

## Potential energy functions for atomic solids

### IV. Reproducing the properties of more than one solid phase

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Potentials have been derived for carbon and tin by optimizing to the energies, bond lengths and phonon frequencies of the diamond structures and the energies and bond lengths of the other experimentally known solid phase, graphitic carbon and  $\beta$ -tin, respectively. In both cases the other cubic solids (SC, BCC and FCC) and 2-dimensional networks (triangles and squares) are shown to have higher energies. Potentials have also been produced for silicon and germanium which reproduce the diamond structure data, and the lattice energies and distances predicted by electronic structure calculations for the SC, BCC and FCC solids.

#### 1. Introduction

In the first three papers of this series [1-3] we have shown that a potential function consisting of two-body and three-body terms can give, as the most stable phase, the commonly found crystal structures of atomic solids, and that the parameters arising in this function can be optimized to experimental phonon frequencies and elastic constants.

Papers II and III have dealt in detail with the diamond structure solids, C, Si and Ge. The potentials published in III [3] reproduce the lattice energies and lattice constants exactly, the elastic constants with only small errors, and the main features of the phonon dispersion curves along the  $(q, 0, 0)$ ,  $(q, q, 0)$  and  $(q, q, q)$  vectors. The largest difference between calculated and observed frequencies is in the low frequency TA modes, and that may be due to the neglect of anharmonicity in the standard Born-von Karman harmonic analysis.

The principal objective of this series of papers is to develop a general strategy for determining potential functions which cover a wide range of configuration space; paralleling a series of papers which tackled the same task for small polyatomic molecules [4]. There is, of course, no guarantee that, by fitting parameters to the properties of a diamond structure, we shall obtain a satisfactory picture of other regular structures, and it is even less likely that we shall reproduce the properties of impurities and surfaces. Taking the molecular analogy, there is no reason why a potential optimized to the properties of HCN (say) should reproduce the properties of its isomer HNC or of the transition state between these two minima on the potential surface.

One of the most important features of our work so far is that fitting parameters

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to the properties of the diamond structure gives potentials for which the other cubic structures, SC, BCC and FCC, are less stable; this is not a condition that we had to impose. This suggests that by increasing the flexibility of our potentials we should be able to reproduce the diamond properties as well as before and, in addition, reproduce explicit properties of other solid phases.

The stability of a solid phase is determined by its free energy and to deduce this from a potential requires a statistical analysis. However, the electronic energies of structures can now be calculated quite reliably from the Schrödinger equation using pseudo potentials and the density functional model; the lattice energies and geometries of silicon have been calculated for several structures using this technique, and for the diamond structure the results agree well with experimental values [5]. In two of the cases that we study in this paper, Sn and C, other phases are known which are stable at normal pressures and temperatures, and their enthalpies of formation can be estimated.

The potential function proposed in papers I–III contains three types of parameter. Energy ( $D$ ) and distance ( $r_e$ ) scaling parameters are determined at the end of the optimization routine to reproduce the lattice energy and lattice distance of one structure exactly (this presupposes a cubic lattice with only one distance parameter). Second, there are exponential parameters for the two-body and three-body terms; in all previous work these have been taken as equal, since no significant improvement was found by making them different. In the current work, we gain considerably by relaxing this condition. Finally, we chose a set of coefficients in the three-body polynomial which is optimized to phonon frequencies and elastic constants of the lattice and to other properties that are specified.

The full potential is defined by the following expressions

$$V^{(2)}/D = (1 + a_2\rho) \exp(-a_2\rho), \quad \rho = \frac{r - r_e}{r_e} \quad (1)$$

$$\begin{aligned} V^{(3)}/D = & (c_0 + c_1Q_1 + c_2Q_1^2 + c_3(Q_2^2 + Q_3^2) + c_4Q_1^3 \\ & + c_5Q_1(Q_2^2 + Q_3^2) + c_6(Q_3^3 - 3Q_3Q_2^2) + c_7Q_1^4 + c_8Q_1^2(Q_2^2 + Q_3^2) \\ & + c_9(Q_2^2 + Q_3^2)^2 + c_{10}Q_1(Q_3^3 - 3Q_3Q_2^2))e^{-a_3Q_1}, \end{aligned} \quad (2)$$

where

$$\begin{bmatrix} Q_1 \\ Q_2 \\ Q_3 \end{bmatrix} = \begin{bmatrix} \sqrt{\frac{1}{3}} & \sqrt{\frac{1}{3}} & \sqrt{\frac{1}{3}} \\ 0 & \sqrt{\frac{1}{2}} & -\sqrt{\frac{1}{2}} \\ \sqrt{\frac{2}{3}} & -\sqrt{\frac{1}{6}} & -\sqrt{\frac{1}{6}} \end{bmatrix} \begin{bmatrix} \rho_1 \\ \rho_2 \\ \rho_3 \end{bmatrix}. \quad (3)$$

## 2. Application to Si and Ge

In paper III [3] the best Si and Ge potentials, as judged by their least squares fit to phonon and elastic constant data, gave errors of up to 11% in the nearest neighbour distances of the SC, BCC and FCC phases, and up to 17% in the lattice energies (both relative to diamond), these errors being by reference to the results of electronic structure calculations [5]. Such calculations, which are based on pseudo potentials and density functionals, are found to be remarkably accurate when tested against experimental data. For example, for the Si diamond structure the lattice energy is accurate to 4.5% and the lattice distance to 0.4% [5].

Our computer programs have now been extended to calculate the lattice energies

and interatomic distances of the diamond, SC, BCC and FCC phases, and also of the 2-dimensional hexagonal (graphitic), square, and triangular nets; currently, there are no calculations on these 2-dimensional nets. In addition, the Born-von Karman force constants are calculated for up to the fifth shells of the diamond lattice. These results are then passed to a numerical least squares routine (NAG Library E04FDF [6]) and the coefficients  $c_i$  optimized for a given choice of  $a_2$  and  $a_3$ ; optimization with respect to  $a_2$  and  $a_3$  is by inspection. For certain values of  $c_i$  explored by the NAG routine the lattice collapsed and, to prevent this, we added to the two-body term a sharply rising exponential,  $\exp(-50(\rho + 0.2))$ , which prevents the nearest neighbour distance being significantly less than  $0.8r_c$ .

