Simulations of large multi-atom vacancies in diamond

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1. Introduction

With the recent development in the production of porous carbons with controllable pore size [1] the basic question arises: what are the stable pore sizes and shapes in porous carbons on the nanoscale? The size and shape of pores have a profound effect on the energetics of adsorptive storage, which is of great potential technological importance. The problem of modeling a missing group of atoms—vacancy clusters—has received considerable attention in silicon, providing a basis for comparison for similar experimental [2-5] and theoretical [6-10] work on diamond vacancy clusters. Due to the rich chemistry of carbon with its unique energetics of the close lying sp, sp², and sp³ states (as opposed to the typically sp³ hybridized silicon) [13-18] suggests that stable carbon vacancy clusters might display a dazzling variety of shapes and sizes. These clusters will also greatly affect the optical properties of diamond. The literature on the modeling of vacancy clusters in diamond has been limited to either small clusters or to selecting representative samples from the astronomical number of combinatorially possible structures. Our goal is to:

a. Enumerate all distinct structures of Vₙ vacancy clusters with increasing n.
b. Evaluate a large number of Vₙ vacancy clusters (evaluation of all for large n is not possible) at a realistic level of quantum mechanical theory. Then, describe the optimized structures, their electronic states and total energies and any emerging trends in these descriptors.
c. Interpret the driving forces of the distortions originating in the ability of the dangling orbital electrons to form multicenter combinations that lower the energy of the vacancy clusters.

A simple model of electronic structure of these systems can be obtained by imagining the vacancy cluster as being generated by severing the bonds and removing n atoms following the model developed for V₁ by Coulson and Kearsley [28]. The number of such severed bonds, sb, depends on n and the topology of the given vacancy cluster. E.g. sb = 4 for V₁, sb = 6 for V₂. Each severed bond leaves behind an sp³-like dangling bond orbital with a single electron. These dangling bond orbitals form various multicenter combinations, the lowest one being always the most bonding. In all cases we encountered in this work we found the lowest orbital is sufficiently stabilized to make it appear below the highest occupied band energy level, similar to the a₁ orbital for V₁ found by Coulson and Kearsley. Therefore, the number of dangling bond orbitals within the gap is less than sb. We will refer to these dangling bond orbitals within the gap as s before relaxation and s' after relaxation. These levels in the gap are mostly dangling bond levels.
Given the large number of possible structures for larger \( n \) (for details see later) it was necessary to develop an algorithm that generates low energy structures. The diversity of stable structures without structural bias needs to be known before any atomistic interpretation of medium and large vacancy clusters can begin. If in fact these structures do not show structural diversity that needs to be known as well. Alas, due to the extremely large number of possible structures highly accurate ab initio methods [12] can be used only for a very limited number of vacancy clusters. TB-DFT [11] level of theory offers qualitative and even sometimes quantitative results. Even the more sophisticated conventional \textit{ab initio} methods [7–10] have to be improved to obtain the level of accuracy offered e.g. by Quantum Monte Carlo methods in the relatively simple case of a monoatomic vacancy (\( V_1 \)) in diamond [12].

The paper is structured as follows. First, we briefly review previous work on Si and diamond vacancy clusters. We discuss “adamantane-like” structures which ought to be particularly stable by simply counting the number of bonds cut. Then, we develop an algorithm to generate connected vacancy clusters, \( V_n \), of increasing number of \( n \) missing atoms starting from a monoatomic vacancy, \( V_1 \). This is followed by a description of our results obtained for the most stable \( V_n \) vacancy clusters for \( n = 1, 2, \ldots, 14 \).

