

Structural, electronic, and optical properties of the C-C complex in bulk silicon from first principles

Dilyara Timerkaeva,^{1,2} Claudio Attaccalite,^{3,4,5} Gilles Brenet,^{1,2} Damien Caliste,^{1,2} and Pascal Pochet^{1,2,a)}

¹Université Grenoble Alpes, CS 40700, 38058 Grenoble Cedex, France

²Laboratoire de Simulation Atomistique (L_{Sim}), MEM, INAC, CEA, 38054 Grenoble Cedex 9, France

³CNRS/Univ. Grenoble Alpes, Institut Néel, F-38042 Grenoble, France

⁴Centre Interdisciplinaire des Nanosciences de Marseille, Aix-Marseille Université, Campus de Luminy, Marseille, 13288 Cedex 09, France

⁵University of Rome Tor Vergata, Rome, Italy

(Received 24 October 2017; accepted 1 March 2018; published online 28 March 2018)

The structure of the C_iC_s complex in silicon has long been the subject of debate. Numerous theoretical and experimental studies have attempted to shed light on the properties of these defects that are at the origin of the light emitting G-center. These defects are relevant for applications in lasing, and it would be advantageous to control their formation and concentration in bulk silicon. It is therefore essential to understand their structural and electronic properties. In this paper, we present the structural, electronic, and optical properties of four possible configurations of the C_iC_s complex in bulk silicon, namely, the A-, B-, C-, and D-forms. The configurations were studied by density functional theory and many-body perturbation theory. Our results suggest that the C-form was misinterpreted as a B-form in some experiments. Our optical investigation also tends to exclude any contribution of A- and B-forms to light emission. Taken together, our results suggest that the C-form could play an important role in heavily carbon-doped silicon. *Published by AIP Publishing.*

<https://doi.org/10.1063/1.5010269>

I. INTRODUCTION

Carbon, as an isovalent impurity to the silicon, initially occupies a substitutional position (C_s). High-energy irradiation (electron, ion, proton, or gamma) creates fast-diffusing self-interstitials, some of which interact with carbon atoms and eject them from the substitutional sites to create carbon interstitials (C_i). C_i are mobile at temperatures above room temperature and can thus interact with other impurities to form defect complexes. C_iC_s is one of the defects induced by secondary irradiation. This complex is perhaps the most studied defect due to its rich physics and interesting structural, electronic, and optical features.

The pair is associated with a G-center which emits light at 0.97 eV (1280 nm).^{1,2} It was discovered in the 1960s as a by-product in the silicon crystal caused by the radiation damage due to bombardment with high-energy electrons, ions, and gamma rays. In recent years, significant efforts have been deployed to increase the concentration of G-centers,¹⁻³ generally through surface alteration of silicon, followed by laser annealing. These technologies have promising applications in the development of a silicon laser.

The structure of the complex has been debated for a long time and is the subject of numerous experimental and theoretical studies.⁴⁻¹² Early Electron Paramagnetic Resonance (EPR) studies, conducted by Brower *et al.*,⁴ identified a signal, Si-G11, corresponding to a vacancy occupied by two carbon atoms in a positive charge state. The angular dependence of the Si-G11 Zeeman spectrum suggests that two carbon atoms lie in the $\langle 110 \rangle$ plane, whereas the C-C bond is oriented

along the (111) direction. Subsequent experiments, based on optical detection of magnetic resonance (ODMR) studies of the 0.97 eV optical peak, linked the G-center to the C_iC_s complex in its neutral state.⁵ These authors proposed an alternative model for the C_iC_s complex, where the substitutional carbon atoms are separated by an interstitial silicon atom. Two modifications of the complex are possible: the A-form, where the interstitial silicon is in a three-bond configuration, and the B-form, where the Si is bound to two neighboring C_s atoms. The bistable C_iC_s complex [A- and B-forms in Figs. 1(a) and 1(b)] and its charged states have been experimentally studied.⁶ Song *et al.*⁶ extensively analyzed bistable C_iC_s complexes in p- and n-doped silicon using EPR, Deep Level Transient Spectroscopy (DLTS) and Photoluminescence spectroscopy (PL) techniques. Their results provided a complete configurational-coordinate energy diagram. The A-form was found to have lower energy for all the charge-states except neutral, for which the B-form had slightly lower energy. Later, the Localized Vibrational Modes (LVMS) of the bistable complex were determined by Infrared (IR) spectroscopy.⁷ The spectra obtained for the B-form (540.4, 543.3, 579.8, 640.6, 730.4 and 842.4 cm^{-1}) and the A-form (594.6, 596.9, 722.4, 872.6, 953.0 cm^{-1}) agreed fairly well with the values determined by *ab initio* calculations.^{8,9}

In 2002, Laiho *et al.*¹⁰ used EPR to detect new low-symmetry configurations of a complex containing an interstitial silicon and two carbon atoms. These signals, named Si-PT4 and Si-WL5, have yet to be characterized; however, their presence proves the existence of additional forms of the C_iC_s complex. The emergence of these new forms was linked to the cooling procedure employed in the experiments, and they were found to have varying magnetic properties.

