14] Waseda Y and Suzuki K 1975 *Z. Phys.* B **20** 339
Gabathuler J P and Steeb S 1979 *Z. Naturf.* a **34** 1314
Davidovic M, Stojic M and Jovic Dj 1983 *J. Phys. C: Solid State Phys.* **16** 2053
[15] Luedtke W D and Landman U 1989 *Phys. Rev.* B **40** 1164.