Ab initio elastic constants for the lonsdaleite phases of C, Si and Ge

Ab initio elastic constants for the lonsdaleite phases of C, Si and Ge

S Q Wang[1,2] and H Q Ye[1]

[1] Shenyang National Laboratory for Materials Science, Institute of Metal Research,
Chinese Academy of Sciences, 72 Wenhua Road, Shenyang 110016, People's Republic of China
[2] Institute of Physical Metallurgy and Metal Physics, RWTH, Kopernikusstraße 14,
D-52056 Aachen, Germany

E-mail: sqwang@imr.ac.cn

Abstract
The elastic constants of lonsdaleite C, Si and Ge are calculated by using the
plane-wave pseudopotential method in the scheme of density functional theory
and the local density approximation. For comparison, the elastic constants of
the cubic diamond phases of these elements, zincblende SiC and 6H–SiC, are
also calculated.

1. Introduction

The elastic constants of solids give important information on their mechanical and dynamical
properties. These parameters provide a link between the mechanical and dynamic behaviour
of crystals, and may be used as a means of probing the inter-atomic forces. In particular, they
provide information on the stability and stiffness of materials. Although various experimental
techniques are available nowadays for the measurement of elastic constants, such as ultrasonic
wave propagation, neutron scattering and Brillouin scattering etc, the theoretical calculation
of elastic constants is also indispensable due to the difficulties in preparing suitable specimens
for many materials. First-principles calculation has demonstrated its success in theoretical
studies of elastic properties on various materials [1–6].

The lonsdaleite phases of C, Si and Ge are fantastic new crystalline structures compared
to their common cubic diamond phases. However, only the poly-crystal of lonsdaleite C has
been fabricated successfully. To date, the bulk solid forms of lonsdaleite Si and Ge are still
unavailable experimentally, despite the existence of these structures having been confirmed by
many experimental observations [7–14].

In this paper, we investigate the elastic behaviour and the stability of the structure of
lonsdaleite C, Si and Ge by using plane-wave pseudopotential (PW-PP) calculations. The
accuracy and reliability of our realization are tested by calculating their well known cubic
phases and the relevant SiC phases.

2. Details of the calculations

Our PW-PP calculations are realized by using the ABINIT computer code [15]. The LDA pseudopotentials used in these calculations are the Hartwigsen–Goedecker–Hutter (HGH) relativistic separable dual-space Gaussian pseudopotentials [16]. The equilibrium properties of these lonsdaleite phases can be found in a separate paper [17].

The theoretical elastic constants are calculated from the energy variation by applying small strains to the equilibrium lattice configuration. The elastic energy of a solid under strain is given by

$$\Delta E = \frac{V}{2} \sum_{i=1}^{6} \sum_{j=1}^{6} C_{ij} e_i e_j \tag{1}$$

where V is the volume of the undistorted lattice cell, ΔE is the energy increment from the strain with vector $e = (e_1, e_2, e_3, e_4, e_5, e_6)$, and C is the matrix of the elastic constants. For cubic phases there are three independent elastic constants, C_{11}, C_{12} and C_{44}. The hexagonal phases add two more independent elastic constants, C_{13} and C_{33}. The cubic diamond structure is constructed by interpenetrating two face-centred cubic Bravais lattices. Its primitive vectors are defined as

$$\begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix} = \begin{pmatrix} 0 & \frac{a}{2} & \frac{a}{2} \\ \frac{a}{2} & 0 & \frac{a}{2} \\ \frac{a}{2} & \frac{a}{2} & 0 \end{pmatrix} \tag{2}$$

where a is the lattice constant. The primitive vectors of the hexagonal phase are defined by

$$\begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix} = \begin{pmatrix} \frac{\sqrt{3}}{2}a & \frac{1}{2}a & 0 \\ -\frac{\sqrt{3}}{2}a & \frac{1}{2}a & 0 \\ 0 & 0 & c \end{pmatrix} \tag{3}$$

where a and c are lattice constants. The primitive vectors a_i $(i = 1, \ldots, 3)$ are transformed to the new vectors under strain by

$$\begin{pmatrix} a'_1 \\ a'_2 \\ a'_3 \end{pmatrix} = \begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix} \cdot (I + \varepsilon) \tag{4}$$

where ε is the strain tensor. This links with the strain vector e by

$$\varepsilon = \begin{pmatrix} e_1 & \frac{e_6}{2} & \frac{e_5}{2} \\ \frac{e_6}{2} & e_2 & \frac{e_4}{2} \\ \frac{e_5}{2} & \frac{e_4}{2} & e_3 \end{pmatrix}. \tag{5}$$