The phonon frequency parameters and elastic constants on which the least squares fit is based are defined in paper III (which also gives the experimental data), and the only modification we have made to our earlier work is to take all weighting factors for these data as unity. A decision had then to be made on how to introduce the lattice energies and distances of the other cubic phases into our least squares routine, and what weighting factors to use. Our choice was to take the dimensionless ratios of quantities relative to their diamond lattice values and to use weighting factors so as to obtain a roughly equal balance between the phonon and elastic constant data on the one hand and the lattice energies and distances on the other.

Potentials were first derived for a weighting factor of one and the exponents  $a_2$  and  $a_3$  covering a grid from 3.0 to 8.0. Two regions were found to give low RMS values: low exponents ( $a_2 = 4-6$ ,  $a_3 = 3-4$ ) and high exponents ( $a_2 = 5-8$ ,  $a_3 = 6-8$ ). An important difference between these is that in the low exponent region the 2D structures have high energies (low stabilities) and in the high exponent region they have low energies; often lower than the energy of the diamond structure. Currently there are no *ab initio* data on the 2D structures, although calculations for such structures are now being made for some elements, and are clearly of great importance for the type of analysis we are undertaking.

The best potentials derived in the low exponent region were satisfactory with respect to the available data, gave good-looking potential energy curves, smooth with a single minimum, and were easily found by the NAG minimization routine starting from the initial point  $c_i = 0$ . However, the convergence of these potentials with added shells was poor. Our calculations have been made by summing over all atoms in shells around a central atom which are less than 2.6 times the first shell radius; this brings in 5 shells for diamond (which is necessary for a good phonon description) and 6, 7 and 6 shells for SC, BCC and FCC, respectively. However, for low exponents, the atoms in shells at a distance greater than 2.6 make a significant contribution to the lattice energy.

We examined a model with an arbitrary cut-off of the potentials to zero beyond a specific distance. This is straightforward for the 2-body term (say, put  $V^{(2)} = 0$  for distances greater than  $2.6r_0$ ,  $r_0$  being the nearest neighbour distance). For the three-body terms the recipe is less obvious. We investigated a model in which three-body terms are set to zero if any one of the three distances is greater than  $2.6r_0$ , but found that this gave a poor least squares result in the low exponent region. For this reason we have concentrated our attention on solutions in the high exponent region where convergence is not a problem.

When potentials were obtained in the high exponent region solely from the phonon and elastic constant data, the energy ordering of the cubic structures was generally qualitatively satisfactory and the 2D structures had a higher energy than the

Table 1. Potential function for Si and Ge and the calculated force constants ( $10^4$  dyne  $\text{cm}^{-1}$ ).<sup>a</sup>

	Si	Ge		Si	Ge
$a_2$	6.50	6.50	$\alpha$	5.663	5.086
$a_3$	6.50	6.50	$\beta$	3.650	3.332
$D/\text{eV}$	2.918	2.330	$\mu$	0.472	0.428
$r_c/\text{\AA}$	2.389	2.559	$\lambda$	-0.358	-0.294
			$\nu$	0.203	0.132
$c_0$	3.598	2.986	$\delta$	0.040	0.044
$c_1$	-11.609	-13.778	$\mu'$	-0.090	-0.089
$c_2$	13.486	29.843	$\lambda'$	0.202	0.126
$c_3$	-18.174	-14.291	$\nu'$	0.060	0.055
$c_4$	-5.570	-28.628	$\delta'$	0.006	-0.023
$c_5$	79.210	61.935	$\mu''$	0.061	0.055
$c_6$	-6.458	-1.418	$\lambda''$	-0.328	-0.327
$c_7$	23.383	33.565	$\mu'''$	0.036	0.041
$c_8$	-111.809	-99.248	$\lambda'''$	-0.025	-0.024
$c_9$	9.705	8.881	$\nu'''$	0.035	0.043
$c_{10}$	38.297	30.103	$\delta'''$	-0.027	-0.021

<sup>a</sup>The force constants  $\alpha \dots \delta'''$  refer to Cartesian displacements of atoms in first to fifth shells and are defined explicitly in paper III [3]. It should be noted that there is an additional repulsive contribution to the 2-body term, as defined in the text, whose object is to prevent collapse of some structures at small lattice distances.

diamond structure. When the structure weighting factor was greater than unity, the 2D squares structure was more stable than the diamond structure, and sometimes the SC structure was also more stable than diamond. The most satisfactory weighting factor for Si was found to be 0.8 and potentials with  $a_2$  and  $a_3$  in the region of 6.5 gave the best results. Varying these exponents by  $\pm 0.5$  gave little change in the RMS value, and it would be necessary to have additional data, particularly on the energies and geometries of 2D structures, to give a firmer tolerance to the exponents.

Our optimum potential for Si and its associated Born-von Karman force constants is given in table 1. According to the weighting criteria for phonons now being used, this potential gives a better fit to the phonon data than the potentials given in paper III and is also much better in respect of the energies and interatomic distances of the non-diamond structures. It can be seen from table 2 that the stability of SC is overestimated and that of FCC underestimated, and the interatomic distances are all a little too large. Another fault that we have noted is that the potential curve for the 2D hexagonal lattice has a second minimum (just) at an interatomic distance approximately 0.8 of the true minimum; a better potential without this feature could presumably be obtained if we had specific data on the 2D structures, but in any case it is unlikely to have a significant effect on observable properties of Si systems.

The properties of the Ge lattices were reproduced by potentials very similar to those for Si and, following our practice in paper III, we took the same exponents for Ge and Si to simplify future studies on Si/Ge mixtures. The same weighting factor for the structural data (0.8) was also used. The Ge potentials and resulting data are also shown in tables 1 and 2. All potential curves in this case were smooth, with a single minimum.