2. Vacancy clusters in diamond

In diamond, more than 500 electronic and more than 150 vibrational optical centers have been documented [37–39]. The purpose of this section is to review key information relevant to the discussion. About half of these defects are believed to be related to impurity atoms which are outside of our scope. In our paper we shall study the defects related to connected \( V_n \) vacancy clusters. Single vacancies and interstitials can be produced by irradiation of diamond and the interstitials can be obtained by annealing at about \( T = 400 \, ^\circ C \) [23]. It was found [20] that by annealing at \( T = 600 \, ^\circ C \), single vacancies \( V_1 \) migrate and form divacancies \( V_2 \). Divacancies anneal out at \( T = 800 \, ^\circ C \) producing a series of EPR active \( S = 1 \) centers labeled \( R \), \( 0 \), \( 1 \), \( R \), \( 10 \), \( R \), \( 11 \), and KUL11 [6,23,24]. These centers are respectively associated with \( \langle 110 \rangle \)-oriented vacancy chains with \( n = 3 \) to 8 by Lakouboukovski and Stesmans [2], although the concentration of the \( n \)-vacancy chains rapidly decreases with \( n \). At \( T = 1150 \, ^\circ C \) all of these vacancy chains anneal out producing more stable vacancy clusters [2].

Baker’s model for vacancy cluster formation [6] assumes that the clusters of vacancies must have been created by accumulation of migrating vacancies such that a “family tree of ancestors” with sufficient stabilities and life times can be identified. From this genealogical approach it follows that the steps to accumulate any particular cluster must involve precursors with the same configuration of vacancies, less one or two adjacent vacancies. These precursors must have been relatively stable and they should be observable as independent defects [6]. Baker’s approach revealed some shortcomings of earlier models and provides useful guidelines for vacancy cluster growth. The consideration of genealogy of vacancy construction [6] is built into our algorithm described in Section 4.

Hounsome et al. [25] studied \( \langle 110 \rangle \) vacancy chains, multi-vacancy clusters and vacancy discs in diamond using DFT with the AlMPRO and DFTB codes [26,27]. The multi-vacancy clusters under study were the clusters \( a-V_n \) \( \langle n = 1 \text{ to } 14 \rangle \) of Fig. 1 and their formation energies were calculated in the \( S = 0 \) and \( S = 1 \) spin states with the AlMPRO method. These clusters were obtained by minimizing the number of dangling bonds in analogy to Si vacancy clusters. In all cases, the more compact adamantane-like clusters were more energetically favorable than the \( \langle 110 \rangle \) chains. Exceptionally stable clusters were found with the \( V_6, V_{10} \) and \( V_{14} \) adamantane-like vacancy clusters just as in the case of silicon, but for the diamond \( V_6 \) they did not obtain the healing phenomenon described by Hastings et al. [16]. Further, they observed that the \( \langle 111 \rangle \) vacancy disc, consisting of a \( \langle 111 \rangle \) double plane of vacancies, had a much lower formation energy per vacancy at 1.20 eV than any of the multi-vacancy point defects. However, as stated in the introduction, no systematic large scale generation of clusters and their geometry optimization has been performed so far.

3. Energy calculations and structural descriptors

In our total energy calculations we used TB-DFT [11] in the framework of periodic boundary conditions for the conventional cubic supercell of \( (N-n) \) atoms, \( n \) varied from 1 to 14, and \( N \) was 216. This parametrized non-SCF method uses only one \( s \) and three \( p \) orbitals on each carbon atom and has well known limitations but it is very fast computationally. The equilibrium positions of the atoms were determined by the conjugate gradient method and due to the large number of possible cases we restricted ourselves to the \( \Gamma \)-point approximation. In each \( V_n \) cluster calculation, we first doubly occupied the lowest \( 2(N-n) \) energy levels of the available \( 4(N-n) \) levels. For determining the most stable structures we developed an algorithm to generate \( V_n \) vacancy clusters from those of the previous generation \( V_{n-1} \) by adding a \( V_1 \). The most stable vacancy cluster generated is \( V_{n-1} \) and \( V_{n-1} \) is the \( k \)-th in the order of stability.