^{a)}pascal.pochet@cea.fr

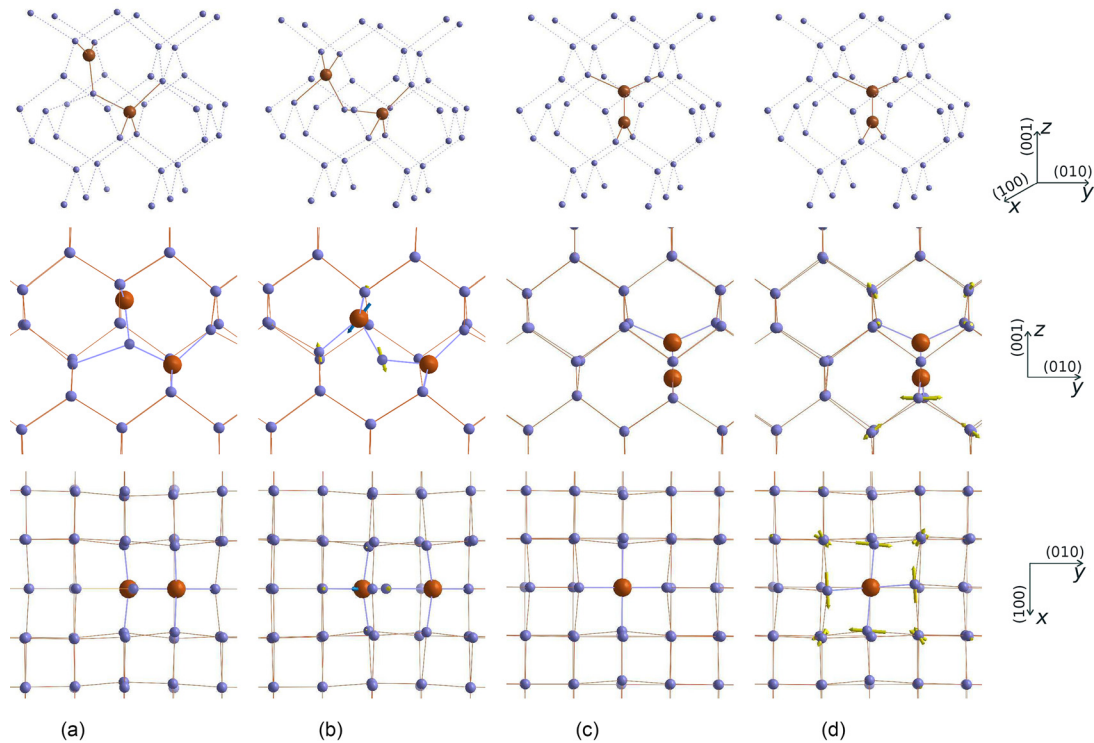


FIG. 1. Schematic view (top line), “side” view (middle line), and “top” view (bottom line) of the four C_7C_8 complex forms. Blue spheres correspond to silicon atoms; red spheres correspond to carbon atoms. Yellow and blue arrows indicate distortion of the B-form with respect to the A-form and of the D-form with respect to the C-form. (a) A-form, (b) B-form, (c) C-form, and (d) D-form.

The precise geometry of carbon-pair configurations can be investigated by first principles studies. A few attempts to theoretically determine their geometry have been made in recent years. By applying density functional theory (DFT) calculations, Liu *et al.*¹³ proposed a third configuration for the C_7C_8 complex [see Fig. 1(c)], the C-form, with two carbon atoms situated in a vacancy and oriented along the (100) direction. Although this configuration was found to be at least 0.2 eV more stable than the A and B forms for all charge states, it has never yet been experimentally observed.

Most theoretical studies since the proposal of the C-form have investigated the three forms of C_7C_8 complexes^{14–16} [see Figs. 1(a)–1(c)]. However, their results were not always in agreement. For example, Mattoni *et al.*¹⁴ and Docaj and Estreicher¹⁶ reported that binding of the A-form is as strong as that of the C-form, but that both forms are less stable than the B-form in a neutral state. In these two studies, non-spin-polarized calculations were performed. Zirkelbach *et al.*,¹⁵ in contrast, calculated the stability of dicarbon pairs taking the spin into account. Their results identified the C-form as the most stable. In this article, we propose another stable configuration of the C_7C_8 complex, which we call the D-form. This form is produced by torsion of the C-form along the C-C bond axis [see Fig. 1(d)].

Here, we present an extensive theoretical characterization of all four C_7C_8 complex forms from first-principles. The results will help to sort out which complex type is observed in different experimental growth procedures. We focused on both the ground state properties (geometries, binding energies) and the excited state properties (bandgaps and optical absorption/emission spectra) of all four forms.

The paper is organized as follows: in Sec. II we summarize the computational methods used to calculate the atomic structure and the electronic and optical properties; in Sec. III, we present the actual numeric parameters used in the calculations; in Sec. IV, we present and discuss our results on the electronic, structural, and optical properties of the C_7C_8 complex forms, and we finally conclude in Sec. V.

II. METHODS

The C_7C_8 structures were embedded in 216-atom silicon supercells, applying periodic boundary conditions. Geometric optimizations were performed using BigDFT wavelet-based code¹⁷ with Hartwigsen-Goedecker-Hutter pseudo-potentials¹⁸ and the GGA-PBE functional.¹⁹ The locality of the wavelet basis-set and the appropriate parallelization of BigDFT ensure a very good efficiency for large supercells with localized orbitals, such as defect states. Structures were relaxed using the Fast Inertial Relaxation Engine (FIRE).²⁰ To calculate the phonon modes, we employed a finite-difference method to the frozen phonon approximation. To accelerate computations, only the defect and its first-shell neighbors were precisely considered; remote atoms contributed to the dynamical matrix as unperturbed bulk atoms.

The excited states were calculated by applying the many-body perturbation theory on a plane-wave basis set. Therefore, we took optimized structures from BigDFT and generated occupied and empty states²¹ using the plane-wave based QuantumEspresso²² code, norm-conserving Troullier-Martins pseudo-potentials,²³ and the GGA-PBE functional.¹⁹

The Kohn-Sham levels were then corrected by applying many-body perturbation theory to obtain the quasi-particle (QP) band structure and determine the system's optical response. The QP band structures were obtained within the GW approach.²⁴ Specifically, we used non-self-consistent GW (denoted as G_0W_0) where the screened Coulomb potential, W , and Green's function, G , were built from the KS eigenstates $\{\varepsilon_{n\mathbf{k}}; |n\mathbf{k}\rangle\}$ (where \mathbf{k} is the crystal wave vector and n is the band index). The quasi-particle energies were then obtained from

$$\varepsilon_{n\mathbf{k}}^{\text{QP}} = \varepsilon_{n\mathbf{k}} + Z_{n\mathbf{k}} \Delta \Sigma_{n\mathbf{k}}(\varepsilon_{n\mathbf{k}}). \quad (1)$$