Finally, we comment on convergence of the NAG minimization routine; this was much more difficult for the high exponent than for the low exponent region, and we

Table 2. Comparison of output and input data for Si and Ge.  $C_{ij}$  are elastic constants (units  $10^{12}$  dyne  $\text{cm}^{-2}$ )  $V^* = V/V(\text{dia})$ ,  $r^* = r/r(\text{dia})$ .<sup>a</sup> Hex, sq, and tri refer to the 2D nets of hexagons, squares and triangles, respectively.

	Si		Ge	
	Input	Output	Input	Output
$C_{11}$	1.657	1.672	1.32	1.34
$C_{12}$	0.639	0.623	0.49	0.46
$C_{44}$	0.796	0.757	0.68	0.63
$V^*$ (SC)	0.93	0.97	0.93	0.98
$V^*$ (BCC)	0.89	0.88	0.90	0.89
$V^*$ (FCC)	0.88	0.84	0.89	0.85
$r^*$ (SC)	1.07	1.12	1.09	1.13
$r^*$ (BCC)	1.13	1.21	1.17	1.22
$r^*$ (FCC)	1.16	1.26	1.21	1.27
$V^*$ (hex)	—	0.74	—	0.74
$V^*$ (sq)	—	0.88	—	0.95
$V^*$ (tri)	—	0.94	—	0.98
$r^*$ (hex)	—	1.05	—	1.08
$r^*$ (sq)	—	1.20	—	1.21
$r^*$ (tri)	—	1.09	—	1.10

<sup>a</sup>The elastic constants are from reference [7] and the lattice energies and distances from reference [5].

frequently converged on potentials with good RMS values which were unsatisfactory in other respects: notably, curves with large negative values for  $c_2$  and  $c_7$  and positive values for  $c_4$ , which collapsed at short intermolecular distances (negative values of  $Q_1$ ). The best procedure we found was first to converge to a cubic polynomial ( $c_0$ – $c_6$ ) from starting values with all coefficients zero, and to use the resulting coefficients, plus  $c_7$ – $c_{10} = 0$ , as starting values to converge to the full quartic polynomial.

### 3. Application to Sn

$\alpha$ -Sn or grey tin has the diamond structure and is a semiconductor, but it is unstable above 286 K, converting to  $\beta$ -Sn or white tin, which is metallic.  $\beta$ -Sn is more dense than  $\alpha$ -Sn and has a body-centred tetragonal structure. One can picture a reaction path from  $\alpha$  to the  $\beta$  form as a compression along the  $c$  axis and an expansion along the  $a$  and  $b$  axes ( $a = b$ ) (see figure 1), although this is not necessarily the lowest energy pathway for the phase transition [8]. The  $c$  axis compression effectively changes the coordination number of all atoms from 4 to 6.

The lattice energy and lattice distance are normally converged quite well for the diamond structure by summing out to fifth neighbours, but for  $\beta$ -Sn this is not the case as the  $c$  axis compression brings in four relatively close atoms from what are seventh neighbours in diamond; in the diamond cubic unit cell they are at (1, 1, 5), (–1, –1, 5), (1, –1, –5) and (–1, 1, –5). These atoms have therefore been included in the two-body and three-body sums for  $\beta$ -Sn.

The phonon dispersion curves for  $\alpha$ -Sn at 90 K have been determined by Price, Rowe and Nicklow [9] along the  $[q, 0, 0]$ ,  $[q, q, 0]$  and  $[q, q, q]$  wave-vectors using inelastic neutron scattering. There are as yet no experimental measurements of the elastic constants of  $\alpha$ -Sn, and we have therefore used values estimated by Price and Rowe from their phonon data [10]. For the  $\beta$ -Sn structure we have an estimated

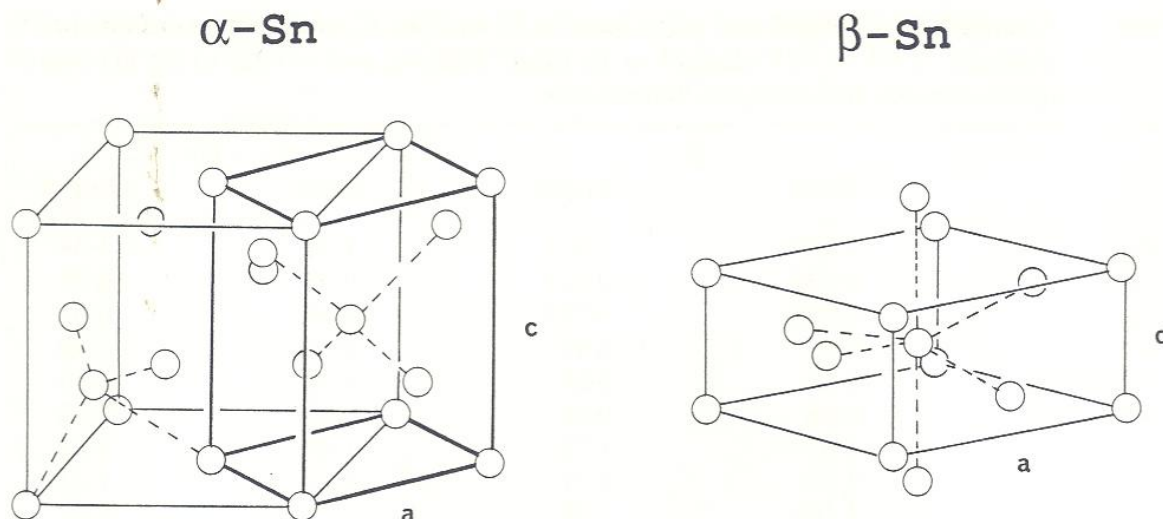


Figure 1. Relationship between the  $\alpha$ - and  $\beta$ -Sn structures. For  $\alpha$ -Sn the body-centred tetragonal cell is indicated by the thicker lines.  $\alpha$ -Sn:  $a = 4.584 \text{ \AA}$ ,  $c = 6.483 \text{ \AA}$ ,  $c/a = \sqrt{2}$ .  $\beta$ -Sn:  $a = 5.832 \text{ \AA}$ ,  $c = 3.181 \text{ \AA}$ ,  $c/a = 0.545$ .

enthalpy at 0 K, relative to  $\alpha$ -Sn (0.016 eV) [11] and its lattice parameters ( $a = b = 5.832 \text{ \AA}$ ,  $c = 3.181 \text{ \AA}$ ) [12].

