

# A family of low-energy low-density silicon allotropes built from the diamond structure

L. PIZZAGALLI

*Institut P', CNRS UPR 3346, Université de Poitiers, SP2MI - BP 30179, Boulevard Marie et Pierre Curie, 86962 Futuroscope Chasseneuil Cedex, France*

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**Abstract** – First-principles calculations have been performed to investigate structural and energetic properties of a family of silicon allotropes, built from the cubic diamond structure. These phases are characterized by a lower density compared to silicon diamond, and low relative energies ranging from 0.067 eV/at. to 0.089 eV/at. only. One of its members, the  $L1_{\beta}$  phase, is shown to become more stable than the diamond structure for hydrostatic tensile pressure of 7.5 GPa. Its low density and the presence of 8-fold rings in the structure also suggest that it might have potential use as a lithium container.



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Recent years have witnessed an intense research activity regarding carbon allotropes, with the aim to discover new materials exhibiting specific properties like high hardness [1–4]. Hence, a large number of new phases have been proposed over the last few years, especially with the use of state-of-the-art prediction techniques [5,6]. Many of these phases exhibit  $sp^3$  bonding, which makes them suitable allotrope candidates for silicon, too. Using first-principles calculations, few groups have investigated the stability and other properties of several of these possible structures [7–10]. The results indicate that all these phases are stable, with energy differences ranging from 0.06 to 0.16 eV/at. compared to the most stable cubic diamond structure. These hypothetical materials may have potential uses in photovoltaic applications [9], or as high-capacity lithium container in battery [8].

It is well documented how several metastable silicon phases can be obtained by first applying a hydrostatic pressure on the cubic diamond structure. In fact, the metallic  $\beta$ -tin is already formed at about 12 GPa, followed by the *Imma* and *Cmcm* phases [11]. In addition, pressure release from  $\beta$ -tin leads to several metastable structures depending on the conditions, such as R8 and BC8 [12,13]. All these phases are characterized by a larger density than in cubic diamond. It is interesting to note that most of the recently proposed allotropic phases exhibit a lower density instead [7–10]. One might then assume that such structures could be obtained by applying

a hydrostatic tensile pressure, although it remains unclear how such a feat could be achieved. For instance, Bautista-Hernández *et al.* predicted that M-Si and bct-Si would be more stable than cubic diamond for tensile pressures of 11.3 GPa and 12.3 GPa, respectively [10]. Then one may wonder whether it could be possible to find other silicon phases which could be stable at lower pressure. The Si-46 clathrate is predicted to be more stable than the diamond phase at a tensile pressure of 6 GPa [14], but its quite different topology makes a direct transition from diamond-related structures very unlikely.

Following an analysis of the cubic diamond structure and optimized by first-principles calculations, a family of low-energy low-density phases is described in this paper. These structures are characterized by two narrowly spaced layers along the  $\langle 111 \rangle$  cubic phase direction, plus a variable number of additional layers of fully hybridized  $sp^3$  atoms. The resulting energies range from 0.067 eV/at. to 0.089 eV/at., and the densities from 93% to 97%, relative to the diamond phase. The structures with the smallest elementary cells are shown to become more stable than the cubic phase for tensile hydrostatic pressures greater than about 7.5–7.6 GPa.

Calculations were performed in the framework of the density functional theory [15,16], using the PWscf package of the Quantum Espresso project [17]. The Perdew-Burke-Ernzerhof functional [18] was used for describing exchange-correlation contributions, and electron-ion

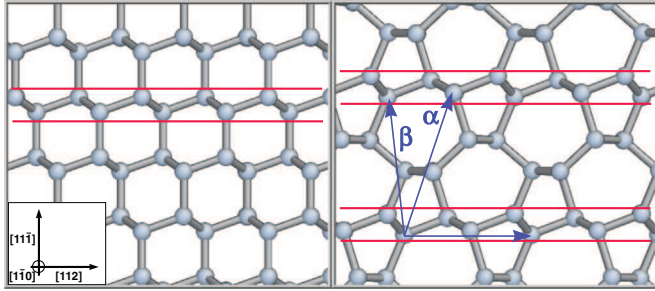


Fig. 1: (Color online) Cubic diamond (left) and  $L2_\beta$  (right). The red horizontal lines frame a structural unit including two inequivalent layers, which is repeated along the  $[11\bar{1}]$  direction to form the cubic diamond structure. The  $L2_\beta$  phase includes two additional layers between this unit along the same orientation. There are two possible ways to repeat the stacking, with a  $\frac{1}{2}[1\bar{1}0]$  shift ( $\beta$ ) or not ( $\alpha$ ).