In Eq. (1)

$$Z_{n\mathbf{k}} = [1 - \partial \Delta \Sigma_{n\mathbf{k}}(\omega) / \partial \omega|_{\omega=\varepsilon_{n\mathbf{k}}}]^{-1}$$

is the re-normalization factor, and

$$\Delta \Sigma_{n\mathbf{k}} \equiv \langle n\mathbf{k} | \Delta \Sigma | n\mathbf{k} \rangle,$$

where

$$\Delta \Sigma = \Sigma - V^{\text{xc}}$$

is the difference between $\Sigma = GW$, the GW self-energy, and V^{xc} , the exchange-correlation potential used in the KS calculation.²⁵

The optical-spectra were calculated by solving the Bethe-Salpeter equation (BSE)²⁶

$$(\varepsilon_{c\mathbf{k}}^{\text{QP}} - \varepsilon_{v\mathbf{k}}^{\text{QP}}) A_{v\mathbf{k}}^s + \sum_{v'\mathbf{k}'} \langle v\mathbf{k} | K_{eh} | v'\mathbf{k}' \rangle A_{v'\mathbf{k}'}^s = \Omega^s A_{v\mathbf{k}}^s. \quad (2)$$

Here, electronic excitation was expressed in an electron-hole pair basis $|v\mathbf{k}\rangle$ corresponding to transitions at a given \mathbf{k} from a state in the valence band (v) with energy $\varepsilon_{v\mathbf{k}}^{\text{QP}}$ (hole), to a conduction-band (c) state with energy $\varepsilon_{c\mathbf{k}}^{\text{QP}}$ (electron). $A_{v\mathbf{k}}^s$ are the expansion coefficients of the excitons in the electron-hole basis, and the Ω^s are the excitation energies for the system. With spin-polarized defects, we performed spin-polarized calculations both at the GW and BSE levels.

III. CALCULATION DETAILS

In this section, we report the convergence parameters entering into the different calculations discussed in Sec. II.

As recently shown by Wang *et al.*,^{11,12} the formation energy of the neutral states of A-, B-, and C-forms are the lowest among all charge states for a wide range of Fermi energy levels. Therefore, we focused on the neutral states of C_iC_s . Structures were optimized using a 0.42-Bohr grid spacing on the wavelet mesh, and a cutoff of 80 Ry in plane-wave to generate the KS wave-functions. In the G_0W_0 calculation, 1500 bands were used to expand the Green's functions and calculate the screened interaction W , 30 000 G -vectors to expand the Kohn-Sham orbitals, 2-Ha cutoff for the G -vectors contributing to the dielectric constant. The dielectric contribution to the definition of W was calculated using a double-grid technique to integrate the Brillouin zone with a single \mathbf{k} -point (gamma point) for the matrix elements, and a $2 \times 2 \times 2$

shifted grid for single-particle energies, see Kammerlander *et al.*²⁹ for details. The same double-grid technique was used to calculate the optical response. For the BSE, we used the static part of the screening calculated in the GW, 100 valence bands and 100 conduction bands to calculate the optical absorption, and 15 000 G -vectors to describe the Kohn-Sham wave-functions. Then, the BSE equation was also inverted and interpolated on the double grid.²⁹ All the GW and BSE calculations were performed in Yambo code.³⁰

IV. RESULTS AND DISCUSSION

Here, we will address the structural, vibrational, electronic, and optical properties of the different C_iC_s complexes.

A. Structures and binding energies of the various forms of the C_iC_s complex

In Figs. 1(a)–1(d), the four optimized configurations of the C_iC_s complex are shown (A-, B-, C-, and D- forms). In the A-form, carbon atoms occupy neighboring lattice sites, while the Si atom is an interstitial bonded to both carbon atoms and one silicon. The B-form is similar to the A-form, but the interstitial Si only bridges the two carbon atoms and is not bonded to another Si. The third configuration, the C-form, consists of two carbons in a vacancy aligned in a (100) crystallographic direction. The D-form is a slight variation on the previous configuration: all Si atoms bonded to two C atoms are slightly twisted around the C-C axis compared to the C-form. The D-form was obtained through non-spin-polarized geometry optimization. The initial configuration for this optimization was chosen as slightly different from the C-form. Thus, we can conclude, that the D-form is another local minimum, which is similar to the C-form but with almost 0.4 eV higher energy.

The twisted shape of the D-form could be the result of the rotation of the π -orbitals of two C atoms to form a π bond [see Figs. 1(c) and 1(d)]. In the C-form, the two corresponding π -orbitals are perpendicular to each other; each is occupied by a single electron, making this complex paramagnetic.

All four forms of the C_iC_s complex can be created from identical ingredients, i.e., from mobile interstitial carbon and immobile carbon in a substitutional site. Depending on the topology of the reaction, either A and B or C and D forms can emerge. In a neutral state, A will directly transform to B, as B is more stable. The A to B transformation barrier has been estimated to be as low as 0.1 eV.¹⁵ Transformation from either A (or B) to C and back is less likely as the transformation barrier is estimated to be up to 2–3 eV.¹⁶ The kinetics of C_iC_s complex formation and reorientation, i.e., various migration barriers, is beyond the scope of the present study. Interested readers can find information in Zirkelbach *et al.*¹⁵

The binding energies of the complex were calculated as $E_b(\text{C}_i\text{C}_s) = -E_{\text{tot}}(215\text{SiC}_i\text{C}_s) - E_{\text{tot}}(216\text{Si}) + E_{\text{tot}}(215\text{SiC}_s) + E_{\text{tot}}(216\text{SiC}_i)$, and the values obtained are listed in Table I. The C-form was found to be the most stable. These results contradict some recent theoretical studies;^{14,16} however, they concur with findings reported by Zirkelbach *et al.*¹⁵ and Liu *et al.*¹³ We demonstrate the crucial role of the spin in

TABLE I. Binding energies in eV for four configurations of C_iC_s . References 8, 9, 13, and 14 reported relative values of their binding energies. E_{b0} indicates the binding energy of the most stable configuration within each study. SP indicates spin-polarized calculations.

