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Abstract. Carbon substitution in bulk silicon has been investigated using the super-cell approach, in conjunction with the periodic *ab initio* Hartree–Fock method. The convergence of the defect formation energy and of the relaxed defect geometry as a function of the super-cell size is discussed with reference to super-cells containing 8, 16, 32 and 64 atoms.

It turns out that the convergence of the *unrelaxed* defect formation energy is rapid, in spite of the large local charge redistribution around the defect (the net charge on carbon is $1.2|e|$); the relaxation effects are very large (about 2.0 eV) and involve mainly the first and second neighbours; however, the relaxation of the fifth neighbours of the defect (which is possible only with the biggest super-cell considered) lowers the energy by a further 0.06 eV. The defect formation energy and the atomic displacements obtained with the 32 and 64 atoms super-cells are similar, whereas the energy difference between the 16 and 32 atoms cells is as large as 0.4 eV.

1. Introduction

The super-cell (SC) approach is probably the most widely adopted scheme for the study of local defects in bulk [1–8]. It is also used in the study of chemisorption at the surface of crystalline compounds [9, 10], where the semi-infinite substrate is simulated by a slab periodic in the two directions parallel to the surface.

In the SC scheme, a periodic array is build from a unit cell which contains the defect at the centre; the larger the unit cell, the smaller the interaction between the defects, and the higher the computational cost.

The most appealing feature of the SC scheme is that periodic *ab initio* (or *first-principle*) programs implemented for the study of perfect crystals can be used; all the technology implemented in the last twenty years for *ab initio* periodic calculations is also exploitable for the study of local defects.

There are two kinds of limitation which correspond to two different levels of complexity: (A) the super-cell size must be such as to contain the 'perturbed zone', that is all the atoms involved in the ionic and electronic relaxation; (B) the distance between the defects must be large enough to reduce their electrostatic interaction to negligible values; two (B) sub-cases must be distinguished, according to whether the defect is neutral (B1) or not (B2).

For neutral defects (B1), the SC scheme is expected to converge to the isolated defect limit with 'reasonable' speed; in the following, we shall try to determine quantitatively how fast energies and geometries converge.

In the case of charged defects (B2), the electrostatic energy of the super-cell diverges (infinite array of charged cells), and 'tricks' must be adopted in order to (i) neutralize the unit cell, and (ii) cancel the interaction between the neutralized defects. The treatment of charged defects within the SC formalism presents more theoretical problems than neutral defects; only partial and *ad hoc* solutions have been proposed (see for instance the corrective scheme proposed in [5] and used in [7]).

As regards problems (A) and (B1), up to now most SC calculations have been performed with relatively small cells (8, 16 or 32 atoms), and in only a few cases has the stability of results been checked with respect to the SC size; therefore, no general conclusion can be drawn, both because the number of SCs explored is too small and because, in most cases, the calculations referring to different SCs have been performed in different conditions. An example is the calculation of De Vita *et al* [7] concerning vacancies in MgO; SCs containing 16 and 32 atoms (to be indicated in the following as S16 and S32) have been considered; in the first case, an energy cut-off of 1000 eV has been used in the plane wave expansion, whereas the cut-off was 600 eV for the larger SC; as a consequence, the quality of the basis set is not the same for the two sets of calculations; the total energy per molecular unit of the perfect system evaluated with S16 and S32 differs by as much as 2.3 eV, although energy differences (defect formation energy; energy relaxation around the defect) are claimed to be affected to a much lower degree by basis set effects.

As a matter of fact, no clear evidence has been given till now of the speed of convergence of the defect formation energy, relaxation effects and charge redistributions as a function of the SC size in different kinds of compounds (ionic, covalent, metallic systems).

The aim of the present paper is to study convergence trends of the SC results in a covalent system, when a relatively large perturbation is introduced. Carbon has a higher electronegativity than silicon, so that a large charge transfer is to be expected (the Mulliken net charge in bulk SiC is $\pm 1.81|e|$ [11]). Besides, the covalent radius of carbon is much smaller than that of silicon (the inter-atomic distances are 1.56, 1.90 and 2.36 Å in diamond, SiC and silicon respectively), so a large atomic relaxation is to be expected. The substitution of C in bulk Si is then a good paradigm for the study of the convergence of the SC with size.