interactions were modelled using an ultrasoft pseudopotential [19] from the Quantum Espresso repository [20]. A plane-wave cut-off of 30 Ry and 500 irreducible  $k$ -points were found to be largely sufficient to obtain well-converged forces and energies. Ions coordinates and cells geometry were optimized using the Broyden-Fletcher-Goldfarb-Shanno algorithm.

The new phases discussed in this work were built from the cubic diamond structure. Considering the orientations shown in fig. 1, the latter can be viewed as the stacking of a structural unit containing two inequivalent  $(111)$  layers (framed by the red horizontal lines). In the new proposed phases, additional layers composed of fully hybridized  $sp^3$  atoms are introduced between each structural unit. According to how the periodicity is recovered, two possible structures, denoted by  $\alpha$  and  $\beta$ , can be obtained (see fig. 1). The new phases are designated by “ $L n_{\alpha/\beta}$ ”, “L” for “Layered” and  $n$  being the number of additional layers.

Relaxed structures for  $n$  ranging from 1 to 4 are shown in fig. 2. They are characterized by 5-fold and 7-fold rings at the junction between the preserved cubic diamond layers and the additional ones, except for the  $L1_{\alpha/\beta}$  phases for which 5-fold and 8-fold rings are obtained. Between additional layers, 6-fold rings are present. A careful review of the existing literature reveals that the  $L2_\beta$  phase is the so-called M-phase and has already been studied for carbon [1,3] and silicon [8–10]. Also, the  $L2_\alpha$  phase is equivalent to the M-10 structure [9,21]. It seems that the other  $L n_{\alpha/\beta}$  phases have not been previously described. It is important to emphasize here that because of the way these new structures are built and the low symmetry, there is no need to perform phonon calculations to check for dynamical stability. In fact, the structures were obtained after a significant number of relaxation steps, with non negligible displacements of all atoms, confirming they are metastable.

Tables 1 and 2 report structural information about all the structures, as well as their energies relative to the most