It was convenient for our analysis to describe the  $\beta$ -Sn lattice in terms of two parameters:  $T = \sqrt{2(a/c)}$ , a parameter which is 1 for diamond and 2.593 for the experimental  $\beta$ -Sn structure, and  $S = r_{\beta}/r_{\alpha}$ , the ratio of the nearest neighbour distances in the  $\beta$  and  $\alpha$  lattices whose experimental value is 1.076. However, optimizing the  $\beta$ -Sn structure in two dimensions was found to be quite time-consuming as the topography of the surface was very sensitive to small changes in the 3-body coefficients. We therefore chose to optimize in the constant volume approximation which has been used by others for electronic structure calculations on such systems [13]. For  $\beta$ -Sn structures in which the volume per atom is constant, and equal to that in the diamond structure,  $S$  and  $T$  are related by

$$S = ((2T^2 + 1)/3T^{4/3})^{1/2}. \quad (4)$$

The optimum values of  $S$  and  $T$  derived in this way were very close to the exact optima for the potentials we produced.

Fitting only to the data for  $\alpha$ -Sn (twelve phonon derived quantities and three elastic constants) could be achieved with high accuracy using only a cubic polynomial in the 3-body term and exponents in the region  $a_2 = a_3 = 7$ . Moreover, for these potentials the diamond structure was generally the most stable cubic structure. However, the value of  $T$  for these potentials was generally much too high (typically  $> 3.5$ ) so the geometry of  $\beta$ -Sn was poorly given by these potentials. Adding the lattice energy and  $T$  to our minimization procedure (various weighting factors were explored) led to potentials which gave a reasonable representation of the phonon frequencies, but the diamond structure was less stable than some of the other cubic structures; this was true for either a cubic or quartic polynomial.

Two further problems were found with potentials that fitted the above data. Firstly, when the  $(T, S)$  surface was examined, it was either very flat around the  $\beta$ -Sn geometry or there were more than two minima on the surface. Second, the value of  $r_e$  necessary to fit the  $\alpha$ -Sn lattice distance was rather large. For our current study there is nothing wrong in this as the diamond lattice distance is always reproduced exactly

Table 3. Potential function for Sn and associated force constants ( $10^4$  dyne  $\text{cm}^{-1}$ ) for the diamond structure.<sup>a</sup>

$a_2$	6.25	$\alpha$	3.238
$a_3$	3.55	$\beta$	3.018
$D/\text{eV}$	1.000	$\mu$	0.129
$r_e/\text{\AA}$	2.805	$\lambda$	0.239
		$\nu$	-0.115
$c_0$	1.579	$\delta$	0.384
$c_1$	-0.872	$\mu'$	-0.058
$c_2$	-4.980	$\lambda'$	-0.053
$c_3$	-13.145	$\nu'$	0.248
$c_4$	-4.781	$\delta'$	-0.104
$c_5$	35.015	$\mu''$	-0.089
$c_6$	-1.505	$\lambda''$	-0.319
$c_7$	2.949	$\mu'''$	0.174
$c_8$	-15.065	$\lambda'''$	0.013
$c_9$	10.572	$\nu'''$	0.096
$c_{10}$	12.830	$\delta'''$	0.112

<sup>a</sup>The potential was based on a lattice energy (0 K) of 3.14 eV [14] and a lattice constant (90 K) of 6.483  $\text{\AA}$  [12].

by our scaling procedure, but if the potentials are used to study small Sn clusters then they are found to have large interatomic distances, in conflict with theoretical estimates [15].

In summary, no satisfactory potential was found to reproduce just the  $\alpha$ -Sn phonon data and the  $\beta$ -Sn lattice energy and geometry. To solve the problem, we therefore added to our least squares data set two further constraints. The first was to remove the flatness of the surface around the  $\beta$ -Sn minimum by making the potential at  $T = 2.0$  and  $3.0$  greater than that at  $T_{\text{opt}}$  by  $0.1D$ , and the second was to make  $r_e$  equal to the nearest neighbour distance in the diamond lattice, both conditions introduced into the minimization program with various weighting factors. All potentials were examined over the full  $(T, S)$  surface to confirm that they had only two minima (those for  $\alpha$ -Sn and  $\beta$ -Sn) and it was established that the energies of the other cubic structures and the two dimensional lattices of triangles, squares and hexagons were all less stable. The most satisfactory potential according to the above criteria is given in table 3, and the quality of the fit can be seen from the data quoted in tables 4 and 5.

Table 3 includes the Born-von Karman force constants for our optimum potential but these are not, of course, optimum for the phonon elastic constant data alone. Indeed, it can be seen from table 2 that some of the phonon parameters are rather poor. Much better potentials in this respect are obtained in the high exponent region; the parameters of such a potential are given in table 6. The main defect with this potential is that the SC structure is more stable than diamond.

We also give in table 6 the force constants deduced by Zdetsis [16, 17] from his analysis of the phonon data alone. Going out to fifth neighbours, Zdetsis obtains a near perfect fit to the phonon curves but, as can be seen from table 4, his force constants do not fall off appreciably at long range, with  $\lambda'''$ , for example, being greater than all but the first neighbour force constants. In paper III [3], we made similar observations concerning Zdetsis' force constants for C, Si and Ge. In fact, Zdetsis himself points out that any force constants obtained in such a manner need not

Table 4. Comparison between experimental and calculated values of the phonon parameters, and elastic constants for  $\alpha$ -Sn (see paper III for definitions); units of  $10^{12}$  dyne  $\text{cm}^{-2}$ .