Recent improvements in the CRYSTAL code [12] now permit the investigation of super-cells of up to 64 atoms for the system investigated here, and the relaxation up to the fifth neighbours at a relatively low cost and with a basis set of good quality. The accuracy of the code in the treatment of the Coulomb and exchange infinite series, and in the reciprocal space integration is fairly high; the total energy per Si atom of the perfect host system evaluated for S2, S8, S16, S32 and S64 lies always within a range of less than 10^{-5} Hartree (-3.77042 Hartree).

2. Computational details

We refer to previous papers [12–14] for a description of the periodic Hartree–Fock crystalline orbitals (LCAO) self-consistent field computational scheme as implemented in the CRYSTAL92 code [12]. The calculations have been carried out using pseudopotentials [15] for both C and Si atoms; the Gaussian basis set adopted is reported in the appendix; it is a 'split valence plus polarization functions' basis (two sp and one d shell for each atom), which was used in a previous study of bulk C, Si and SiC [16]; atomic and binding energies, lattice parameters and bulk moduli of the three systems are also reported in the appendix.

As regards the computational conditions for the evaluation of the Coulomb and exchange series, the following values have been used for the truncation tolerances as defined in [12]

and [13]: 5, 5, 6, 6, 12. The shrinking factors defining the reciprocal space nets are 4, 4, 4, 2 corresponding to 11, 11, 11, 4 reciprocal space points for which the Fock matrix is diagonalized for S8, S16, S32 and S64 respectively.

All the cells considered maintain the full symmetry of the original crystal (S8 and S64 are simple cubic; S16 is face centred; S32 is body centred). The relaxation around the defect has been studied optimizing the geometrical parameters point by point in subsequent cycles involving first, second, third ... neighbours. Two complete cycles were sufficient to obtain a total energy stable to 5×10^{-4} Hartree/cell with respect to the previous cycle of optimization. The number of stars of neighbours that can be relaxed is 1, 1, 3, 4 for the four SC, from S8 to S64 respectively; it must be noticed that, in S64, the star of the fourth neighbours is not complete within the reference cell, whereas the fifth is complete, so only the latter has been included in the relaxation process.

3. Results and discussion

The energy data are reported in table 2; tables 3 and 4 give information on the relaxed geometry; table 5 reports Mulliken charges and bond population data.

In the following, silicon atoms are labelled with roman numbers I, II, ... to indicate that they are first, second, ... neighbours of the defect atom. Symbols such as Si_1, Si_{11} indicate, on the contrary, first neighbours and first neighbours of the first neighbours of the defect; table 1 shows the relations between the two sets; note that $I = Si_1$, $II = Si_{11}$, but $III \neq Si_{111}$.

Table 1. Composition of the super-cells considered in the present study. N labels the star of the Nth nearest neighbours of the carbon impurity at a distance R (in Å) from it (with no relaxation); there are M of them, M' of which are contained in the reference cell; incomplete stars are marked with an asterisk. The Bonds column indicates to which star(s) the atoms coordinated to an atom in the Nth star belong; for example, in the fourth row 2II–1IV–1VI means that an atom of the third star is linked to two atoms of the second, one of the fourth and one of the sixth star. No atom beyond the sixth star has been considered.

| N | R | M | Bonds | M' | | | |
				S8	S16	S32	S64
0	0.0	1	4I	1	1	1	1
I	2.36	4	10–3II	4	4	4	4
II	3.86	12	1I–2III–1V	3*	6*	12	12
III	4.53	12	2II–1IV–1VI	—	4*	12	12
IV	5.46	6	2III	—	1*	3*	3*
V	5.95	12	1II–2VI	—	—	—	12
VI	6.69	24	2V	—	—	—	12*

The substitutional defect formation energy E_S is defined as follows:

$$E_S = E_C^{SCn} - (n - 1)E_{Si}^{Crys} - E_C^{Crys}$$

where E_C^{SCn}, E_{Si}^{Crys} and E_C^{Crys} are the total energy of the defect super-cell containing $(n - 1)$ Si atoms and the C defect, and the energy per atom of perfect bulk silicon and diamond respectively. If reference is made to the isolated atoms, according to the equation

$$E_S' = E_C^{SCn} - nE_{Si}^{Cryst} - E_C^{at} + E_{Si}^{at}$$

(where E_{Si}^{at} and E_C^{at} are the atomic energies, reported in the appendix), the substitution energies must be shifted downwards by 1.99 eV (2.59 eV for the correlated energies).