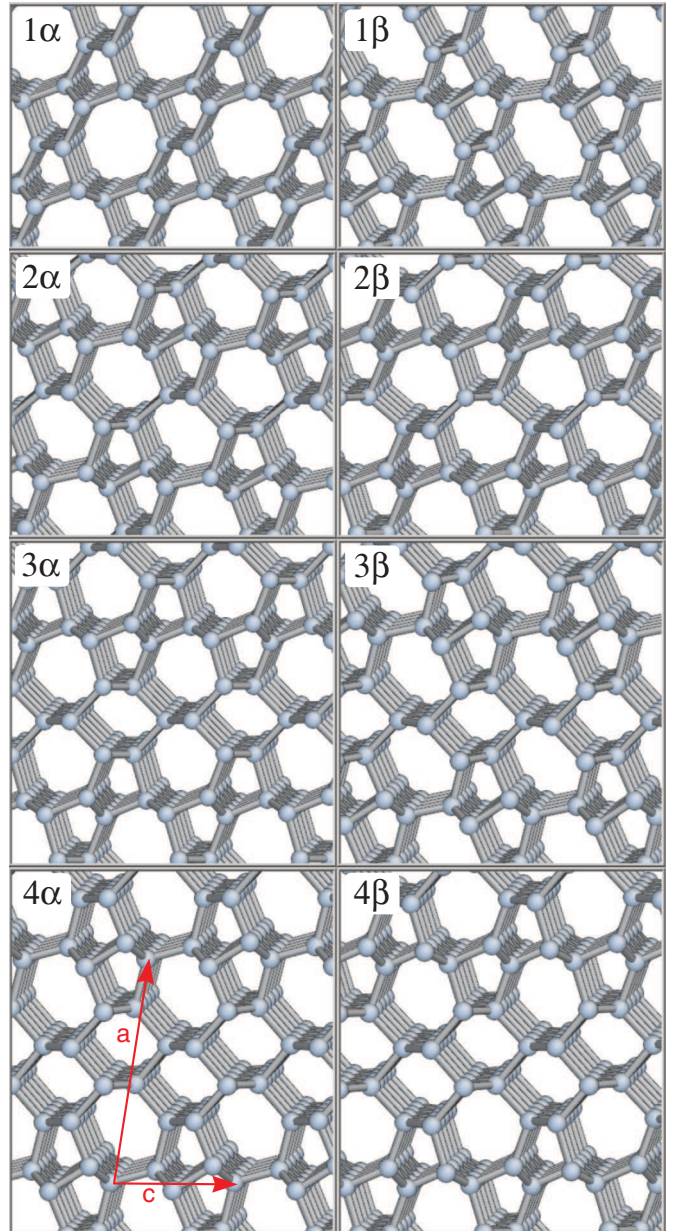


Fig. 2: (Color online) Optimized structures of the  $L n_{\alpha/\beta}$  phases investigated in this work.

stable cubic diamond phase, their bulk moduli obtained by fitting the energy-volume relation (fig. 3) with a 3rd-order Birch-Murnaghan equation, and the DFT-PBE computed band gap. It is noteworthy that all  $L n_\beta$  phases are triclinic and belong to the  $C2/m$  space group.  $L n_\alpha$  phases are all monoclinic, but belong to different space groups. In fact,  $L1_\alpha$  is in the  $Cmcm$  group.  $L2_\alpha$  and  $L4_\alpha$  are in the  $P2/m$  space group, while  $L3_\alpha$  is in the  $P2_1/m$  group.

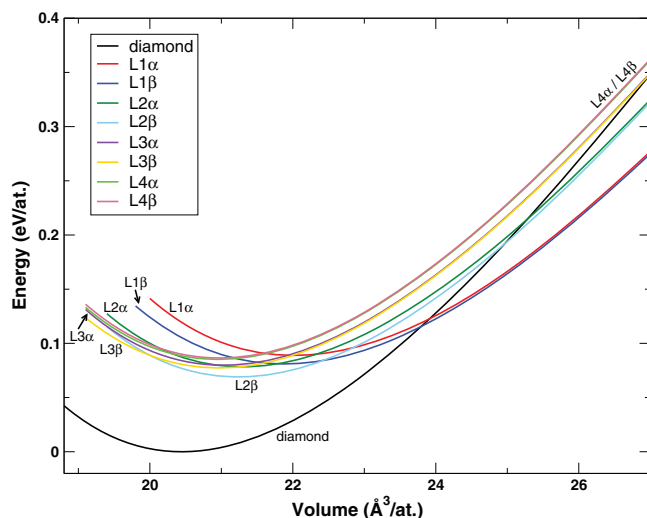
Concerning density, all phases are less dense than the cubic diamond structure, with atomic volumes of about 2.5% to 7.7% greater. Smallest differences are obtained for  $L n_{\alpha/\beta}$  phases with the largest “ $n$ ”, while the lowest densities are associated with the  $L1_{\alpha/\beta}$  structures. This

Table 1: Cell parameters, volume, energy relative to the cubic diamond phase, bulk modulus, and DFT-PBE band gap for the different structures reported in this work.

Structure	$a$ (Å)	$b$ (Å)	$c$ (Å)	$\beta$ (°)	$V$ (Å <sup>3</sup> /at.)	$\Delta E$ (eV/at.)	$B$ (GPa)	Gap (eV)
Cubic dia.	5.468	5.468	5.468	90	20.437	0.0	89.1	0.67
L1 $\alpha$	11.964	3.845	5.743	90	22.017	0.089	77.9	0.83
L1 $\beta$	10.755	3.859	6.579	105.99	21.869	0.081	74.7	1.00
L2 $\alpha$	7.262	3.869	6.300	105.84	21.288	0.078	79.8	0.98
L2 $\beta$	13.911	3.865	6.364	96.86	21.233	0.069	80.9	0.55
L3 $\alpha$	9.127	3.866	6.167	104.96	21.022	0.080	80.3	0.60
L3 $\beta$	17.882	3.877	6.112	96.38	20.961	0.077	78.3	0.87
L4 $\alpha$	10.981	3.877	5.987	99.57	20.948	0.085	80.3	0.59
L4 $\beta$	21.620	3.869	6.031	93.95	20.969	0.086	81.3	0.35

Table 2: Space group and Wickoff positions for the different structures reported in this work (obtained using the FINDSYM utility [22]).