After generating a list of \( V_{n,k} \) vacancy clusters having decreasing stability with increasing \( k \), we recalculated the geometry of the most stable ones for testing our results obtained by only 50 conjugate gradient steps using partial occupation numbers when the highest orbitals were degenerate. The surface atoms are defined as those with one or more cut bonds. A bond is considered cut if either it has a neighbor in the \( V_n \) or if its original first neighbor distance increased due to relaxation to a distance greater than 1.9 Å. A vacancy atom with three cut bonds defines three adjacent surface atoms. The distances among these are denoted by \( r_1, r_2, r_3 \). A vacancy atom with two cut bonds defines two surface atoms; their distance is marked by \( r_4 \). Distances between a four coordinated atom and its neighbors are referred to as \( r_5, r_6, r_7, r_8 \). The deformation of the surrounding of such a motif adjacent to vacancies leads to the shortening of three bonds, and the lengthening of a bond perpendicular to the plane of these three bonds defined by the corresponding three neighboring atoms. We used tetrahedra to describe these locally distorted “graphitized” structures helping to identify these situations effectively. We use the term tetrahedron of graphitization, TOG, to identify these structural motifs that play a key role in this work.

For comparison we provide the corresponding distances of the ideal diamond structure in parentheses when needed. For reference, our optimized diamond structure corresponds to \( r_{CC} = 1.5487 \) Å. The symmetry of a \( V_n \) is defined by the symmetry of its surface atoms. We have calculated the symmetries of the orbitals using only its coefficients...
on the surface atoms. Thus, \( m_n \) is the \( n \)-th molecular orbital that belongs to the irreducible representation \( \lambda \). Thus e.g. 429\( m_n \), refers to the 429-th orbital \( \lambda \) irreducible representation. For the \( N=216 \) supercell without vacancies \((n=0)\), we obtained for the Highest Occupied Molecular Orbital and Lowest Unoccupied Molecular Orbital: \( \text{HOMO} = -5.17 \text{ eV} \) and \( \text{LUMO} = 2.27 \text{ eV} \) which were used as the gap of diamond. We also refer to the total weight on the dangling orbitals that play an active role in the properties of a given \( \nu_n \). These are normalized sums or atomic orbital coefficients on the surface atoms of a vacancy cluster and help identify bulk vs. surface states.

4. Algorithm for generating connected vacancy clusters

In the Supporting data section we discussed two procedures for generating vacancy clusters. They are the hexagonal ring clusters (HRC) and the spherically shaped clusters (SPC) method. The HRC method can be seen as a procedure for minimizing the number of dangling bonds, \( N_{\text{DB}} \). Both procedures remove atoms one after the other from an ideal diamond structure. If a vacancy cluster \( V_n \) has already been generated, the next \( V_{n+1} \) cluster can be generated in several ways by removing one atom that is directly connected to another in \( V_n \). The number of such sites grows fast as \( n \) increases. A particular \( V_{n+1} \) cluster so generated can be identical to another if they can be transformed into each other by translation, rotation, reflection or any combination of these transformations.

The following algorithm generates our vacancy clusters of \( n \) missing adjacent atoms from the lattice for each \( n \), starting with \( V_1 \). The algorithm uses a diamond lattice (the \( U_r \) lattice) on which some of the steps of the algorithm are executed. All calculations refer to periodic boundary conditions using a supercell with \( N \) sites, \( n \) vacancies.

1. Start with the monoatomic \( V_1 \) vacancy, and increase \( n \) one by one.
2. Generate all possible \( V_n \) vacancy clusters on the lattice by adding one neighboring atom in all possible positions for each of the \( V_{n-1} \) vacancy clusters that were generated in the previous step with sufficiently low energies to be kept on the list.
3. Eliminate the equivalent vacancy clusters on the \( U_r \) lattice based on the eigenvalues of the modified adjacency matrix and only one of each equivalent set is kept. The number of the equivalent structures in step \( n \) is \( \nu_n \).
4. Optimize the geometries of all \( \nu_n \) structures.
5. Calculate the formation energies for all \( V_n \) vacancy structures obtained.
6. Keep only the \( M_n \) lowest energy vacancy clusters. \( M_n \) should be as large as permitted by the computational facilities.
7. \( n \rightarrow n + 1 \), and GO TO 2. The process terminates at a predetermined \( n \) value.