In order to understand the relative importance of the electrostatic and covalent effects in the substitution mechanism, it is useful first of all to discuss the results referring to the unrelaxed geometry. The first row in table 2 shows that the substitution energy (E_S) is the same for the four SCs; this is surprising because, in view of the large charge accumulation on the carbon atom, one would expect a relatively large interaction between the 'charged' carbons (the net charge evaluated according to the Mulliken partition is about $0.9|e|$ for the unrelaxed geometry and $1.2|e|$ for the fully relaxed one) belonging to different cells, and this electrostatic interaction should obviously decrease from S8 and S64, producing different E_S.

Table 2. Hartree–Fock substitutional energy E_S (in eV) in bulk silicon as a function of the super-cell size. N is the number of stars of neighbours of the central defect that are allowed to relax. Numbers in parentheses refer to energies corrected for correlation effects (see the text).

	E_S			
N	S8	S16	S32	S64
0	3.93 (4.98)	3.94 (5.00)	3.93 (4.98)	3.92 (4.98)
I	2.86 (3.74)	2.81 (3.68)	2.41	2.42
II	—	—	2.06	2.07
III	—	—	2.06 (2.87)	2.07
V	—	—	—	2.01 (2.83)

Table 3. Relaxation effects in carbon-substituted bulk silicon as a function of the super-cell size. Roman numerals indicate the number N of neighbours of the central defect that are allowed to relax; arabic numerals identify the neighbour that relaxes (for example, the value -0.06 in row III column 2 under the S32 heading gives the relaxation of the second neighbours in S32 when up to the third neighbours are allowed to relax). ΔR is the variation (in Ångström) of the distance R (see table 1) between the defect and its neighbours. Positive ΔR indicates increased distances. The star IV is not fully contained in the reference cell also in S64 (see table 1), so it cannot be relaxed.

					ΔR Super-cell					
		S8	S16	S32			S64			
N	R	1	1	1	2	3	1	2	3	5
I	2.364	−0.19	−0.20	−0.24			−0.24			
II	3.861	—	—	−0.27	−0.06		−0.28	−0.05		
III	4.527	—	—	−0.27	−0.06	0.00	−0.28	−0.05	0.00	
V	5.950	—	—	—			−0.28	−0.05	0.00	−0.02

Table 5 (referring to the relaxed geometry, but the following considerations also apply to the unrelaxed situation) shows, however, that the four Si nearest neighbours of the defect have a positive net charge that compensates to a large extent the negative charge of carbon; the resulting Mulliken net charge of the CSi_4 'cluster' is about $+0.3|e|$. Actually, the energy data show that the compensation is much more effective than the Mulliken charges indicate; this is confirmed by the maps reported in figure 1, where the charge density difference

Table 4. Relaxation effects in carbon-substituted bulk silicon as a function of the super-cell size. Bond lengths D in Å. Si_1 is the nearest neighbour of the defect, Si_{11} is the first-nearest neighbour of Si_1 etc. In the first set of data (I in first column) only the first set of neighbours of the defect are allowed to relax; in the second set (V entry) all the stars of neighbours which are complete in the given cell are relaxed. The unrelaxed Si–Si distance is 2.364 Å. The number of neighbours at the indicated distance is given in parentheses.

		D (A–B) Super-cell			
N	Bond	S8	S16	S32	S64
	$C-Si_1$	2.175(4)	2.166(4)	2.122(4)	2.123(4)
	Si_1-Si_{11}	2.175(1)	2.166(1)	2.122(1)	2.123(1)
		2.434(3)	2.437(3)	2.456(3)	2.455(3)
I					
	$Si_{11}-Si_{111}$	2.434(4)	2.364(2)	2.364(3)	2.364(3)
			2.437(2)	2.456(1)	2.455(1)
	$C-Si_1$			2.090(4)	2.090(4)
	Si_1-Si_{11}	—	—	2.090(1)	2.090(1)
				2.418(3)	2.418(3)
V					
	$Si_{11}-Si_{111}$			2.368(2)	2.363(2)
				2.409(1)	2.384(1)
				2.418(1)	2.418(1)

between the CSi_{n-1} and the Si_n ($n = 8$ and 64) unrelaxed clusters is represented, and in figure 2, where the corresponding electrostatic potential maps are shown. The substituted and unsubstituted clusters have the same number of electrons (we are using pseudopotentials for both C and Si), so the maps represent the charge redistribution due to the substitution (figure 1) and the electrostatic potential so generated (figure 2); the two figures clearly show that the rearrangement of the electronic charge strongly affects the first nearest neighbours of C, whereas second and further neighbours are essentially unaffected.