Group	Wickoff positions
L1 $_{\alpha}$ $Cmcm$ (63)	c (0, -0.056, 1/4) g (0.2063, 0.305, 1/4)
L1 $_{\beta}$ $C2/m$ (12)	i (0.0176, 0, 0.18433) i (-0.44, 0, -0.31715)
L2 $_{\alpha}$ $P2/m$ (10)	i (-0.23813, 0, -0.39036) m (0.16673, 0, -0.04158) m (0.1741, 0, -0.37826) n (-0.36583, 1/2, -0.08057)
L2 $_{\beta}$ $C2/m$ (12)	n (-0.3953, 1/2, 0.38831) i (-0.2270, 0, -0.08561) i (-0.2871, 0, -0.4429) i (0.44432, 0, -0.37416) i (0.05923, 0, 0.1536)
L3 $_{\alpha}$ $P2_1/m$ (11)	e (0.10374, 1/4, 0.03562) e (0.41258, 1/4, -0.06052) e (0.1135, 1/4, 0.49473) e (0.45758, 1/4, -0.30952)
L3 $_{\beta}$ $C2/m$ (12)	e (0.30671, 1/4, 0.29726) i (0.01344, 0, 0.18931) i (-0.4646, 0, -0.32661) i (-0.24551, 0, -0.11369) i (-0.14613, 0, -0.3398)
L4 $_{\alpha}$ $P2/m$ (10)	i (0.34321, 0, 0.42527) m (0.17555, 0, -0.02727) m (0.10376, 0, 0.41334) m (-0.20971, 0, 0.2442) n (-0.35356, 1/2, -0.05477) n (-0.44141, 1/2, 0.25385)
L4 $_{\beta}$ $C2/m$ (12)	n (0.34389, 1/2, 0.41596) i (-0.23379, 0, -0.08251) i (-0.27428, 0, -0.44102) i (-0.45774, 0, -0.35896) i (-0.37615, 0, 0.39727) i (0.12679, 0, 0.16346) i (0.0431, 0, -0.11982)


Fig. 3: (Color online) Energy vs. atomic volume for the  $Ln_{\alpha/\beta}$  phases, relative to the cubic diamond energy, obtained from constant-pressure calculations.

could be explained by the decreasing relative proportion of 7-fold rings in the structure for increasing “ $n$ ”. It is more difficult to understand why the more stable member of the  $Ln_{\alpha/\beta}$  family is  $L2_{\beta}$ , with  $\Delta E = 0.069$  eV/at. One explanation could be that layers added between cubic diamond structural units are slightly strained, about 1% compared to the ideal diamond silicon. Then it becomes less and less energetically favorable to increase the number of additional layers. Besides, the presence of several additional layers help to reduce bond distortions associated with 5-fold and 7-fold rings. It is then likely that the  $L2_{\beta}$  corresponds to the best compromise. Bulk moduli are typically in the range 78–81 GPa, thus about 10% lower than the diamond value. Although a bulk modulus is not *stricto sensu* a measure of hardness, these reduced values suggest that  $Ln_{\alpha/\beta}$  phases are softer than the diamond phase as expected. This is probably due to the presence of 5-fold and 7-fold rings. Finally, DFT-PBE calculations revealed that several of the  $Ln_{\alpha/\beta}$  phases, especially  $L1_{\beta}$  and  $L2_{\alpha}$ , are characterized by band gaps larger than for cubic diamond. Additional calculations, for instance in