E_b , eV	This work	Reference 15	Reference 16	Reference 14	Reference 8	Reference 9	Reference 13
A-form	0.86	0.93	0.92	E_{b0}	$E_{b0}-0.35$	$E_{b0}-0.11$	$E_{b0}-0.2$
B-form	0.93	0.95	1.28	$E_{b0}-0.4$	E_{b0}	E_{b0}	$E_{b0}-0.2$
C-form	1.11		0.90	$E_{b0}-0.2$			
C-form(SP)	1.28	1.28					E_{b0}
D-form	0.88						

complex respective stabilities as it increases the binding energy by about 0.17 eV compared to non-spin polarized calculations (0.2 eV in Ref. 15). The D configuration has a binding energy of 0.88 eV, which is close to that of the A-form.

Generally speaking, all these forms may be present in a heavily carbon-doped silicon, and their relative concentrations should depend on their binding energies if thermal equilibrium is reached, or otherwise on the thermal history of the sample. It should also be noted that formation kinetics can significantly affect the balance between the four complex concentrations. That is why, even if the A- and B-forms are indeed less stable than the C-form, they may nevertheless be present in the sample and could be detected by various experimental techniques, such as IR and EPR spectroscopy.

To reproduce the sample preparation process, we simulated the experimental sample preparation, tracking concentrations of various compound point defects in silicon exposed to electron irradiation. The concentrations of defects were extracted from Kinetic Mass Action Law (KMAL) simulations.³¹ KMAL is a theoretical model based on a rate theory, which we use to reproduce temperature-driven diffusion-limited reactions. To account for the temperature effect, activation energies derived from *ab initio* computation were used.²⁷ The lattice type, the geometry of each defect, and their binding energies are the main factors affecting diffusion, defect formation and subsequent stability.

Figure 2 shows the concentrations of various carbon-related defects in silicon produced during isochronal annealing (20 min) up to 500°C. KMAL simulation results were

compared to experimental data.^{27,28} We performed two simulations varying a single parameter: the C_iC_s binding energy. Figure 2(a) shows results for the B-form of C_iC_s , whereas Fig. 2(b) shows results for the C-form of C_iC_s .

The two simulations highlight the main features of the experiment: species, their concentrations, and the reaction temperatures. When considering the C-form, the simulation reproduces the following two experimental parameters: the C_iC_s dissociation temperature of 280–300°C and the experimentally observed evolution of the C_iO_i pair. This evidence favors the existence of the C-form. With the B-form, decay of C_iC_s pairs at lower temperatures (190°C) releases mobile C_i species, causing the C_iO_i concentration to increase just before its dissociation. This increase is not seen experimentally, adding further proof that the C-form is the one detected in this experiment.

These observations are strong evidence for the presence of the C-form in irradiated silicon, but more detailed analysis of other properties will be required to definitively assign the observed properties of the dicarbon pair to any single form. Hereafter, we will consider all four forms of C_iC_s pair, namely, A-, B-, magnetic C-, and D-form as they are the most interesting configurations. In particular, we will define the proportion of their vibrational and excited states.

B. Vibrational properties

One of the easiest ways to decipher the precise configuration of defects present in a sample by combined

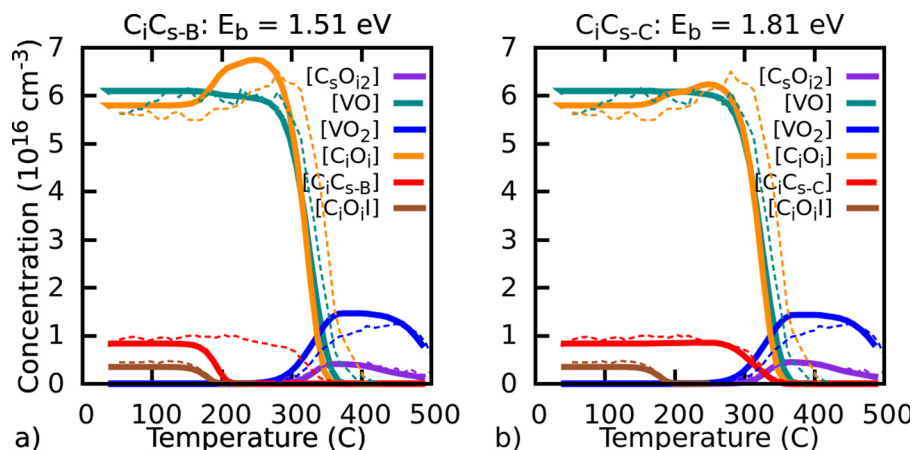


FIG. 2. The C-form predominates in the experiments under consideration. Isochronal annealing simulations of carbon/oxygen related defects in silicon were compared to experimental observations.^{27,28} In experiments, carbon-containing silicon was first exposed to electron irradiation to provoke the appearance of Frenkel pairs. Fast-migrating vacancies and interstitials led to the formation of defect complexes. The concentrations of these formations were examined as a function of temperature. Continuous lines correspond to simulated curves; dashed lines represent experimental data. (a) KMAL simulations of the B-form of the C_iC_s complex: simulation data fail to reproduce experimental data. (b) KMAL simulations of the C-form of the C_iC_s complex. Experimental and simulated data show good matching.

TABLE II. Frequencies in cm^{-1} of the four A-, B-, C-, and D-forms of C_7C_8 pair. Frequencies in bold are calculations from the present work; they are compared to previously published theoretical and experimental values. In Lavrov *et al.*,³² the authors did not match frequencies to the form of the C_7C_8 complex.

