

Pressure-induced symmetry breaking in tetrahedral networks

G. J. Ackland

*Department of Physics, The University of Edinburgh,
Mayfield Road, Edinburgh, EH9 3JZ, Scotland*

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Recent experiment and theoretical studies appear to show a great deal of complexity in the high-pressure behavior of tetrahedral semiconductors. We show that the structural stability of silicon and the order of its phase transitions is identical to that of a tetrahedrally coordinated network of rigid rods with spring-loaded joints. We further show how this parameter-free model resolves the recent controversy regarding the first high-pressure phase in silicon.

Recent refinements in high-pressure crystallography have revolutionized the field of high-pressure phases of tetrahedral semiconductors. Until recently, all these materials appeared to fit a simple scheme with the zincblende or wurtzite low pressure phase transforming to either β -Sn or NaCl structures at the metallization transition. A tidy phenomenological theory explained these two structures in terms of ionicity and bond length,¹ and *ab initio* electronic structure calculations confirmed the high-pressure instability of the diamond phases.² A second phase transition, to the simple hexagonal phase, was also reported in Si,^{3,4} and its stability again demonstrated by electronic structure calculation.⁶ Similar hexagonal phases have been reported in GaAs and InSb.⁵

The discovery of orthorhombic distortion in the III-V compounds⁷ was initially associated with their lying in a region of intermediate ionicity between β -Sn and NaCl regimes, the structure being intermediate between the two. However, the orthorhombic phase in InSb and GaAs is actually *Imm2*,⁷ an intermediate between β -Sn and simple hexagonal. Soon after these experimental results appeared, electronic structure calculations demonstrated the instability of β -Sn with respect to *Imm2* in InSb.⁸

The most recent, and remarkable, report⁹ is that the first high-pressure phase silicon itself, the archetypal pressure-induced metallization, may have been misinterpreted. Careful x-ray crystallography using imaging plates and synchrotron radiation showed that for most of its range of existence the β -Sn phase of silicon was in fact unstable with respect to an orthorhombic distortion to *Imma* (the monatomic analogue of *Imm2*). Once again, electronic structure calculations on the *Imma* phase confirmed this instability, although at the low end of the pressure range the energy difference was within the computational uncertainty.¹⁰

It thus appears that the complex behavior of even the simplest of covalent materials is at the limit of both experimental and computational feasibility. There may seem to be no reason why still more complexity should not lie undetected awaiting further improvements in resolution or computation.

In this paper it is shown that far from being complex,

the observed behavior can be understood by a simple consideration of the bonding nature of the materials: the various phases observed in silicon are isomorphic to those found for a simple network model of rods and springs.

The network in question is one in which atoms are represented by hard spheres, each connected to four other atoms by rigid rods. These rods have the same length as the hard sphere diameter and interact with each other by means of torsional springs. In constructing the *PVT* phase diagram for this model there are no free parameters, the "pressure" being given in reduced units of the spring constant and bondlength and the "temperature" expressed as the energy barrier appropriate to the Landau-type W-shaped well.¹¹ The topological connectivity of the network remains fixed throughout, although the effect of relaxing this condition for sixfold-coordinated structures is discussed.

To obtain analytic expressions for enthalpy it is necessary to assign a suitable functional form to the energy of the springs. Since they represent bond-bending of covalent bonds and the distortions away from tetrahedral will be large, a simple spring constant is not ideal. From a tight binding analysis¹² it has been shown that¹³ the natural minimum of a three body sp^3 term is in the range $115^\circ - 118^\circ$, and hence for the spring energy a trigonometric expansion about $\theta_m = 116^\circ$: $U \propto (\cos \theta - \cos \theta_m)^2$ is appropriate. This form gives the relation between geometry and energy a simple analytic form, and it turns out that similar stability behavior is obtained with other reasonable choices. Use of the covalent approximation and sp^3 term implies that the current model will be inapplicable to atomic structures with greater than fourfold coordination. Remarkably, the symmetry predictions of the rigid rod model mimic those of real systems well beyond this regime. There is some support for the extension of the idea of covalent bonding from the significant bond charges observed in *ab initio* calculations of β -Sn and simple cubic phases¹⁴.

The connectivity of the network is determined with respect to the diatomic *Imma* cell, since it is the maximal subgroup linking diamond, β -Sn, and simple hexagonal, and allows a unique fourfold bonding topology. This enables us to go by continuous distortion of the network

from diamond to β -Sn to $Imma$ to simple hexagonal without stretching or breaking any of the bonds. The general $Imma$ structure is determined by four parameters, three lattice constants a , b , and c and one internal parameter u .⁹ β -Sn is a special case of this with $u = \frac{1}{4}$ and $a = b$; diamond further requires $c/a = \sqrt{2}$. Simple hexagonal is also a special case with $u = 0$ and $b/c = \sqrt{3}$. By varying the angle between a and b axes it is further possible to go to face-centered cubic, while by considering a cell doubling it is possible to form hexagonal close packing. The simple cubic structure can also be obtained in this topology ($u = 1/2$, $c = a = \sqrt{2}$, $b = 2$) although two neighbors are not connected by rods.