Table 5. Net atomic charges and Mulliken bond populations of the relaxed super-cells as a function of the super-cell size. Si(I) is the net charge of the silicon atoms belonging to the first star of neighbours of the carbon arom; Si_1-Si_{11} is the bond population (in electrons) between the atoms indicated. The bond population between first neighbours in the perfect crystal is $0.383|e|$. The asterisk indicates that the star of neighbours is not complete.

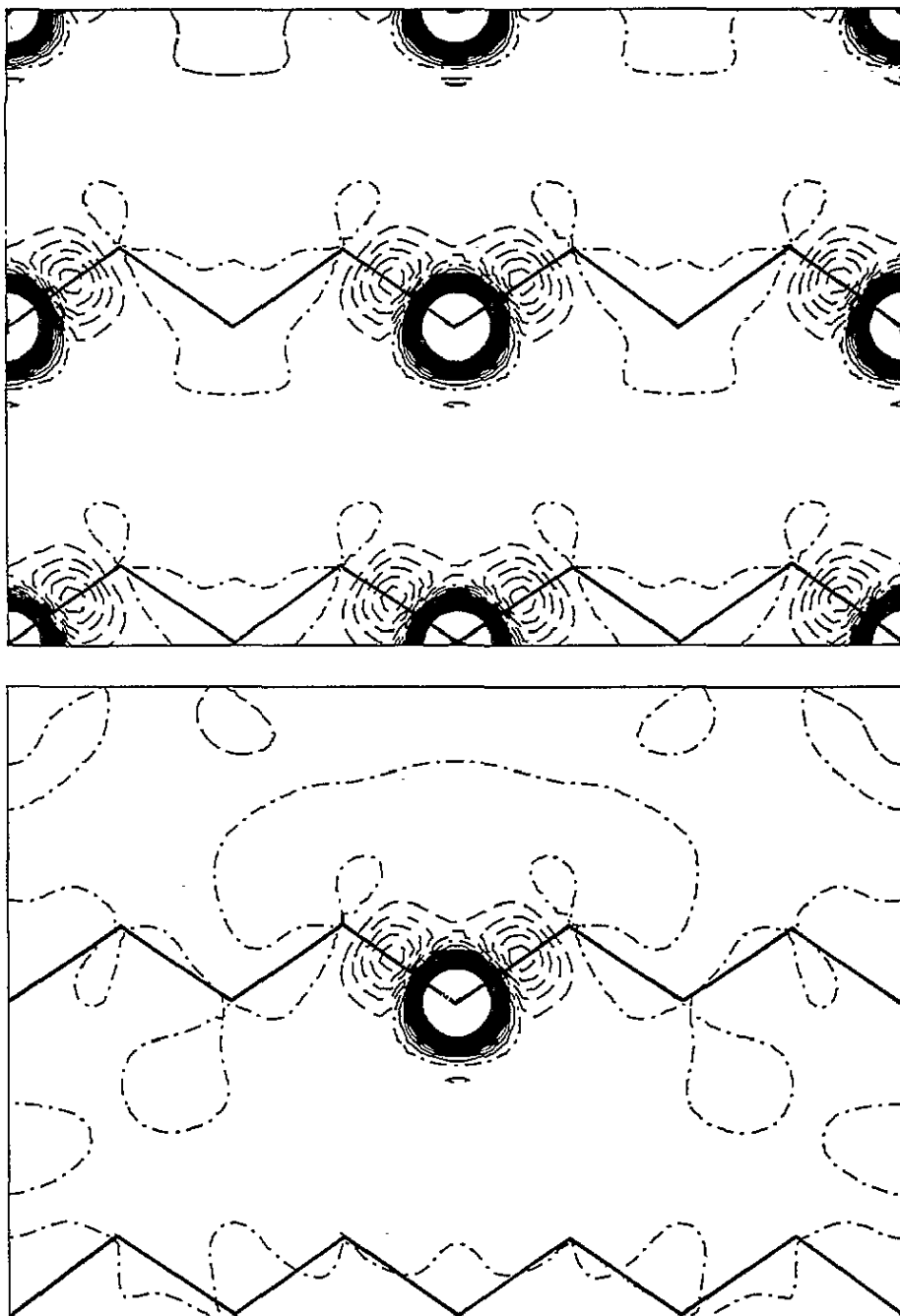|	Super-cell			
	S8	S16	S32	S64
C	−1.085	−1.101	−1.201	−1.202
Si(I)	+0.341	+0.367	+0.375	+0.376
Si(II)	−0.094*	−0.049*	−0.022	−0.025
Si(III)	—	−0.015*	−0.004	−0.009
Si(IV)	—	—	+0.005*	−0.003*
Si(V)	—	—	—	+0.006
Si(VI)	—	—	—	+0.003*
$C-Si_1$	0.306	0.306	0.301	0.301
Si_1-Si_{11}	0.369	0.370	0.379	0.379
$Si_{11}-Si_{111}$	—	0.382	0.374	0.378
			0.382	0.384