Steps 2 and 3 are executed on the ideal \( U_r \) lattice, not on the optimized structures (even if those are available), turning the process into a discrete problem. In Step 2, the algorithm checks all atoms on the inner surface of each of the \( V_{n-1} \) vacancy clusters adding one more missing atom from that surface. The surface is defined as atoms that have less than four adjacent (connected) atoms. A practical element of this modeling is that the connectivities of each structure can be easily reconstructed. Selection of equivalent structures in Step 3 was done by diagonalizing the modified adjacency matrix, \( D \) which is defined as the transformed interatomic distances, \( r_{ij} \):

\[
D_{ij} = \exp \left( -a r_{ij} \right). \tag{1}
\]

Two structures are considered equivalent if their eigenvalues are the same. In our calculations we used \( a = 1.0 \text{ Å}^{-1} \). The conventional adjacency matrix, \( A \), is obtained from \( D \) when only first neighbor distances are considered which are all taken to be the same. The advantage of diagonalizing \( D \) instead of \( A \) is that certain structures that are degenerate for \( A \) are not degenerate for \( D \) allowing a finer discrimination of structures. This is important, since in the selection process degenerate structures, if kept, would create a computational overload and may significantly reduce the diversity of the final structures. Using the above-mentioned algorithm, we have calculated the number of all possible vacancy clusters in the range from \( V_1 \) to \( V_{14} \). The notation \( n(p/q) \) means that the number of all possible \( V_n \) vacancy clusters is \( p \) which was reduced to \( q \) inequivalent ones. We obtained the following results: 1(1/1), 2(4/1), 3(6/1), 4(8,3), 5(30/7), 6(83/24), 7(328/88), 8(1357/385), 9(6617/1713), 10(32,417/8112), 11(167,511/38,865), 12(869,139/190,081), 13(4,574,468/937,194), 14(24,139,560/4,660,000). (The last \( q \) value for \( n = 14 \) was extrapolated.) Thus the algorithm generated, for example, 167,511 \( V_{11} \) vacancy clusters with only 38,865 inequivalent ones.

In Step 4, the geometry optimization was done with a conjugate gradient method for each of the \( \nu_n \) structures. The geometry relaxation process typically required at least 50 steps. The most stable structures were determined by filling up the lowest one electron energy levels. In the case of degeneracy, we used the accidental order of the eigenvalues generated by the computer. We choose \( N=216 \) for the diamond supercell with \( n \) up to 14. In Tables S1 through S11 we present the genealogy of all \( V_n \)'s with their respective formation energies. For \( 8 \leq n \leq 14 \) the same information is given only for the ten lowest energy structures in Table SIV.

In Step 5, the relative stability of the \( n \)-vacancy clusters was expressed by the formation energy \( E_n^f \):

\[
E_n^f = E_{\text{vac}}^n - \frac{N-n}{N} E_{\text{cryst}}. \tag{2}
\]

The formation energy per vacancy is \( E_n^f = E_n^f / n \). Here \( E_{\text{vac}}^n \) is the total energy of a supercell with \((N-n)\) atoms and \( E_{\text{cryst}} = E_{\text{vac}}^0 \).

Step 6 refers to the choice of \( M_n \). For small \( n \) the maximum value of \( M_n \) is \( \max(M_0) \). This number is limited (e.g. \( \max(M_2) = \max(M_3) = 1 \)) but \( \max(M_n) \) rapidly raises with \( n \) to astronomical numbers. Up to \( n = 7 \), we included all possible vacancy clusters, for \( n > 7 \) we used the following parameters \( M_2 = M_6 = M_8 = M_{10} = M_{11} = 5 \) and \( M_{12} = M_{13} = 7 \). Table SIV contains genealogical information on how the different structures can be generated from their “parents”.

5. Results

We present the outcomes for each of the \( V_n \) vacancy clusters. Fig. 1 contains the atomic numbering, Figs. 2 and 3 show the most stable vacancy clusters, and Figs. 4 and 5 contain specific vacancy clusters used in the analysis or because of earlier discussions of these structures in the literature. Figs. 2–5 contain relaxed (columns 5 and 6) and unrelaxed (columns 2 and 3) geometries of the respective \( V_n \)'s. Column 4 shows the removed atoms which are also indicated in columns 2 and 6 in addition to the surface atoms of each \( V_n \). Notation used in the earlier literature is adjacent to the symmetry labels of the relaxed structures in column 7. Column 1 contains the symmetry of the ideal unrelaxed structures. Figs. 6–9 illustrate specific cases and their geometrical descriptors. Figs. S1–S3 (see the Supporting data section) show the energy levels and symmetries of the dangling bond orbitals. In Table 1, we collected characteristic distances obtained for the relaxed geometries. These are analyzed after the discussion of the specific diamond vacancy clusters with \( n = 1 \) through 14. Further detailed analysis of the specific vacancy cluster energy levels and geometrical characteristics is given in the Supporting data section. For several vacancy clusters we confirm earlier assignments, while for some vacancy clusters a novel interpretation is offered based on the presented modeling.
5.1. \textit{V}_1\text{ vacancy}