In the calculation of the elastic constants for the cubic phase, we apply the tri-axial shear strain $e = (0, 0, 0, \delta, \delta, \delta)$ to the crystal. Then, C_{44} can be calculated from

$$\frac{\Delta E}{V} = \frac{3}{2} C_{44} \delta^2. \tag{6}$$

Similarly, the shear modulus $C' = \frac{1}{2}(C_{11} - C_{12})$ is calculated from the volume-conserving orthorhombic strain $e = (\delta, \delta, (1 + \delta)^{-2} - 1, 0, 0, 0)$ by using

$$\frac{\Delta E}{V} = 6C' \delta^2 + O(\delta^3). \tag{7}$$

The bulk modulus B can be obtained by using the strain under hydrostatic pressure $e = (\delta, \delta, \delta, 0, 0, 0)$:

$$\frac{\Delta E}{V} = \frac{9}{2} B \delta^2. \tag{8}$$

Then C_{11} and C_{12} are hence given by

$$C_{11} = \frac{3B + 4C'}{3}, \tag{9}$$

$$C_{12} = \frac{3B - 2C'}{3}. \tag{10}$$

The calculation of the elastic constants for the hexagonal phases is a little more arduous. Firstly, one applies the strain $e = (\delta, \delta, 0, 0, 0, 0)$ to calculate $C_{11} + C_{12}$:

$$\frac{\Delta E}{V} = (C_{11} + C_{12})\delta^2. \tag{11}$$

Then $C_{11} - C_{12}$ is calculated using the strain $e = (0, 0, 0, 0, 0, \delta)$:

$$\frac{\Delta E}{V} = \frac{1}{4}(C_{11} - C_{12})\delta^2. \tag{12}$$

C_{33} can be obtained by using the strain $e = (0, 0, \delta, 0, 0, 0)$:

$$\frac{\Delta E}{V} = \frac{1}{2}C_{33}\delta^2. \tag{13}$$

Also, C_{44} can be obtained by using the strain $e = (0, 0, 0, \delta, \delta, 0)$:

$$\frac{\Delta E}{V} = C_{44}\delta^2. \tag{14}$$

Under the condition of hydrostatic pressure, $e = (\delta, \delta, \delta, 0, 0, 0)$, the bulk modulus, $B = \frac{2}{9}(C_{11} + C_{12} + 2C_{13} + C_{33}/2)$, is calculated:

$$\frac{\Delta E}{V} = \frac{9}{2}B\delta^2. \tag{15}$$

Therefore, C_{13} is determined.

In this study, firstly 21 sets of $\Delta E/V \sim \delta$ data for each phase were obtained from PW-PP calculations by varying δ from -0.02 to 0.02 in steps of 0.002. These data were fitted by using a quadratic polynomial and then the relevant elastic constant was acquired from the coefficient of the quadratic term in the corresponding equations (6)–(15). As an example, the computational procedures for the elastic constants of lonsdaleite Si are illustrated in figure 1. We found that the coordinate optimization of ions in the strained lattice is quite important for achieving accurate results. The coordinate optimization of ions in the strained lattice is realized using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) minimization algorithm by taking into account the total energy as well as the gradients [18].

In the theoretical calculations of elastic constants we used a plane-wave energy cutoff of 50.0 hartree and $4 \times 4 \times 4$ and $4 \times 4 \times 2$ Brillouin zone samplings, respectively, for the diamond and lonsdaleite phases. These values will retain errors in the total energy of 0.001 hartree. In studies of the stability of the structures, the differences in energy between various crystallographic configurations are usually quite small. Therefore, the cohesive energies of cubic and hexagonal phases are calculated using a higher plane-wave energy cutoff of 100 hartree, together with $8 \times 8 \times 8$ and $10 \times 10 \times 6$ Brillouin zone samplings, respectively, for the diamond and lonsdaleite phases, to guarantee a consistent error in the total energy of 0.0001 hartree.