Parameter	Input [10, 11]	Output
Ram	0.540	0.528
$P_1$	0.432	0.519
$P_2$	0.100	0.087
$P_3$	0.479	0.477
$P_4$	0.057	0.041
$P_5$	0.031	0.057
$P_6$	0.015	0.065
$P_7$	0.039	0.038
$P_8$	0.012	0.004
$P_9$	0.383	0.308
$P_{10}$	0.355	0.401
$P_{11}$	0.324	0.224
$C_{11}$	0.690	0.662
$C_{12}$	0.293	0.338
$C_{44}$	0.362	0.328

necessarily be unique [17]. The elastic constants calculated by Zdetsis [16] are also given in table 6; these differ from most other estimations of the elastic constants which have  $C_{44} > C_{12}$  [11, 18, 19]. Figure 2 shows the phonon dispersion curves deduced from the force constants given in table 6, and compares them with experimental values.

The potential curves  $V(r)$  for all the cubic and 2D structures are smooth with a single minimum. The lattice energies and nearest neighbour distances for these structures are given in table 5. Cohen and co-workers have carried out pseudo potential calculations on  $\alpha$ -Sn and  $\beta$ -Sn, and on a number of high pressure forms [20, 21]. They calculate  $\beta$ -Sn to be less stable than  $\alpha$ -Sn by about 0.04 eV (cf., the experimental value of 0.16 eV) and BCC and HCP to be only 0.12 eV less stable than  $\alpha$ -Sn [21]. Although our  $\alpha$ - $\beta$  energy gap, 0.03 eV, is also smaller than the experimental value, our BCC and FCC energies at 0.5 eV are probably a little too high (assuming the latter is close to the HCP energy).

Figure 3 shows the potential plotted as a function of the parameter  $T$  with  $S$  optimized.  $S$  is 1 for diamond and 1.08 for  $\beta$ -Sn the experimental structure; at the maximum of the curve in figure 3 (a saddle point on the tetragonal surface),  $S = 1.03$ . Also shown on this figure is the nearest neighbour distance, which is a minimum for

Table 5. Calculated ratios of lattice energies  $V^* = V/V(\text{dia})$  and the nearest interatomic distances  $r^* = r/r(\text{dia})$  for Sn.

	$V^*$	$r^*$
$\beta$ -Sn <sup>a</sup>	0.99	1.16
SC	0.98	1.18
BCC	0.85	1.32
FCC	0.84	1.36
Hex	0.12	1.17
Sq	0.13	1.35
Tri	0.12	1.49

<sup>a</sup>  $\beta$ -Sn geometry:  $T(\text{exp}) = 2.592$ ,  $T(\text{calc}) = 2.593$ ,  $S(\text{exp}) = 1.076$ ,  $S(\text{calc}) = 1.162$ .



Table 6. Phonon-elastic constant optimized potential and comparison of the resulting force constants for  $\alpha$ -Sn with those of Zdetsis [15, 16] (units  $10^4$  dyne  $\text{cm}^{-1}$ ).

Parameter	Value	Parameter	Value	Zdetsis
$a_2$	8.0	$\alpha$	3.571	3.048
$a_3$	6.0	$\beta$	2.616	2.098
$D/\text{eV}$	1.428	$\mu$	0.228	0.170
$r_e/\text{\AA}$	2.896	$\lambda$	-0.276	-0.397
		$\nu$	0.088	0.231
$c_0$	3.374	$\delta$	0.059	0.089
$c_1$	-4.981	$\mu'$	0.003	0.064
$c_2$	9.695	$\lambda'$	0.002	-0.190
$c_3$	-27.182	$\nu'$	0.032	-0.023
$c_4$	-13.165	$\delta'$	-0.019	-0.065
$c_5$	70.892	$\mu''$	0.040	0.013
$c_6$	12.903	$\lambda''$	-0.180	0.016
$c_7$	10.478	$\mu'''$	0.025	0.068
$c_8$	-77.093	$\lambda'''$	0.006	0.362
$c_9$	12.002	$\nu'''$	0.011	0.009
$c_{10}^a$	0.000	$\delta'''$	-0.003	0.145
		$C_{11}$	0.684	0.699
		$C_{12}$	0.293	0.327
		$C_{44}$	0.347	0.319

<sup>a</sup>  $c_{10}$  was constrained to zero as optimization with a full quartic potential gave unstable results.

the  $\alpha$  (diamond) structure. The barrier between the  $\alpha$  and  $\beta$  structures is very pronounced, as it should be given the kinetic stabilities of the two phases. We would not wish to speculate on the actual mechanism for interconversion.

Both of the Sn potentials we have given have good convergence. For the phonon optimized potential of table 6 this is not surprising, as the exponents are large, but for the low value of  $a_3$  in table 3 we would normally expect poor convergence. However, taking the diamond lattice energy for five shells (47 atoms) as 100%, the lattice energies calculated on adding successive shells are 92%, 95%, 97%, 100%, 100%; the last mentioned being for a total of eleven shells and 159 atoms. Thus, although there is a dip in the lattice energy on adding the sixth shell, the five-shell result is essentially the same as the converged result. This is also true of the other cubic structures; the FCC structure for six shells (87 atoms) is almost exactly the same as for ten shells (225 atoms).

In conclusion we can say that we have a potential for Sn which reproduces the structural data quite well and is tolerable for the phonons of  $\alpha$ -Sn, and another potential which is much better for the phonon data but which makes the SC structure more stable than the diamond and which gives too high a value for  $T$  for the  $\beta$ -Sn structure.