Figure 1. Difference charge density maps. The maps are drawn in the (110) plane through the carbon atom, and refer to super-cells with 8 (top) and 64 (bottom) atoms. We report the difference between the electron density in the unrelaxed defective crystal and the perfect crystal calculated with the same basis set. Consecutive iso-density lines differ by 0.005 electrons Bohr^{-3}. Continuous, dashed and dot-dashed lines correspond to positive, negative and zero differences. The zig-zag chain of atoms is shown.
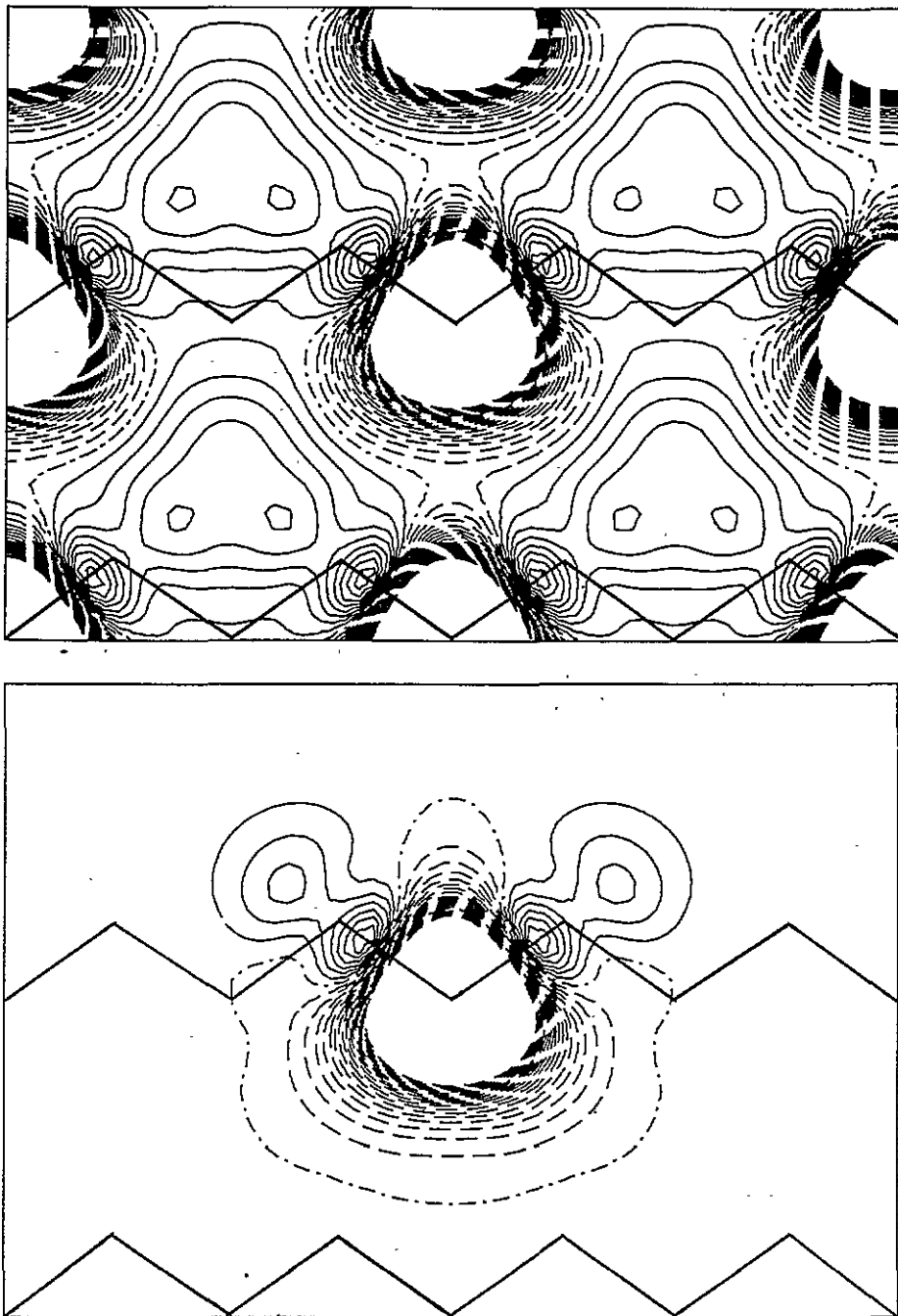
Figure 2. Difference electrostatic potential maps for the C substitution in bulk silicon. We report the difference between the electrostatic potential in the unrelaxed defective and perfect crystal. Consecutive iso-difference lines differ by 0.005 au (0.136 V). The top figure refers to S8, the bottom to S64. The symbols are as in figure 1.