This study theory				Docaj ¹⁶ theory			Leary ⁸ theory	Capaz ⁹ theory		Lavrov ⁷ experiment		Lavrov ³² experiment
A	B	C-SP	D	A	B	C-NSP	B	A	B	A	B	not identified
933	819	1135	1182	917	805	1181	838	890	841	953	842	749
861	702	801	744	912	704	810	715	874	716	873	730	527
699	608	733	732	710	663	806	649	722	643	722	641	
572	548	549	525	598	567	580	582	567	567	597	580	
566	525			591	563		552	557	514	594	543	
	521				549		543		503		540	

theoretical-experimental investigation of LVMs. Convergence between the values obtained unambiguously indicates a correct structure, while the line-intensity can be used to estimate concentration. Therefore, we present our theoretical investigation of LVMs for the four C_7C_8 forms and compare them with already published results (see Table II). Our values for the A- and B- forms are in excellent agreement with experimental values and previous calculations. For the C-form, our results differ to a larger extent. These differences may be related to the geometries of the C-form studied, which were not the same here and in Docaj's study.¹⁶ Spin polarization was not taken into account by Docaj; as a result, they could be dealing with the D-form or another local minimum. The results obtained could serve as a reference for future IR experiments. While the A and B forms present vibrational peaks at no more than 950 cm^{-1} , we propose to justify the existence of C or D forms by the appearance of a peak in the 1100 to 1200 cm^{-1} range. Up to now, this peak was not observed since, like in the study of Lavrov *et al.*,⁷ the spectral range is often only scanned up to 1000 cm^{-1} .

The experimental data presented in Fig. 2 rely on a 546 cm^{-1} band to measure the C_7C_8 complex concentration. Our vibrational analysis indicates that this band can be attributed to the B-form or the C-form and the (less stable) D-form. The A-form does not have a band at this frequency. Therefore, combining the vibrational simulations with the KMAL simulations, it appears that the C-form was detected in the experimental studies we examined.^{27,28}

C. Electronic and optical properties

The dicarbon pairs are associated with a light-emitting defect, the G center. The electronic structure and light spectrum associated with each of the forms described could provide information on which one is linked to the G center. We start our discussion of the electronic properties of the four complexes at the Kohn-Sham level. In Fig. 3(a), a schematic representation of the electronic band structure of the four defects is shown. Although we used a large supercell (more than 200 atoms), due to resonant defect states, the presence of the defects slightly affects the bulk gap, shifting it by about 0.13 eV in the worst case—complex A. All four complexes produced deep energy levels in the bandgap. In the A and B cases, a single level is present within the gap, located at 0.36 eV and 0.40 eV , respectively, from the top valence band. The C- and D-forms produced more complex structures. In

the case of the C-form, the defect was spin-polarized and the level presented in the gap splits into two levels, one for each spin polarization. Finally, the D-form is also associated with two levels in the gap: one fully occupied and one empty. Next, we used quasi-particle correction to obtain the band structure schematically represented in Fig. 3(b).

The GW corrections broaden the gap from 0.76 eV to 1.1 eV in pure Si. These corrections increase the energy of the unoccupied defect levels while decreasing that of the occupied levels. In the A and B cases, these levels remain within the gap whereas in the C and D cases the defect levels almost merge with the lowest conduction and top-most valence lines [see Figs. 3(a) and 4(b)]. This difference has important implications for the optical properties, as we will

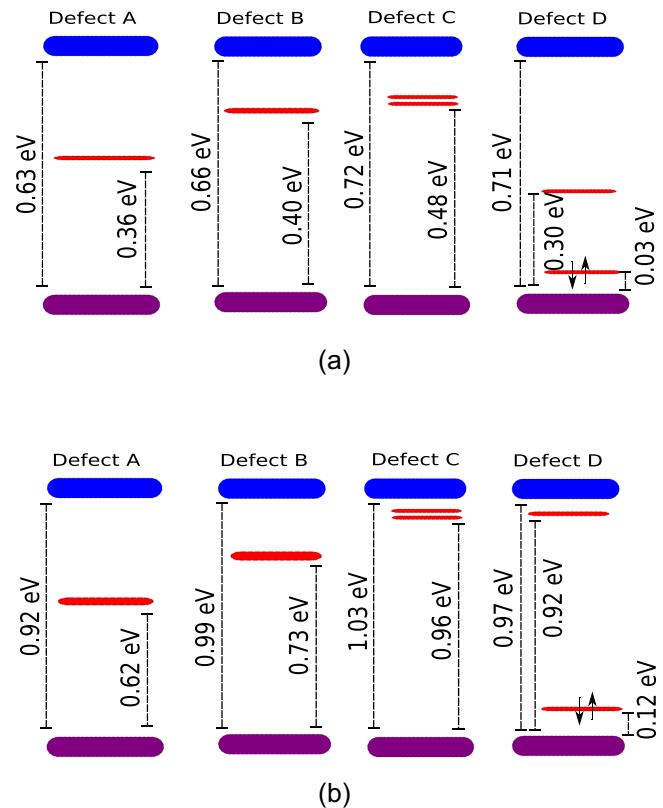


FIG. 3. Schematic band structure of the defects levels in the different complexes. Purple and blue colors correspond to valence and conduction bands, while red color corresponds to defect levels. All defects levels are empty except in the D case where there is a fully occupied level in the gap, indicated by the two arrows. (a) DFT level and (b) G_0W_0 level.