#### 4. Carbon

It is difficult to think of a bigger challenge for solid state potentials than to find a common function to represent both diamond and graphite, and one which is also applicable to other crystalline structures. The valence states of the atoms and the nature of the electronic wavefunctions are quite different for diamond and graphite. However, if one is looking ahead to find potentials for carbon clusters, including the

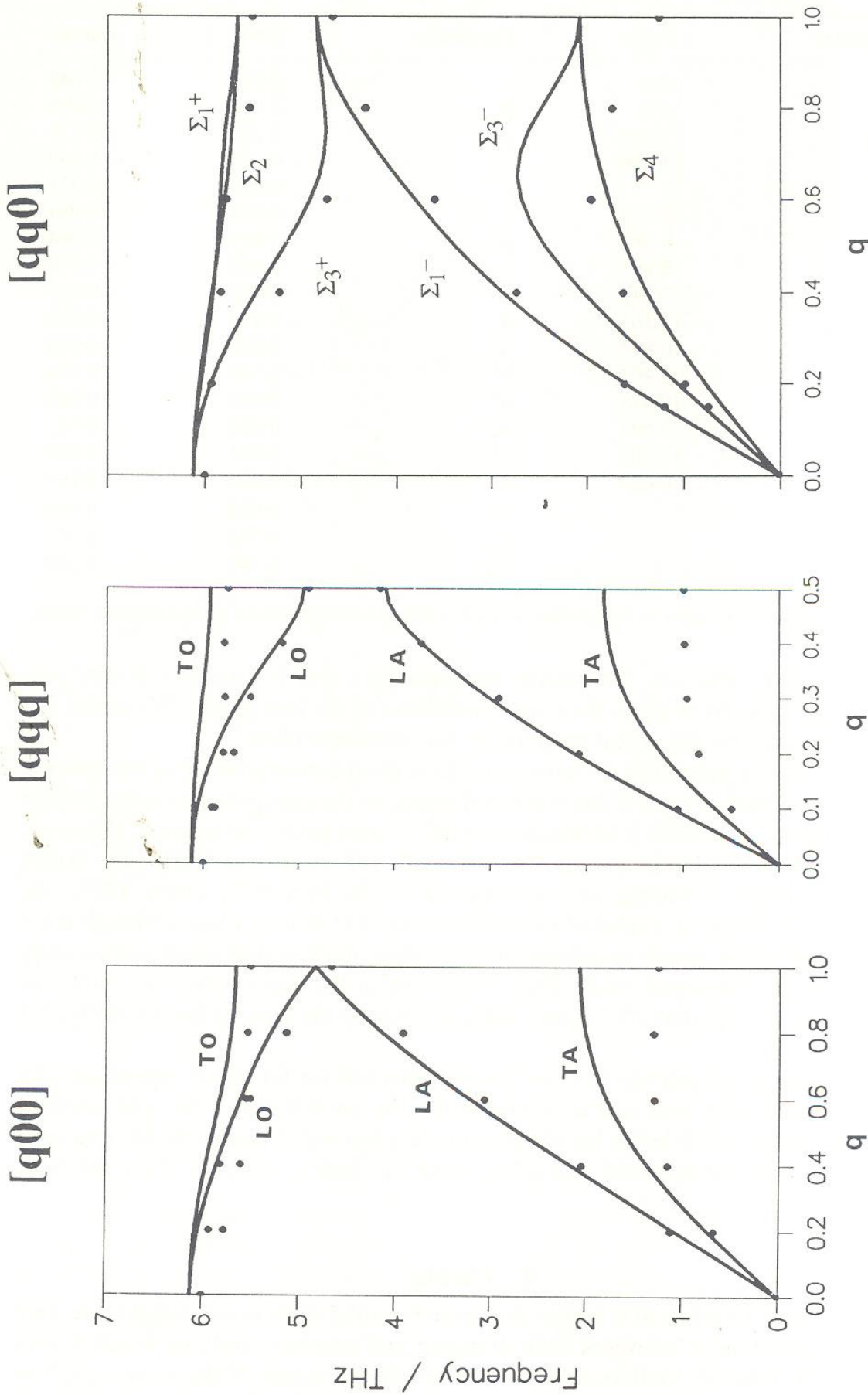


Figure 2. Phonon dispersion curves for  $\alpha$ -Sn calculated using the potential of table 6. Experimental frequencies are represented by points. Wave-vectors  $q$  are in units of  $2\pi/r_1$ .

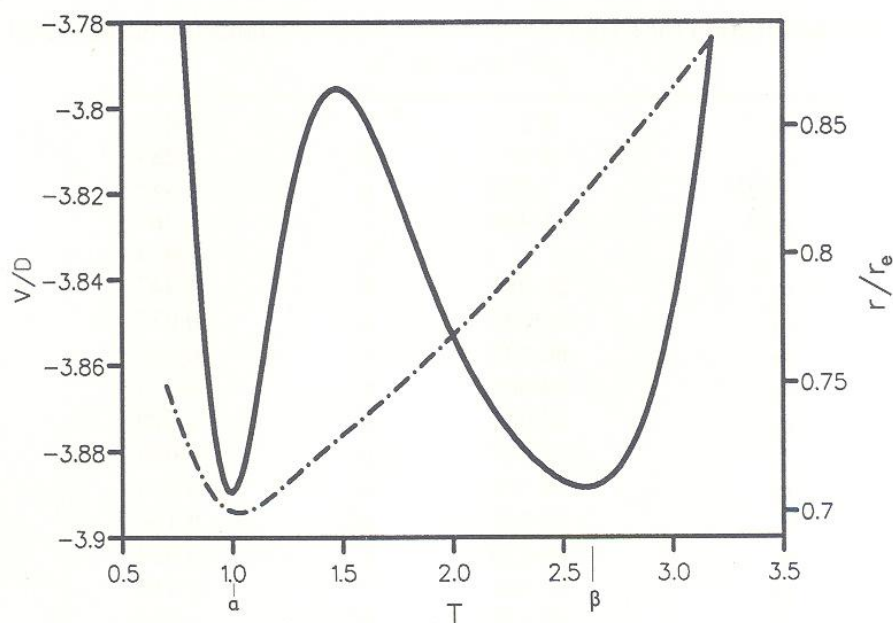


Figure 3. Plot of potential energy  $V$  (in units of  $D$ , solid line) and nearest neighbour distance  $r$  (in units of  $r_e$ , broken line) as a function of  $T$  with  $S$  optimized.

novel fullerene structures [22], then a common functional form for all crystalline structures would be a major step in that direction.