According to experimental and theoretical results [20–22,29,30] the neutral monovacancy in diamond has \textit{T}_d symmetry (Figs. 2 and 6). \textit{V}_1\text{ in Si undergoes a \textit{T}_d to \textit{D}_{2d} distortion [19]. Coulson and Kearsley [28] and later Yamaguchi [31] assumed that the electrons in the dangling orbitals surrounding the vacancy primarily determine the electronic properties. In our TB calculations, the HOMO was a triply degenerate non-bonding \textit{t}_2 orbital containing two electrons, that is \textit{s}_b=4 and \textit{s}_s=3. In order to obtain a \textit{T}_d symmetry relaxed structure in the conjugate gradient procedure we used a fractional occupation number of 2/3 in the HOMO (Fig. S1). In the relaxed
structure, the four three-coordinated carbon atoms define the size of the tetrahedron-like void with a side of 2.61 (2.52) Å. The first neighbors of the vacancy atom experience an outward displacement of 0.044 Å while the second neighbors undergo a 0.024 Å inward displacement. These values are similar but smaller than in previous work [21]. We obtained a formation energy of 7.538 eV for V1. Local density calculations gave 7.2 eV formation energy on a supercell of 64 atoms [32]. Without any constraint to the symmetry, we obtained 7.272 eV for the formation energy with a geometrical distortion to C2v symmetry (Table SI).

5.2. V2 vacancy

The removal of two neighboring atoms from the diamond structure yields a defect with D3d symmetry [20,33–35] (Figs. 2, S1) that contains six dangling bonds (sb = 6) and six electrons. Upon geometry relaxation, a Jahn–Teller distortion drives the structure to C2h (Fig. S1). The two equilateral triangles formed by the dangling bond atoms around the three-fold axis changed to two isosceles triangles with the following distances: r1 = 2.50 (2.52) Å, r2 = 2.63 (2.52) Å, r3 = 2.63 (2.52) Å (Fig. 7). Besides the changing of the symmetry we observe on average a small increase of the interatomic distances of the two triangles. The relaxed interatomic distances are the following: r1 = 2.50 (2.52) Å, r2 = 2.61 (2.52) Å, r3 = 2.61 (2.52) Å. The distance r1 is perpendicular to the mirror plane containing the vacancy atoms (Fig. 2). The distance r4 = 2.49 (2.52) Å is also perpendicular to this plane and the corresponding surface atom has cut bonds with the middle atom of the vacancy cluster as illustrated in Fig. 8. In our most stable structure with S = 0 spin, the HOMO(426b2)–LUMO(427a2) energy difference is 0.24 (0.11) eV. Inclusion of electron correlation may show a triplet ground state when the gap is this small. EPR measurements on irradiated diamond attributed the R5 center to the neutral V3 vacancy with S = 1 spin state [2,6].

5.3. V3 vacancy

The void of the V3 vacancy has C2v symmetry and sb = 8 (the two terminal atoms have 3 dangling bonds and the center atom has 2) which are on the eight neighboring (or surface) atoms of the void (Figs. 8, S1). During the relaxation, the relative position of these orbitals remain unchanged (s = s′ = 5).