Let us now consider relaxation effects. As can be easily anticipated on the basis of a comparison between the covalent radii of C and Si, the distance between the central atom

and its nearest neighbours shortens considerably. As a consequence, the Si_1–Si_{11} bond is stretched and also Si_{11} must relax; the relaxation process is dominated by the covalent network and does not depend on the electrostatic effects of the central double shell of negative and positive charges, so it is better described in terms of inter-atomic distances, as in table 4, rather than in terms of distances from the defect, as in table 3.

The relaxation energy is large; when only Si_1 are relaxed, the energy gain is 1.1 eV for S8 and S16, and increases to 1.5 eV at the S32 and S64 level; the reason for this difference is that, in S8 and S16, the second-nearest neighbours are in common to defects in neighbouring cells.

A further energy gain of 0.35 eV is obtained by relaxing the second-nearest neighbours (this is possible only in S32 and S64, as results from table 1: the star of second neighbours is not complete in S8 and S16); the relaxation of the third neighbours gives no energy gain because, in spite of the fact that two of the neighbours of an atom II are of type III, their displacement has no effect on the Si_1–Si_{11} distance, which is stressed. On the contrary, atoms V, being linked to atoms II, cooperate in the minimization of the stress of the bonds involving atoms II. This explains the differences shown in table 3 and 4 between S32 and S64, for atoms V can only be relaxed in S64 and the relaxation of I and II is the same in the two cases. The energy gain is small but not negligible (0.06 eV). When relaxing atoms V, the Si_{11}–Si_{111} bonds reduce from 2.410 Å (after the relaxation of I and II) to 2.384 Å; as a consequence, all bonds of atom II but one (pointing towards atom I) approach the equilibrium Si–Si length. It is possible that the inclusion of other stars of neighbours could further reduce the total energy of the system, but it is reasonable to suppose that the residual energy gain would not exceed 0.1 eV.
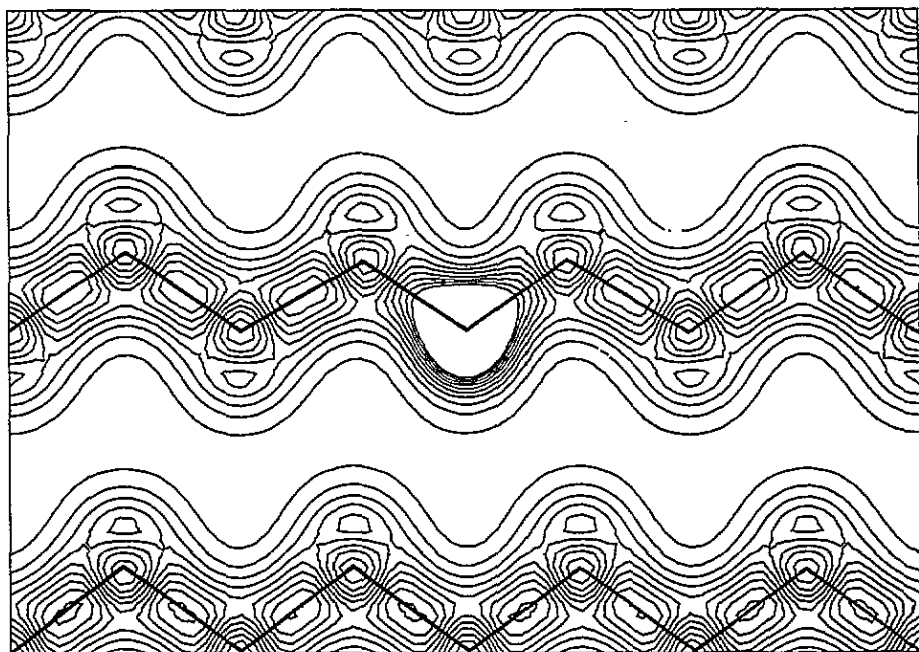