In our view the most successful attempt to date is that of Heggie [23]. Unfortunately, his potential contains parameters which depend on the hybridization states of the atoms, and these are not always directly determined from the geometry of the system. It is not yet clear how these parameters should be defined except for diamond, graphite and the transition structures between the two.

We have tackled the problem by treating graphite as a single 2-dimensional hexagonal sheet. An estimate has been made of the interlayer interaction energy in graphite of 0.11 eV per atom [24] and, when this is added to the experimental heat of formation of graphite, it makes the diamond structure slightly more stable than graphite. The phonon, elastic constant and structural data on diamond have been given in paper III [3].

Fitting the phonon and elastic constant data above was a task tackled in paper III and the best sum of squared deviations that can be obtained is approximately 0.1. However, potentials satisfying these criteria give poor energies and potential curves for the other cubic structures and the graphitic sheet has only about 75% of the lattice energy of diamond. As in the case of Si, there was also a tendency for the 2D lattice of squares to be unreasonably stable.

In addition to the graphite and diamond experimental data we have calculations by Yin and Cohen [25] on the SC, BCC and FCC phases, so that the lattice energies and nearest neighbour distance of these, relative to diamond, can be added to the minimization routine. There are no calculations of comparable quality on the 2D lattices of squares and triangles although there are calculations by Weinert and co-workers [26] which predict that the 2D square lattice has a cohesive energy 62% of that of 2D hexagons; these calculations overestimate the absolute cohesive energy of 2D hexagons. In our calculations we have included an arbitrary constraint on the energy of 2D squares to prevent this structure being too stable;  $V^*(\text{sq}) = 0.8$ . We took weighting factors of 10 for all structural data, except for  $V^*(\text{hex})$  where we took

Table 7. Potential function for  $C$  and the calculated force constants for the diamond structure ( $10^4$  dyne  $\text{cm}^{-1}$ ).

$a_2$	8.2	$\alpha$	16.077
$a_3$	8.2	$\beta$	2.289
$D/\text{eV}$	7.954	$\mu$	2.345
$r_c/\text{\AA}$	1.468	$\lambda$	-1.767
		$\nu$	1.954
$c_0$	22.085	$\delta$	1.847
$c_1$	-65.608	$\mu'$	0.032
$c_2$	60.803	$\lambda'$	0.826
$c_3$	-69.806	$\nu'$	0.373
$c_4$	83.062	$\delta'$	0.329
$c_5$	155.927	$\mu''$	0.098
$c_6$	-38.352	$\lambda''$	-0.914
$c_7$	-64.847	$\mu'''$	0.130
$c_8$	-146.058	$\lambda'''$	-0.014
$c_9$	27.741	$\nu'''$	0.116
$c_{10}$	147.137	$\delta'''$	0.026

a factor of 20 to give high priority to the diamond-graphite energy gap. This led to two regions of exponents in which the sum of squares was minimized;  $a_2 = a_3 \approx 6.0$  and  $a_2 = a_3 \approx 8.0$ . There was little to choose between the two but we give in this paper the best potential in the latter region as it provides a better representation of the phonon dispersion curves.

The potential and its force constants are given in table 7. The sum of squared deviations is 1.2 for the phonon data and 0.4 for the structural data. Figure 4 shows the potential energy curves for the cubic and 2D structures, and table 8 gives the relative lattice energies and distances of these structures. The potential energy curve of graphite is not as smooth at its minimum as we would like. The fit to the structural data is excellent (imposed rather by our high weighting factors), but the elastic constants are not as well reproduced as by our potentials of paper III. Although our fitting to the phonon data is poorer than we obtained before, the phonon dispersion curves for diamond, shown in figure 5, are in their overall shape rather better as the avoided crossing of the  $\Sigma_3^+$  and  $\Sigma_3^-$  branches along the  $[q, q, 0]$  vector is more pronounced. However, both the Raman frequency and the frequency of the TA mode are too high.

Our potential gives excellent convergence for lattice energies and lattice distances with added shells because the exponents are high. Note that with higher exponents we also have larger polynomial coefficients; the two must go together because we know that for the diamond structure the long range force constants are not negligible.

Last, there is the question of whether our potential gives a reasonable picture of the real graphite structure, or only for the 2D hexagonal sheet. The simplest calculation is for a fully eclipsed structure and for this we find a shallow minimum at an interplanar separation of 2.58  $\text{\AA}$  with a depth of approximately 1 eV per atom. For hexagonal graphite, which has half the atoms eclipsed and half over the centre of a ring, the minimum is at 2.50  $\text{\AA}$  and is slightly deeper. The experimental value for the interplanar separation is 3.35  $\text{\AA}$  and our estimated contribution to the lattice energy only 0.1 eV so our potential certainly overestimates the interplanar interaction, but not to a wholly unreasonable extent; it is important that our potential does not collapse the interplanar separation to chemical bond distances.