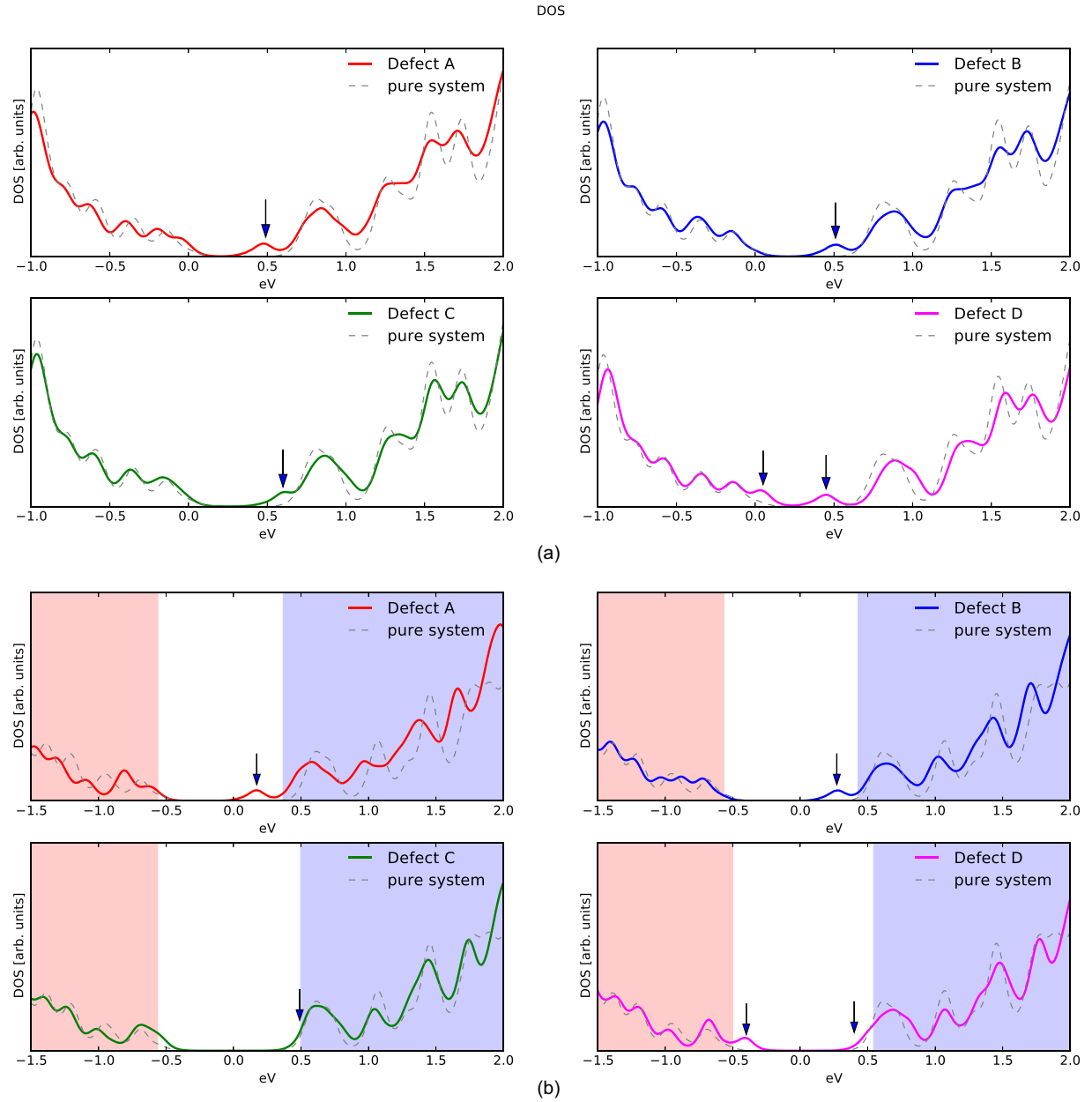


FIG. 4. Top panel: Density of states at the IP level. Bottom panel: Density of states at the G_0W_0 level, in the presence of the different defect complexes, compared to bulk silicon within the same supercell. The arrows indicate the position of the deep-level defects in the bandgap. The red (blue) box indicates the valence (conduction) bands. (a) Density of states in IP approximation and (b) density of states in G_0W_0 approximation.

see below. The corresponding density of states (DOS), interpolated on $2 \times 2 \times 2$ shifted k -points, is reported in Fig. 4(b). The DOS of the four C_7C_8 structures was compared with that of the pure system, aligning the top valence band position. The four complexes share a similar DOS state to the pure system, but the peaks belonging to the bulk silicon are smoother because the defects break symmetries in the supercell. In Fig. 4(b), the arrows indicate the positions of the defect levels shown in the diagram in Fig. 3(b). Now that we have analyzed the electronic structure of the four defects, we can move on to their optical properties.

The optical response was evaluated within independent particle approximation (IP) starting from the G_0W_0 band structure [Fig. 5(a)] and by means of the Bethe-Salpeter equation (BSE), i.e., including both local-field effects and

electron-hole interaction [Fig. 5(b)]. In the IP approximation, the optical response can simply be constructed from transitions between occupied and unoccupied levels depicted in Fig. 3(b) mediated by the optical matrix elements. In Fig. 5(a), we report only the lowest part of the spectra, that is the one more affected by the presence of defects.

Next, we included correlation effect using the Bethe-Salpeter Equation that mixes the single particle transitions, redistributes the spectral weight, and renormalizes the transition energies. In the B-, C-, and D-forms of C_7C_8 complex, these effects simply shift the spectra towards lower frequencies [see the difference between Figs. 5(a) and 5(b)]. In contrast, in the case of the A-form, the spectral weight is significantly redistributed, the peak at 1300 nm disappears, and the peak at 1350 nm becomes more intense. Figure 5(b) shows the final