3. Numerical results

3.1. Elastic constants

Although experimental data for all the diamond phases of C, Si and Ge are available nowadays, we also calculated the theoretical elastic constants of these cubic phases as the first step in the
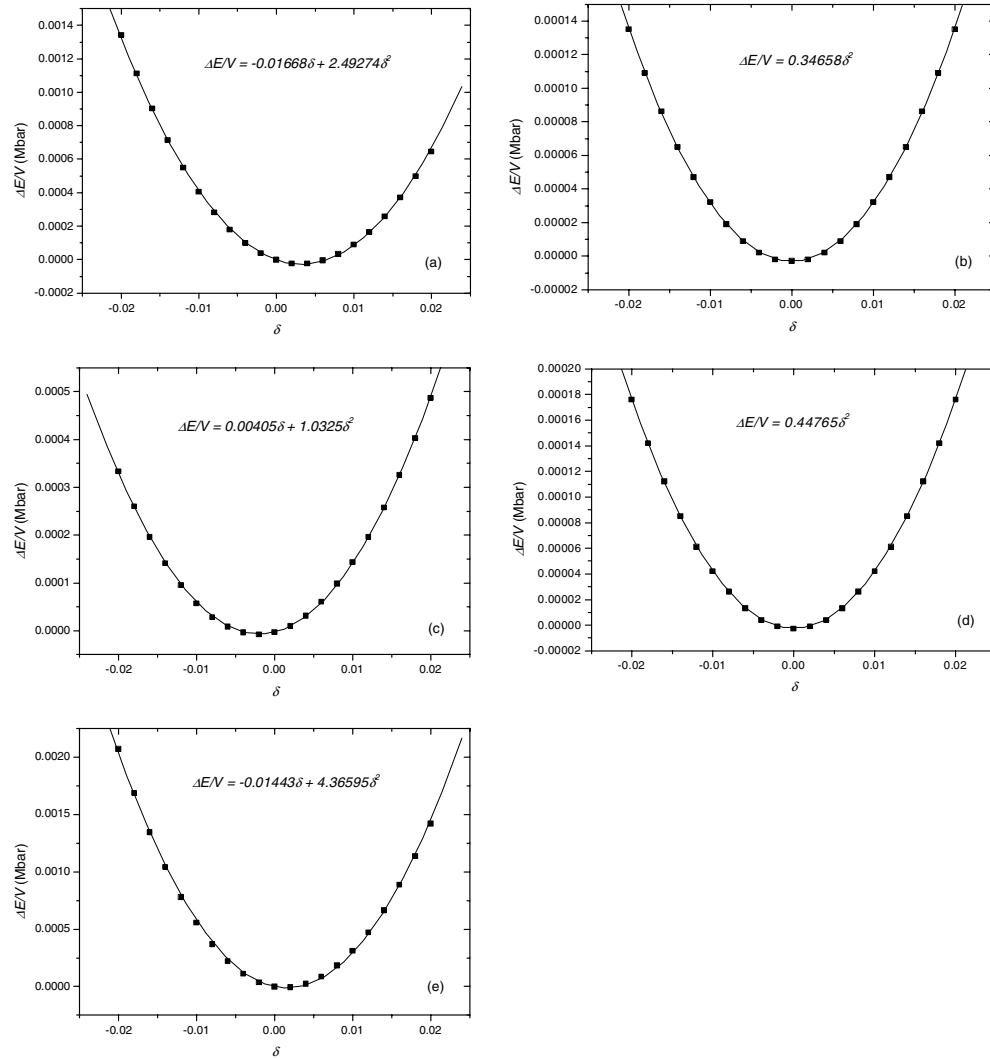
Figure 1. The calculation of the elastic constants of Lonsdaleite Si from the PW-PP ground-state results under various strains: (a) $C_{11} + C_{12}$; (b) $C_{11} - C_{12}$; (c) C_{33}; (d) C_{44}; and (e) bulk modulus B.

present study. The reasons are twofold. Firstly, by comparing theoretical and experimental data we can judge the applicability of the pseudopotentials in the present case. Secondly, we can also test the methodological feasibilities of lattice deformation and ion-coordinate optimization used in this work. We found that, without coordinate optimization, the results of the determination of some elastic parameters may have an error as much as several tens of per cent.

The calculated elastic constants for the cubic diamond phases of C, Si, Ge and zincblende SiC are presented in table 1. The equilibrium geometries of diamond C, Si, Ge and zincblende SiC can be found elsewhere [4, 17]. It is seen that the errors between our theoretical results and the experimental results are generally within 5.0%, except for C_{12} of diamond C, which has the much big error of 15.2%. The origin can be understood since C_{11} and C_{12} are determined

Table 1. The elastic constants of diamond C, Si, Ge and zincblende SiC (in Mbar). The value in parenthesis is the error (in per cent) of our theoretical result compared to the experimental data.