Modeling bonds by rigid rods may appear to be a gross oversimplification. However, the experimental data show that the bond length remains roughly constant as a function of pressure, when compared with the other relevant length scale, the cube root of the atomic volume. Assuming constant bond length moreover introduces two constraints into the $Imma$ -free parameters:

$$x^2 = \frac{1}{4}a^2 + u^2c^2 = \frac{1}{4}b^2 + \left(\frac{1}{2} - u\right)^2 c^2. \quad (1)$$

In conjunction with the constraints introduced by symmetry, the diamond structure is completely defined, the β -Sn structure has one free parameter (c/a), $Imma$ has two [for example, $y = (c/x)$ and u] and simple hexagonal is also completely defined.

The PV equation of state for this model can thus be written in terms of two structural parameters and a pressure. The enthalpy is then given as $H = E + PV$ where, solving for the angles,

$$V = abc/4, \quad (2)$$

$$E = [(1 - 2u^2y^2) + \cos \theta_m]^2 + \left\{ 2 \left[1 - \left(\frac{1}{2} - u\right)^2 y^2 \right] - 1 + \cos \theta_m \right\}^2 + 4 \left[u \left(\frac{1}{2} - u\right) y^2 + \cos \theta_m \right]^2, \quad (3)$$

and

$$y = c/x. \quad (4)$$

The stable phase at a given pressure is then given by minimizing H with respect to the two dimensionless structural parameters u and y . The zero temperature stability of each phase is thus a balance between the E and PV terms, and with pressure being measured in "natural" units of spring constant and bond length, there are no fittable parameters. For simplicity, each phase is examined in turn. The possibility of a symmetry-enhancing phase transition at high temperature will be treated subsequently by Landau theory.

The stability of diamond with respect to β -Sn is illustrated in Fig. 1. Diamond becomes *metastable* at pressure 1.48, and the transformation to β -Sn is therefore first order, accompanied by a large volume collapse. A similar plot for the stability of β -Sn with respect to simple hexagonal via $Imma$ distortion has a single minimum.

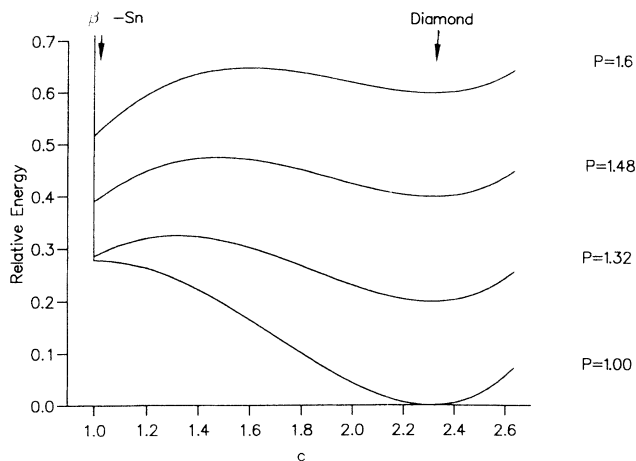


FIG. 1. Graph showing the dependence of enthalpy on c for the β -Sn symmetry, at several different pressures. Diamond is the special case where $c = 4/\sqrt{3}$. The enthalpy zero is taken as the enthalpy of the diamond structure, with each graph displaced upward by 0.2 for clarity. The vertical line at $c=1$ arises from contact between the hard spheres. The phase transition occurs at about $P=1.48$. The double minimum in the graph shows that the transition is first order.

At zero temperature, and above the diamond transition pressure, the β -Sn structure is unstable at *all* pressures with respect to $Imma$. Figure 2 shows the stable value of u at zero temperature which is generally neither $\frac{1}{4}$ nor 0, but an intermediate value which reduces to 0 (simple hexagonal phase) at high pressure and increases to $\frac{1}{4}$ at low pressure (below 1.48), so before β -Sn becomes stable with respect to $Imma$, it has become metastable with respect to diamond. Diamond itself is stable with respect to variation in u , and it is only after the barrier to the first order transition to β -Sn has been overcome that the distortion of u occurs.