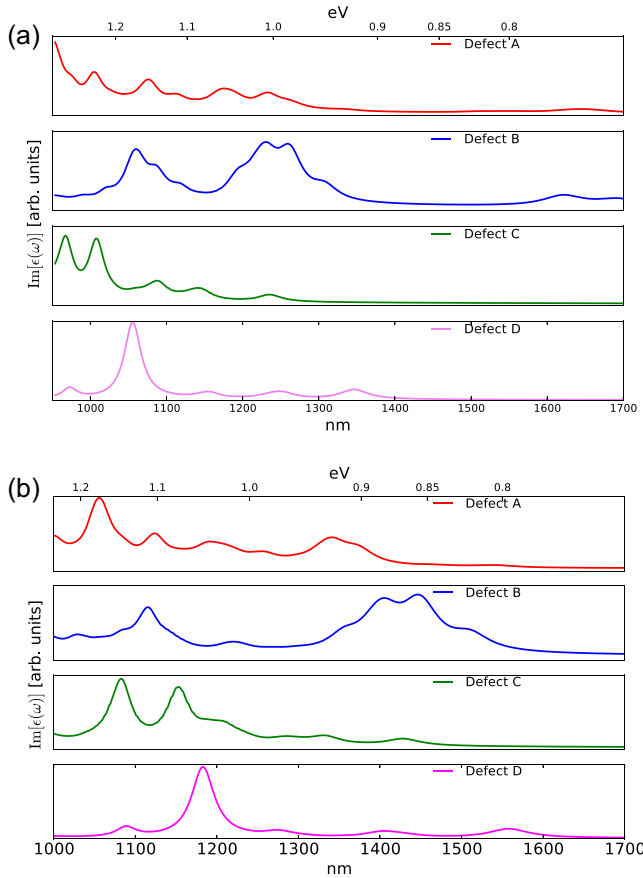


FIG. 5. Top panel: Optical absorption in the presence of the different defect complexes in independent particle approximation, starting from the G_0W_0 band structure. Bottom panel: Optical absorption with the different defect complexes, applying the G_0W_0 approximation plus the Bethe-Salpeter equation. The vertical lines indicate the wavelength of experimental light emission.^{1,2} (a) G_0W_0 + IP and (b) G_0W_0 + BSE.

optical absorption spectra for the four defect forms. Note that the spectra for the A, B, and C complexes are of similar intensity, whereas the spectrum for the D-form is four times more intense. This can be explained by the fact that both occupied and unoccupied levels of the D-defect are present in the bandgap, and therefore transition between them has a larger weight in the spectra due to the small energy difference.

Comparing optical absorption results with luminescence measurements is not easy for several reasons. Firstly, the intensity of the two spectra is unequal due to the different electron distributions. In addition, the luminescence spectrum is usually red-shifted relative to the absorption spectrum due to structural relations (Stoke shift), and this shift has similar energy to that of local vibrations. For these two reasons, it is challenging to identify particular defects from their optical spectra. From the optical response presented here, the defect complexes that could be excluded were the A and B complexes because they cause strong absorption peaks at wavelengths below emission line. Thus, once excited, a defect like the B (or the A) will emit in a range above 1450 nm (below 0.8 eV). As a result, the C- and D-forms appear to be the most likely to emit light. Moreover, the energy shift between their optical absorption peak and the emission peak is compatible with local vibration energies

(see Table II). Finally, the C and D cases also produced small peaks at a lower energy than the emission peak, and these could come into play in the luminescence process. It is therefore challenging to identify the defect complex from our absorption spectra.

V. CONCLUSIONS

In this study, we performed a detailed investigation into the properties of the forms of the C_iC_s complex from first principles calculations. Our aim was to better understand the properties of the possible forms of C_iC_s complexes and why the C-form, which is the most stable according to our calculations, has never yet been experimentally observed. In addition, we tried to theoretically characterize the optical properties of the four carbon-carbon pair forms and attempted to assign one of them to the light-emitting G-center.

Our results indicate that, among all four C_iC_s forms, the C-form is the most stable, with binding energy 0.4 eV higher than that of the B-form. Moreover, KMAL isochronal annealing simulations demonstrated that the dissociation temperature for the 546 cm^{-1} band, which is used to determine the stability of C_iC_s complex, corresponds to the binding energy of the C-form. Meanwhile, the binding energy of the B-form results in a dissociation at a temperature about 100 °C lower, which strongly contrasts with experimental data and therefore further supports the existence of the C-form. We next computed a set of localized vibrational modes for each of the four configurations. The set corresponding to the C-form contains four bands, three of which are within the same range as the A- and B-forms, and even overlap with the latter. The highest band, at 1135 cm^{-1} , is above the registration range in most LVM experiments, and it could therefore have been missed during measurements. The electronic and optical properties of the C_iC_s complexes indicated that correlation effects must be included to describe the optical properties of C_iC_s defect complexes. In fact, the various approximations in standard semi-local functionals fail to describe the appropriate position level for localized and resonant defect states with respect to the bulk levels. Our results thus provide an accurate quasi-particle band structure for the four complexes and their optical absorption using the GW + BSE approximation. However, as a consequence, the form responsible for the light-emitting G-center becomes ambiguous. The C-form seems to be the most stable one, but both the B- and C-forms are compatible with the vibrational measurements. Nevertheless, the optical response tends to exclude the A and B complexes. But defects A and B could contribute to the luminescence process through non-radiative decay. This possibility was not considered in this work. To summarize, all four forms can exist and probably coexist in carbon-rich irradiated silicon. The relative concentrations of the four complexes probably depend on their binding energies if the sample is at thermal equilibrium, or, otherwise, on the thermal history of the sample. It is difficult to identify a single form which would be responsible for the light emission of the G-center in silicon. However, the stability, vibrational properties, and optics provide strong evidence that the C-complex plays an important role in heavily carbon-doped silicon. To our knowledge, no evidence of the

existence of the C-form has been obtained by, the generally effective EPR characterization technique. According to our simulations, the C-form is a magnetic complex, and as a result it would produce a signal in a spectral range far from the signal for neutral species. Hence, additional characterization experiments will be required to investigate the C and D configurations. New experiments should take into account the complexes' vibrational properties, as reported in the current study, as well as their magnetization. From a theoretical point of view, some additional calculations of excited states of C_iC_s forms could provide new information.