The equilateral triangles composed by the surface atoms at the two terminal vacancy atoms changed to isosceles triangles as with the V2 vacancy. The relaxed interatomic distances are the following: r1 = 2.50 Å, r2 = 2.61 (2.52) Å, r3 = 2.61 (2.52) Å. The distance r1 is perpendicular to the mirror plane containing the vacancy atoms (Fig. 2). The distance r4 = 2.49 (2.52) Å is also perpendicular to this plane and the corresponding surface atom have cut bonds with the middle atom of the vacancy cluster as illustrated in Fig. 8. In our most stable structure with S = 0 spin, the HOMO(426b2)–LUMO(427a2) energy difference is 0.24 (0.11) eV. Inclusion of electron correlation may show a triplet ground state when the gap is this small. EPR measurements on irradiated diamond attributed the R5 center to the neutral V3 vacancy with S = 1 spin state [2,6].

5.4. V3_is vacancy

Here we describe a set of three isolated V1 vacancies forming a special kind of three-atom vacancy with C3v symmetry, the V3_is (Figs. 4, S1), where the three vacancy atoms are in second neighbor position in the (111) plane. Their interatomic distance is 2.52 Å and they form an...
equilateral triangle. Relaxation in \( V_{3,1s} \) produces what we call a tetrahedron of graphitization (TOG). If we translate by \( r_{CC} \) the three vacancy atoms of \( V_{3,1s} \) in the (111) direction we find three carbon atoms at these positions. These three carbons have a joint neighbor. During the relaxation process, this neighboring atom will move toward the plane of the vacancy atoms developing \( sp^2 \) hybridization. We use the notation \( ra \) for the increased interatomic bond and \( rb, rc, rd \) for the other interatomic bonds of the moving atom in the tetrahedron. This displaced atom with its original four neighbors form the TOG with the elongation of the \( ra \) bond and the simultaneous shortening of the adjacent bonds. The number of dangling bond states is increased by one due to the formation of the TOG. The corresponding new gap state is antibonding (\( \pi^* \)). TOG displays the smallest unit with traces of \( \pi \)-bonding and helps analyze more complex cases and it can be easily identified for in col. 5 and 6 in Fig. 4. This protrusion is a characteristic of the TOG that is apparent when comparing the diagrams in col. 5 and 6 with the unrelaxed structures in col. 2 and 3 in Figs. 2 through 4. \( V_{3,1s} \) is the smallest vacancy cluster for which such a protrusion occurs.

5.5. \( V_4 \) vacancy

\( V_{4,1} \) is chain-like and has \( C_2 \) symmetry (Fig. 2 and Table SI) and the ten hybridized dangling bonds are listed in Fig. S1. The corresponding energy level of the doubly occupied HOMO orbital 424 and the energy levels around it are defect states that are in the gap. The two equilateral surface triangles at the two ends of \( V_4 \) relaxed to \( r_1 = 2.34 \) (2.52) Å, \( r_2 = 2.66 \) (2.52) Å and \( r_3 = 2.58 \) (2.52) Å. The distance between the surface atoms near the two interior vacancy atoms is \( r_4 = 2.30 \) (2.52) Å.

EPR on irradiated diamond indicated a \( V_4 \) vacancy with \( C_{2v} \) and in the \( S = 1 \) state \([2,6,36]\), labeled the O1 center. It has been associated with a \( \langle 110 \rangle \) chain \([6,36]\) with \( C_{2h} \) symmetry \((\langle V_{4,3} \rangle \) in Table SI and Fig. 4, S1) contradictory to the EPR finding \([2]\) that indicated \( C_{2v} \). In our calculation for the \( C_{2h} \) symmetry structure the HOMO orbital 424 is in the gap with five other surface orbitals (Fig. S1). The situation is the same before and after the relaxation. The parameters for the two equilateral surface triangles at the two ends of the \( V_{4,3} \) vacancy are the following: \( r_1 = 2.54 \) (2.52) Å, \( r_2 = 2.57 \) (2.52) Å and \( r_3 = 2.57 \) (2.52) Å. The distance between the surface atoms near to the two interior vacancy atoms is \( r_4 = 2.37 \) (2.52) Å as defined in Fig. 8. In a connected chain of vacancies each has two dangling bonds, except for the ends which have three each. These trends are different from those found in earlier calculations where the dangling bonds reconstruct in pairs leaving two dangling bonds, one at each end of the chain \([6,36]\). Note that both \( V_{4,3} \) and \( V_{4,2} \) are significantly less stable than \( V_{4,1} \).