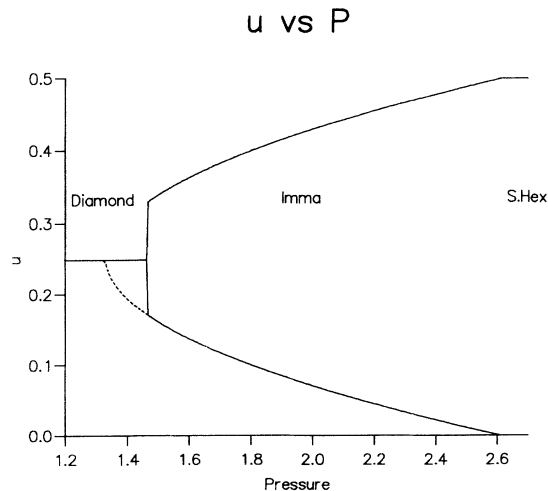


FIG. 2. Variation of internal parameter u with pressure at $T = 0$. Dashed line shows the metastable region of the $Imma/\beta$ -Sn curve. Above 1.48 two values of u (with different b and c) are degenerate.

The simple cubic structure is unstable at all pressures with respect to rhombohedral distortion. The stability of the NaCl structure in compound semiconductors can be understood by considering ionicity, since this compound structure gives six unlike species touching spheres, while β -Sn gives two like species and four unlike species.

For completeness the final transition to close packed has been examined, although considering only four out of 12 neighbors to be bonded is such a drastic approximation as to render the similarity between this system and silicon purely fortuitous. In the close-packed regime the energetics and symmetry depend significantly on the choice of functional form for the spring constant—any form which has a minimum at 180° favors a continuous transition to face-centered cubic via a base-centered monoclinic phase, while with the minimum at 116° the hexagonal close-packed distortion always yields a lower energy than fcc for a given volume. The simplest coordinate system in which to analyze the simple hexagonal to hcp transition is that of the primitive hexagonal unit cell doubled in the c direction. This forms a sandwich of close-packed layers. As with the diamond \rightarrow β -tin transition, the path can be defined by a single parameter, the displacement of the central plane. Defining the basis to be atoms at (000) and $(A, A, \frac{1}{2})$, $A = 0$ represents simple hexagonal in the double-size unit cell and $A = 1/3$ is hexagonal close packed. Considering the energetics, for intermediate values of P there is a continuous variation of A with pressure, thus we might expect to find an intermediate phase with doubling of the unit cell between the simple hexagonal and the hexagonal close packed. An intermediate phase of silicon has been reported in this pressure region, but its structure has not yet been solved.

Once the network is compressed to the hexagonal close-packed phase each hard sphere is in contact with 12 others. Although bonds are still defined only to four neighbors no further volume reduction is possible. It is clear that the covalent hypothesis which differentiates four bonds from the others is now invalid, but the pressure term is now dominant: the model is of hard sphere packing.

For the *Imma* structure, there are two possible distortions leading to the same structure ($u = \frac{1}{4} \pm x$) with a barrier in between (Fig. 2). At sufficient temperature, this barrier can be freely overcome and the resultant structure will have the β -Sn symmetry (u) = $\frac{1}{4}$. Other symmetry-breaking structures also have barriers which can be overcome at sufficient temperature although the diamond \rightarrow β -Sn barrier is very large (Fig. 1). The melting temperature is not well defined because melting requires bond breaking, which is explicitly not allowed. The transition temperature between phases is defined as the barrier height. Since we are working in dimensionless units, this is as detailed an analysis as is possible. The nonlinear relation between T_c and barrier height thus manifests itself in a nonlinear (but monotonic) relationship between the "temperature" used here and an actual thermal energy, as might be determined by molecular dynamic simulation of this system. In view of the nonquantitative nature of the model the exact derivation of free

energy from a double well model¹⁵ has not been done, but the topology of the phase diagram, and the sign of the slopes, which is all one could hope for in a parameter-free model, remains correct.

It is thus possible to define the *PVT* phase diagram [Fig. 3(a)] for this rigid network. As explained above, liquid and gaseous phases are excluded. Within the region of applicability it is topologically equivalent to the experimental diagram for silicon, in which β -Sn appears only as a finite temperature phase, consistent with the finite temperature experiments⁹ and the zero-temperature calculations.¹⁰ For a better comparison to silicon, it is appropriate to allow the choice of bonds in the simple hexagonal phase to vary: it is then possible to define a symmetric W-shaped potential for *Imma* structures around simple hexagonal, with different choices for the four bonds on either side of the $u = 0$ local maximum. This in turn gives a temperature dependence to the *Imma*/(simple hexagonal) boundary and modifies the phase diagram to that shown in Fig. 3(b). Note