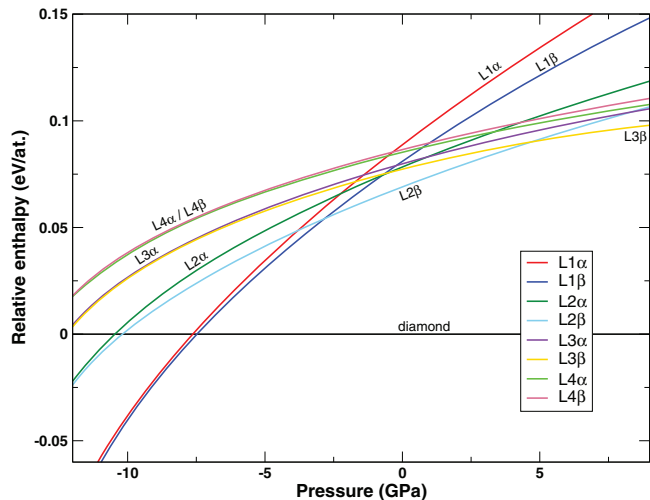


Fig. 4: (Color online) Enthalpy *vs.* hydrostatic pressure for the  $Ln_{\alpha/\beta}$  phases, relative to the cubic diamond structure. Negative pressure values indicate a tensile behavior.

the GW framework, would be required to obtain quantitatively meaningful values though.

These results are in excellent agreement with previous investigations of the silicon M and M-10 phases, which are equivalent to the  $L2_{\alpha/\beta}$  structures. The structural parameters are close to those reported by Wu *et al.* [8], while the energy differences are the same as previous values calculated using the generalized gradient approximation [8,9]. However, local density approximation calculations yield lower dimension values, as expected, but also a larger energy difference of 0.1 eV [10].

Figure 4 represents the enthalpy variation as a function of the applied pressure. Previous investigations revealed that the M phase (the  $L2_{\beta}$  here) would be favored over the cubic diamond phase for hydrostatic tensile pressures larger than 11.3 GPa [10]. The transition pressure computed in this work is 10.2 GPa, the difference being likely due to the use of different exchange-correlation functionals. Surprisingly, another member of the  $Ln_{\alpha/\beta}$  family is favored over diamond for even lower pressure. In fact, a negative relative enthalpy is obtained for the  $L1_{\beta}$  and  $L1_{\alpha}$  phases for tensile pressures of 7.5 and 7.6 GPa, respectively. This is lower than the computed theoretical tensile strength of silicon, computed in this work to be 13 GPa.  $L1_{\alpha/\beta}$  phases are characterized by low relative energies and large volumes at zero pressure, in addition to low bulk moduli which allows for large volumic changes under pressure. This is especially true for the  $L1_{\beta}$  phase.

Obviously, it is easier to conceive pressure-assisted phase transformations in compression than in tension, and it is not clear whether and how phases like  $L1_{\beta}$  could be ever synthesized. Nevertheless, several characteristics of this structure makes its formation not fully unrealistic. In fact, this phase includes few atoms in its elementary cell, and its topology is close to the one of several other silicon allotropes, unlike clathrates for instance. Formation from

other metastable phases is then one option. Recently, it has been suggested that growth on a substrate with the appropriate lattice mismatch could be another option [7]. The  $Ln_{\alpha/\beta}$  phases share with the cubic diamond lattice two layers along the  $\langle 111 \rangle$  direction, a common growth orientation. But even if it seems possible to find an appropriate substrate, with a lattice mismatch corresponding to the required in-plane tensile stress, one may wonder how an out-of-plane tensile stress of several GPa could be applied. Another possible formation route could come from the transformation from higher-energy metastable phases such as R8 or BC8. Finally, a last option could rely on the addition of foreign atoms. In fact, recent calculations indicated that the insertion of lithium in low-density silicon allotropes would be easier than in the diamond structure [8]. The stability of these allotropic phases relative to silicon diamond could then be greatly enhanced, maybe with no need for tensile pressure. The  $L1_{\alpha/\beta}$  would be ideal candidates, since they are characterized by the lowest density of the  $Ln_{\alpha/\beta}$  phases, and the presence of large 8-fold rings which could potentially encompass several Li atoms. Further calculations are clearly needed to explore this aspect.

In summary, a new family of silicon allotropes, built from the cubic diamond structure, is proposed in this work. Structural and basic properties have been computed using first-principles calculations. Among the different phases presented in this work, the  $L1_{\beta}$  is found to become more stable than the diamond phase for hydrostatic tensile pressures of 7.5 GPa. The large computed atomic volume also suggests that the stability of this phase could be further increased by Li insertion. The potentiality of this phase as a possible candidate for structures observed during compression of graphitic carbon, or for photovoltaic applications in silicon-based materials [9] remains to be further investigated.

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