Note added in proof. During review of this paper, we became aware of recent experimental work by Beaufils *et al.*³³ that further explore the properties of G-centers in silicon.

ACKNOWLEDGMENTS

This work was partially funded by ANR as part of the BOLID (No. ANR-10-HABI-0001) and the MECHASPIN (No. ANR-17-CE24-0024) projects. Computing time was provided by the national GENCI-IDRIS and GENCI-TGCC supercomputing centers under Contract Nos. t2012096655 and t2014096107. The research leading to these results has received funding from the European Union H2020 Programme under GrapheneCore2 program.

¹D. Berhanuddin, M. Lourenco, C. Jeynes, M. Milosavljević, R. Gwilliam, and K. Homewood, *J. Appl. Phys.* **112**, 103110 (2012).

²D. D. Berhanuddin, M. A. Lourenço, R. M. Gwilliam, and K. P. Homewood, *Adv. Funct. Mater.* **22**, 2709 (2012).

³K. Murata, Y. Yasutake, K.-I. Nittoh, S. Fukatsu, and K. Miki, *AIP Adv.* **1**, 032125 (2011).

⁴K. L. Brower, *Phys. Rev. B* **9**, 2607 (1974).

⁵K. O'Donnell, K. Lee, and G. Watkins, *Physica B+C* **116**, 258 (1983).

⁶L. W. Song, X. D. Zhan, B. W. Benson, and G. D. Watkins, *Phys. Rev. B* **42**, 5765 (1990).

⁷E. V. Lavrov, L. Hoffmann, and B. B. Nielsen, *Phys. Rev. B* **60**, 8081 (1999).

⁸P. Leary, R. Jones, S. Öberg, and V. J. B. Torres, *Phys. Rev. B* **55**, 2188 (1997).

⁹R. B. Capaz, A. Dal Pino, and J. D. Joannopoulos, *Phys. Rev. B* **58**, 9845 (1998).

¹⁰R. Laiho, M. Vlasenko, and L. Vlasenko, *Solid State Commun.* **124**, 403 (2002).

¹¹H. Wang, A. Chroneos, C. A. Londos, E. N. Sgourou, and U. Schwingenschlögl, *Sci. Rep.* **4**, 4909 (2014).

¹²H. Wang, A. Chroneos, C. A. Londos, E. N. Sgourou, and U. Schwingenschlögl, *J. Appl. Phys.* **115**, 183509 (2014).

¹³C.-L. Liu, W. Windl, L. Borucki, S. Lu, and X.-Y. Liu, *Appl. Phys. Lett.* **80**, 52 (2002).

¹⁴A. Mattoni, F. Bernardini, and L. Colombo, *Phys. Rev. B* **66**, 195214 (2002).

¹⁵F. Zirkelbach, B. Stritzker, K. Nordlund, J. K. N. Lindner, W. G. Schmidt, and E. Rauls, *Phys. Rev. B* **84**, 064126 (2011).

¹⁶A. Docaj and S. Estreicher, *Phys. B: Condens. Matter* **407**, 2981 (2012).

¹⁷L. Genovese, A. Neelov, S. Goedecker, T. Deutsch, S. A. Ghasemi, A. Willand, D. Caliste, O. Zilberberg, M. Rayson, A. Bergman *et al.*, *J. Chem. Phys.* **129**, 014109 (2008).

¹⁸M. Krack, *Theor. Chem. Acc.* **114**, 145 (2005).

¹⁹J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).

²⁰E. Bitzek, P. Koskinen, F. Gähler, M. Moseler, and P. Gumbsch, *Phys. Rev. Lett.* **97**, 170201 (2006).

²¹We checked that the optimized structures did not significantly change if we reoptimize them using plane-waves and Troullier-Martins pseudopotentials.

²²P. Giannozzi *et al.*, *J. Phys. Condens. Matter* **21**, 395502 (2009).

²³N. Troullier and J. L. Martins, *Phys. Rev. B* **43**, 1993 (1991).

²⁴F. Aryasetiawan and O. Gunnarsson, *Rep. Prog. Phys.* **61**, 237 (1998).

²⁵W. G. Aulbur, L. Jonsson, and J. W. Wilkins, *Solid State Physics*, edited by H. Ehrenreich and F. Spaepen (Academic Press, 1999), Vol. 54, p. 1.

²⁶G. Strinati, *Riv. Nuovo Cimento* **11**, 1 (1988).

²⁷E. Sgourou, D. Timerkaeva, C. Londos, D. Aliprantis, A. Chroneos, D. Caliste, and P. Pochet, *J. Appl. Phys.* **113**, 113506 (2013).

²⁸C. Londos, E. Sgourou, D. Timerkaeva, A. Chroneos, P. Pochet, and V. Emtsev, *J. Appl. Phys.* **114**, 113504 (2013).

²⁹D. Kammerlander, S. Botti, M. A. L. Marques, A. Marini, and C. Attaccalite, *Phys. Rev. B* **86**, 125203 (2012).

³⁰A. Marini, C. Hogan, M. Grüning, and D. Varsano, *Comput. Phys. Commun.* **180**, 1392 (2009).

³¹G. Brenet, D. Timerkaeva, E. N. Sgourou, C. A. Londos, D. Caliste, and P. Pochet, *J. Appl. Phys.* **118**, 125706 (2015).

³²E. V. Lavrov, B. B. Nielsen, J. R. Byberg, B. Hourahine, R. Jones, S. Öberg, and P. R. Briddon, *Phys. Rev. B* **62**, 158 (2000).

³³C. Beaufils, W. Redjem, E. Rousseau, V. Jacques, A. Yu. Kuznetsov, C. Raynaud, C. Voisin, A. Benali, T. Herzig, S. Pezzagna, J. Meijer, M. Abbarchi, and G. Cassabois, *Phys. Rev. B* **97**, 035303 (2018).