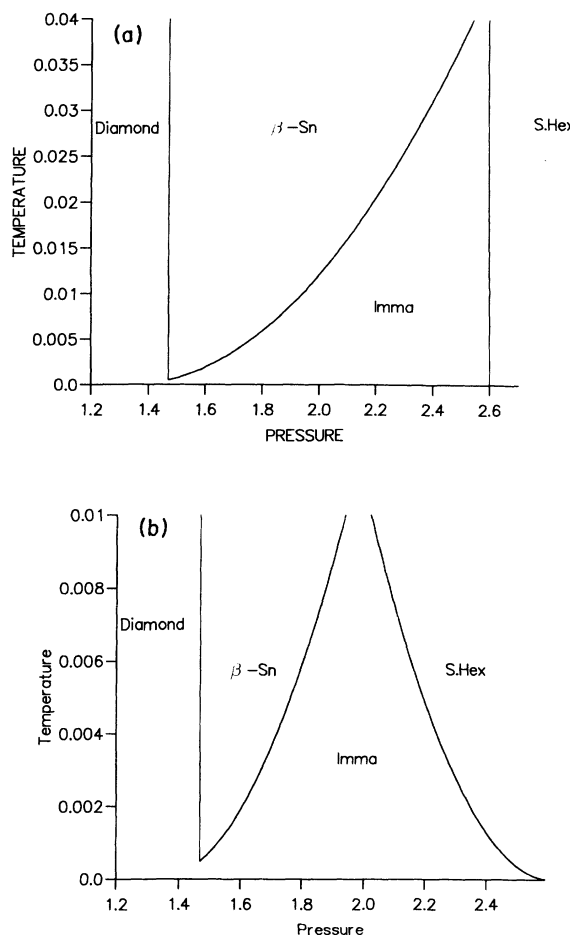


FIG. 3. (a) Phase diagram of the system of hard spheres and rigid rods. Pressure is in units of spring constant per cubic bond length and temperature is taken from the barrier height (Fig. 1), units of spring constant. (b) Phase diagram where the choice of bonded neighbors in structures with greater than fourfold coordination can be varied. Pressure and temperature are defined the same way as in (a).

here that at finite temperature $Imma$ is stable only at a limited range of u values and changes discontinuously to $u = 0$ at the transition to simple hexagonal.

As we have seen for the zero-temperature structures, the diamond $\rightarrow Imma$ is first order while the $Imma \rightarrow$ simple hexagonal is second order. At zero temperature, the metastable β -Sn $\rightarrow Imma$ is also second order (the equivalent graph to Fig. 1, of H vs u , has a single minimum which moves from $u = 1/4$ to $u = 0$ with increasing P). Temperature effects change this: we assume that the β -Sn $\rightarrow Imma$ occurs at the pressure for which the energy maximum at $u=1/4$ (Fig. 2) is higher than the available thermal energy. Since this maximum is already present when the pressure allows the transition from diamond, the minimum u is some way from $1/4$, thus the transition from $u=1/4$ is first order.

The model differs from the wide range of previously postulated empirical silicon potentials in that it has no free parameters. Relaxing the constraint of hard spheres, introducing interactions with more than four neighbors, etc. would allow quantitative fitting to observed data. Several such models exist, with forms based on physical intuition, and it is interesting to note that the rigid rods model can be obtained from some of these with an extremal parametrization.¹⁶⁻¹⁸

For more general topologically connected covalent species, without additional complications such as ionicity, simple rules can also be deduced: At zero pressure we expect high symmetry since equalizing bond angles to minimize energy is the dominant effect. At higher pressures the angles may distort to allow for smaller volumes,

leading to lower symmetry in the intermediate regime between energy-dominated and pressure-dominated (close-packed) regions. A specific case is any transformation from cubic to tetragonal which occurs by one of the three axes breaking symmetry, leaving two axes equivalent. Had the third axis not distorted, the energy could have been reduced by breaking this symmetry. In the absence of a coupling between the three symmetry-breaking modes, the tetragonal phase will thus be unstable with respect to an orthorhombic distortion (as we have seen here). In real systems, such a coupling will exist and its sign will determine whether there is a region of tetragonal stability. At high temperatures, the symmetry can be increased by Landau-type transitions which allow more of the configuration space to be sampled. Finally, we note that even for partially ionic III-V compounds such as InSb, the topology of the phase diagram is the same as for the simple system described here, indicating that the ideas presented here are of rather general application.

To summarize, we have shown that the symmetry-breaking distortions which had remained unconsidered and undiscovered for 30 years since the first crystallographic "solution" of the first high pressure phase,¹⁹ and for 12 years since the first electronic structure calculations on the β -tin phase, could have been anticipated by consideration of a parameter-free model based on a simple mechanical network.

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