	C_{11}		C_{12}		C_{44}		
	PW-PP	Exp.	PW-PP	Exp.	PW-PP	Exp.	C'
C	10.996(1.9)	10.79 [19]	1.428(15.2)	1.240 [19]	5.870(1.6)	5.780 [19]	4.784
Si	1.620(−2.4)	1.660 [20]	0.628(−1.9)	0.640 [20]	0.772(−3.0)	0.796 [20]	0.496
Ge	1.285(2.0)	1.260 [20]	0.457(3.9)	0.440 [20]	0.668(−1.3)	0.677 [20]	0.414
SiC	4.043		1.377		2.556		1.333

using associated methods, for both theoretical calculation and experiment. Since the value of C_{11} is about eight times larger than that of C_{12}, the larger numerical error is consequently hard to avoid in the determination of C_{12}.

The theoretical elastic constants of lonsdaleite C, Si and Ge from our PW-PP calculations are given in table 2. Both the calculated and available experimental elastic constants of hexagonal 6H–SiC are also listed to provide a qualitative evaluation of the reliability of the present calculations. The PW-PP optimized lattice parameters of 6H–SiC in the calculation are $a = 0.3049$ nm and $c = 1.4956$ nm, respectively. The theoretical lattice parameters of lonsdaleite C, Si and Ge were accepted from [17]. It is seen that the errors between our theoretical data and the experimental data for 6H–SiC fall within a reasonable range of −3.9 to 7.8%.

Figure 1 shows the existence of linear terms for the $\Delta E / V \sim \delta$ relations in the calculation of $C_{11} + C_{12}$, C_{33} and B. This means that the optimization procedure for the lattice parameters in the previous study [17] is not perfect. From the relation $\Delta E / V = -0.0144\delta + 4.365\,95\delta^2$ for the bulk modulus B, one obtains an energy minimum at $\delta \approx 0.001\,65$. This indicates an approximate error of about 0.165% for the published lattice parameters of lonsdaleite Si [17] compared to the accurate equilibrium values.

3.2. Stability of structure

The relative stability of the structure of solids can be measured directly from the difference in cohesive energy of the relevant phases. Plentiful information is also incorporated in their elastic parameters. The Zener anisotropy factor A is an indicator of the degree of anisotropy in the solid structure compared to the isotropic material. This can be calculated from the elastic constants of the cubic phase:

$$A = \frac{2C_{44}}{C_{11} - C_{12}}. \tag{16}$$

The procedure for the coordinate optimization of ions releases internal strain in the deformed lattice configuration. From those optimized coordinates, the Kleinman internal-strain parameter ζ [22] can be calculated as

$$\zeta = \frac{(1 + \delta)r_0 - r}{r_0\delta} \tag{17}$$

where r and r_0 are the distances between the two sub-lattices with and without strain, respectively.

Table 3 lists the PW-PP calculated data of the difference in cohesive energy $\Delta E_{\text{H−C}}$ between hexagonal and cubic phases, the Zener anisotropy factor A, and the Kleinman internal-strain parameter ζ of C, Si, Ge and 6H–SiC phases. Here, A and ζ are calculated from the

Table 2. The elastic constants of lonsdaleite C, Si and Ge (in Mbar). The theoretical and experimental elastic constants of hexagonal 6H–SiC are also listed to provide an evaluation of the qualitative reliability of the present calculations. Here, $C_{66} = (C_{11} - C_{12})/2$.

	C_{11}		C_{12}		C_{13}		C_{33}		C_{44}		C_{66}		
	PW-PP	Exp.	PW-PP	Exp.	PW-PP	Exp.	PW-PP	Exp.	PW-PP	Exp.	PW-PP	Exp.	B
C	12.225		1.068		0.475		13.263		4.594		5.578		4.639
Si	1.940		0.553		0.420		2.065		0.448		0.693		0.970
Ge	1.556		0.375		0.277		1.693		0.411		0.591		0.740
6H–SiC	5.273	5.01 [21]	1.067	1.11 [21]	0.559	0.52 [21]	5.631	5.53 [21]	1.654	1.63 [21]	2.103	1.95 [21]	2.283

Table 3. Some structure and mechanical parameters for C, Si, Ge and SiC phases.