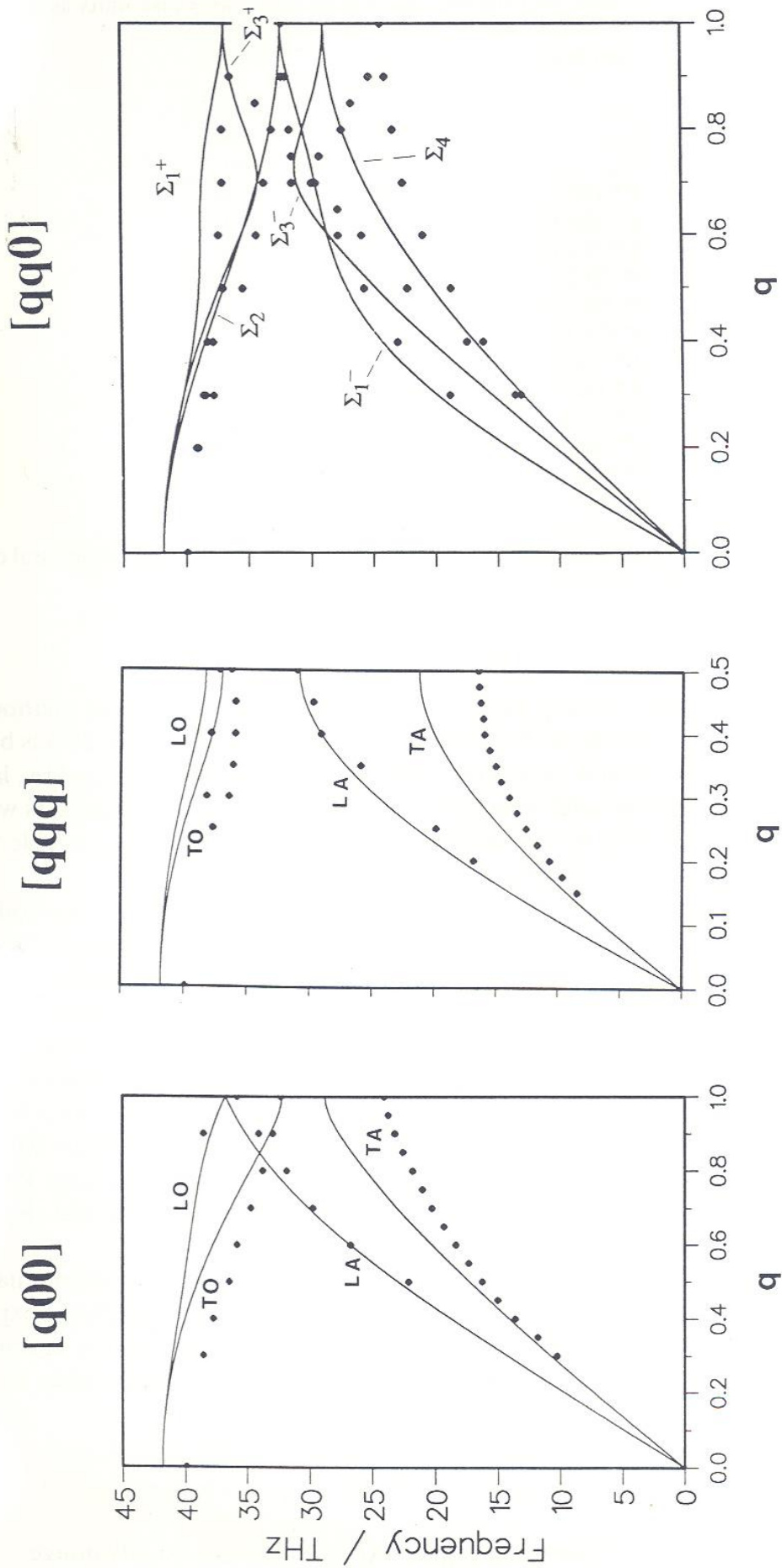


Figure 4. Phonon dispersion curves for C (diamond) calculated using the potential of table 7. Details as in figure 2.

Table 8. Comparison of input and output data for  $C$ ; definitions and units as in table 2.<sup>a</sup>

Parameter	Input	Output
$C_{11}$	10.76	10.492
$C_{12}$	1.25	1.628
$C_{44}$	5.76	6.027
$V^*$ (SC)	0.64	0.68
$V^*$ (BCC)	0.42	0.42
$V^*$ (FCC)	0.38	0.38
$r^*$ (SC)	1.15	1.19
$r^*$ (BCC)	1.34	1.32
$r^*$ (FCC)	1.37	1.36
$V^*$ (hex)	0.99	0.99
$V^*$ (sq)	0.80	0.82
$V^*$ (tri)	–	0.51
$r^*$ (hex)	0.91	0.91
$r^*$ (sq)	–	1.08
$r^*$ (tri)	–	1.28

<sup>a</sup>The experimental elastic constants are from reference [27] and the input structural data for SC, BCC and FCC from reference [25].

## 5. Conclusion

The results presented in this paper are a qualified success for our method. The qualification is that although our fit to the phonon and elastic constant data is broadly satisfactory, except for Si and Ge it is certainly not as good as we obtained by, largely, ignoring the data on other solid structures. The question, yet unanswered, is whether this indicates a basic failing in our method or is just a matter of being unable to find better solutions within our present model.

In terms of basic failings, we have the assumption that only two-body and three-body terms need to be considered. Although this is certainly going to be wrong, we have no evidence yet that it is badly wrong. Another assumption lies in our rather simple form for the two-body term; a single parameter function in reduced units. We found it necessary in the current work to add an exponential hard wall to the two-body potential to prevent collapse of some structures at short interatomic distances, and it is possible that in the future some other two-body function may be more satisfactory. We have explored the use of the Morse function (also a single parameter function) and found no advantage, but there are other functions that could be considered; to introduce more parameters in the two-body term would, however, probably be a difficult step.

The function form of the three-body term is quite flexible in its polynomial, and we do not envisage going beyond the quartic level, but multiplying it by an exponential is only one of the methods of making the function go to zero as any internuclear distance goes to infinity. We have examined another function used widely for molecular studies [4]

$$\frac{1}{2} \left[ 1 - \tanh \frac{aQ_1}{2} \right] \quad (5)$$

which, at large distances, behaves as  $\exp(-aQ_1)$ , but found no advantage.

Our current strategy is to see next how the method behaves for elements which do not have diamond as their most stable phase, and potentials which reproduce the

phonon data for FCC and BCC solids are currently being derived. Preliminary data on Al (FCC) suggests that the fitting is if anything easier than for diamond solids.

Another line we are taking is to use the potentials derived in this paper to examine the structures and stabilities of clusters; others are studying surface reconstruction. It is possible that these studies will also show up basic faults in our model, but to date we are optimistic.

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