Figure 3. The total charge density map through the carbon atom in the (110) plane for S64. The carbon atom is at the centre of the figure. Consecutive iso-density lines differ by 0.01 electrons Bohr^{-3}.
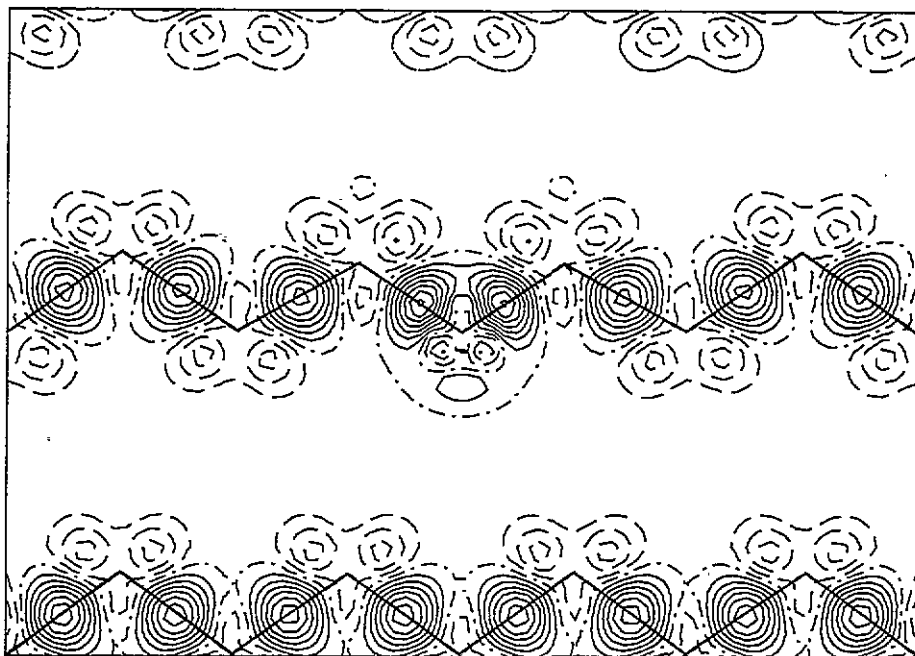
Figure 4. Difference charge density map in the (110) plane through the carbon atom. We report the difference between the electron density in the relaxed defective super-cell with 64 atoms and a superposition of free atomic densities calculated with the same basis set. Consecutive iso-density lines differ by 0.005 electrons Bohr^{-3}. Continuous, dashed and dot-dashed lines correspond to positive, negative and zero difference.

The energy data discussed till now refer to the Hartree–Fock solution, which is affected by the so-called 'correlation error'. It is possible to take electronic correlation effects into account by using '*a posteriori*' correlation-only density-functional-type formulae [17]; the Hartree–Fock charge density (and its gradient) is evaluated in a mesh of points in the unit cell; the correlation function of such density is then integrated over the unit cell to give the correlation energy of the system. The substitution energies including correlation effects are given in parentheses in table 2; the correlation contribution is about 1.0 eV for the unrelaxed geometry, and reduceds to about 0.8 eV for relaxed S32 and S64; the 'cost' for the C substitution is close to 3.0 eV.