	A	ζ	ΔE_{H-C} (meV)
C	1.227	0.107	51.7
Si	1.556	0.533	21.1
Ge	1.614	0.481	33.2
SiC	1.917	0.392	−2.0

elastic parameters of their respective cubic phases. Due to the inequality in the number of atoms in the unit cells of the cubic and hexagonal phases, the difference in cohesive energy ΔE_{H-C} between the two poly-types is given for a pair of dissimilar atoms. It can be seen that all the lonsdaleite phases of C, Si and Ge have higher cohesive energies than their corresponding diamond phases, indicating that the diamond configuration is more stable. This is consistent with the fact that the cubic phases of these elements are more easily fabricated. The table also shows that 6H–SiC is more favoured than zincblende SiC from the viewpoint of energy, as is found by experiment. Carbon has the largest energy difference between its two poly-types. The energy differences of Ge, Si and SiC decrease progressively. A small energy difference may cause a variation in lattice configuration. This explains the vast diversity in SiC and silicon poly-types found to date. The Kleinman parameter of cubic C is the smallest, indicating that the phase has quite a large resistance to bond bending. Materials with larger Zener anisotropy factor tend to differ from cubic configuration, as is seen for SiC. The present results suggest that the lonsdaleite phases of Si and Ge should be easier to prepare than the lonsdaleite phase of C.

4. Conclusions

In conclusion, the elastic constants of lonsdaleite C, Si and Ge have been obtained by using first-principles PW-PP calculations. The reliability of the theoretical data and the calculation procedure are evaluated in detail compared to various experimental results. The stability of the structure and other relevant properties of these lonsdaleite phases are also investigated.

Acknowledgments

References

[1] Kim K, Lambrecht W R L and Segall B 1996 *Phys. Rev.* B **53** 16310
[2] Mehl M J, Osburn J E, Papaconstantopoulos D A and Klein B M 1990 *Phys. Rev.* B **41** 10311
[3] Mehl M J 1993 *Phys. Rev.* B **47** 2493
[4] Wang S Q and Ye H Q 2002 *Phys. Rev.* B **66** 235111
[5] Cheng D Y, Zhao S J, Wang S Q and Ye H Q 2001 *Phil. Mag.* A **81** 1625
[6] Winkler B, Pickard C J, Milman V, Klee W E and Thimm G 1999 *Chem. Phys. Lett.* **312** 536
[7] Zhang Y, Iqbal Z, Vijayalakshmi S, Qadri S and Grebel H 2000 *Solid State Commun.* **115** 657
[8] Silinskas M and Grigonis A 2002 *Diamond Relat. Mater.* **11** 1026
[9] Goswami R, Sampath S, Herman H and Parise J B 1999 *J. Mater. Res.* **14** 3489
[10] Kim J H and Lee J Y 1997 *Thin Solid Films* **292** 313

[11] Tan T Y, Foll H and Hu S M 1981 *Phil. Mag.* A **44** 127

[12] Parisini A and Bourret A 1993 *Phil. Mag.* A **67** 605

[13] Cerva H 1991 *J. Mater. Res.* **6** 2324

[14] Xiao S Q and Pirouz P 1992 *J. Mater. Res.* **7** 1406

[15] Gonze X, Beuken J M, Caracas R, Detraux F, Fuchs M, Rignanese G M, Sindic L, Verstraete M, Zerah G, Jollet F, Torrent M, Roy A, Mikami M, Ghosez P, Raty J Y and Allan D C 2002 *Comput. Mater. Sci.* **25** 478

[16] Hartwigsen C, Goedecker S and Hutter J 1998 *Phys. Rev.* B **58** 3641

[17] Wang S Q and Ye H Q 2003 *J. Phys.: Condens. Matter* **15** L197

[18] Schlegel H B 1982 *J. Comput. Chem.* **3** 214

[19] McSkimin H J and Andreatch P 1972 *J. Appl. Phys.* **43** 2944

[20] Dargys A and Kundrotas J 1994 *Handbook on Physical Properties of Ge, Si, GaAs and InP* (Vilnius: Science and Encyclopedia Publishers)

[21] Kamitani K, Grimsditch M, Nipko J C, Loong C K, Okada M and Kimura I 1997 *J. Appl. Phys.* **82** 3152

[22] Kleinman L 1962 *Phys. Rev.* **128** 2614