Information on the charge distribution of the relaxed system is provided by figure 3, where the total charge density is reported, by figure 4, where the difference with respect to a superposition of atomic charges is shown, and by table 5. It turns out that the net charges (evaluated according to a Mulliken partition scheme) beyond the second star of neighbours are very close to zero (neutral silicon atoms, as in the perfect crystal), the oscillations being always smaller than $0.01|e|$. The bond population, which is a measure of the strength of the covalent bond, reproduces the perfect crystal value at the third bond from the defect in the covalent chain, confirming that the 'saturation' of the defect perturbation is very rapid.

4. Conclusion

In the present paper, the convergence of the carbon substitutional energy and relaxation geometry in bulk silicon as a function of the super-cell size has been investigated; '*a priori*'

two effects can be supposed to dominate the relaxation energetics and geometry, namely the electrostatic interaction with the negatively charged defect (the net charge is $-1.2|e|$) and the propagation of the perturbation through the covalent chain, as a consequence of the displacement of the first four neighbours of the carbon atom.

The present study shows that the electrostatic effects are very short ranged, and completely screened by the nearest neighbours (Si). In forthcoming studies we will investigate whether similar results hold for defects with less symmetric geometry. Covalent effects dominate the relaxation process. The C–Si bond length reduces from 2.36 to 2.12, as a consequence of the small covalent radius of carbon; first neighbours of first neighbours relax in order to minimize the deviation of the Si–Si bond length from the perfect crystal value. The relaxation energy is very high (about 2 eV) and involves at least three sets of Si–Si bonds. Super-cells containing at least 32 atoms are necessary in order to describe relaxation properly.

Appendix

In this appendix we summarize a few data referring to the basis set, atomic energies, and bulk properties of Si, SiC and C (diamond).

Both C and Si are treated at a pseudopotential level; the pseudopotentials of Durand and Barthelat [15] have been adopted, as in a previous paper [16] on the bulk properties of seventeen III–V and IV–IV semiconductors; the basis set is reported in table A1; there are two sp and one d shell for each atom (13 'atomic orbitals'); in the first shell each function is a contraction of two Gaussians; the most diffuse sp and the d shell are single-Gaussian shells.

Table A1. Valence 21G* basis sets. The exponent α (in Bohr^{-2}) and the coefficients c of the two-Gaussian contractions have been optimized in the isolated atoms. The exponents of the single-Gaussian sp and d shells have been optimized in each compound. The coefficients multiply individually normalized Gaussians.

	Two-Gaussian contraction				Outer shell		
	α(sp)	c(s)	c(p)		α(sp)	α(sp)	α(d)
C	2.927 124	−0.146 932	0.165 474	Diamond	0.20	—	0.80
	0.659 924	0.416 847	0.487 652	SiC	0.18	—	0.80
				C in Si	0.18	—	0.80
				Atom	0.18	0.06	
Si	0.882 959	−0.384 853	−0.037 572	Si	0.12		0.50
	0.316 466	0.675 644	0.486 130	SiC	0.19		0.50
				Atom	0.12	0.06	

The atomic energies, used for the evaluation of the defect formation energies, and obtained with the 2–1–1 G basis set reported in table A1, are −5.2876 and −3.6550 Hartree, respectively; one sp shell has been added in both cases for the atomic calculation, in order to describe the tails of the atomic functions; these additional functions are not necessary in the bulk calculations, due to the overlap between neighbouring atoms.

The bulk properties resulting from the above basis sets are reported in table A2, together with the experimental data for comparison.

Table A2. Calculated and experimental bulk properties of diamond, SiC and silicon. BE, a and B are respectively the binding energy, the lattice parameter and the bulk modulus. P91 is the binding energy obtained by taking into account the correlation contribution through an 'a posteriori' (post-SCF) integration of a density functional correlation-only formula proposed by Perdew [17] and using the Hartree–Fock charge density.

System	BE (eV)			a (Å)		B (GPa)	
	HF	P91	Expt	Calc.	Expt	Calc.	Expt
C	10.4	14.7	15.1	3.58	3.57	471	442
SiC	9.0	12.8	13.0	4.39	4.36	245	228
Si	6.3	9.5	9.5	5.46	5.43	109	99

Acknowledgments

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