5.6. \( V_5 \) vacancy

The most stable \( V_5 \) void, the \( V_{5,1} \), has \( C_3 \) symmetry (Figs. 2 and S1). The energy level of the doubly occupied HOMO orbital 422 is in the valence band and the energy levels above it are in the gap. After the
relaxation, the void determined by the atoms having at least one dangling bond can be seen in Fig. 2. The most interesting phenomenon of this void is the appearance of a tetrahedron of graphitization (TOG), which appears as a protrusion in col. 5 and 6 in Fig. 2. The parameters of the TOG are $r_a = 1.99$ (1.54), $r_b = 1.55$ (1.54), $r_c = r_d = 1.47$ (1.54) Å. $V_{5,1}$ has similar to $V_{3,1}$ three atoms which produced the simplest TOG. Baker attributed this $V_{5,1}$ structure to the EPR detected R8 center [6] although its measured symmetry is $C_{2v}$. The R6 EPR center has been attributed to the $V_{5,6}$ chain lying in the (110) plane (Table S1 and Figs. 4, S1) [2,6]. According to our calculation, this structure is the penultimate in the stability order of $V_5$ voids and it has $C_{2v}$ symmetry just as in the EPR experiment.

Fig. 5. Selected $V_n$ vacancy clusters in diamond for $n = 7$ through $n = 13$. The seven columns are the same as in Fig. 2.

Fig. 6. The nearest neighbors to the vacancy cluster $V_1$ (removed atom in red) site maintain $T_d$ symmetry with $r = 2.61$ when the HOMO $t_2$ orbitals all equally occupied by 2/3 electrons.

Fig. 7. The relaxed geometry surrounding $V_{2,1}$ (removed atoms in red). Labeled distances refer to the separations between the three neighbors to the vacancy terminus.
5.7. $V_6$ vacancy

The most stable $V_6$ vacancy cluster has the cyclohexane-like structure with $D_{4d}$ symmetry. As each vacancy atom has two cut bonds, the number of dangling bonds and surface atoms is twelve ($3b=12$) ($V_{6,1}$ in Fig. 2). After the relaxation, we obtained two TOGs as the cyclohexane-like structure of vacancy atoms can be imagined as a pair of connected $V_{3s}$ vacancies as can be seen in Fig. 2. Col. 5 and 6. These two protrusions indicate of two TOGs. The carbon $V_6$ cyclohexane-like vacancy is due to the formation of two TOGs not seen in the Si case.

The number of inequivalent $V_6$ vacancy clusters is 24 and the least stable, $V_{6,24}$, corresponds to the chain lying in the $\langle 110 \rangle$ plane. This structure is usually attributed to the R10 EPR center [2,6] but it has $C_{2v}$ symmetry contrary to the $C_{2h}$ symmetry obtained in EPR experiment. (Table SII and Fig. 4). The extra stability of the carbon $V_6$ cyclohexane-like vacancy is due to the formation of two TOGs not seen in the Si case.

The relaxed geometry surrounding $V_{6,1}$ (removed atoms in red). There are six termini.

![Fig. 8](image)

Fig. 8. The relaxed geometry surrounding $V_{6,1}$ (removed atoms in red). As with the $V_{3s}$, $r_1$, $r_2$, and $r_4$ denote the separations between the three neighbors surrounding the termini. $r_4$ is the separation between the two neighbors of the middle vacant atom.

5.8. $V_7$ vacancy

The most stable $V_7$ void has $C_{s}$ symmetry ($V_{7,1}$ in Table SIII and Figs. 2 and S2). The vacancy cluster contains the previous $V_6$ cyclohexane-like structure plus another atom in equatorial position. After the relaxation we obtained the two TOGs, just as for $V_{6,1}$ (Fig. 2).

In the stability order the next $V_7$ void is the $V_{7,2}$, constructed from the $V_6$ cyclohexane-like structure plus an atom in axial position (Table SIII and Figs. 5, S2). This was assumed to be the most stable $V_7$ vacancy cluster in previous calculations [25]. This defect also has $C_{s}$ symmetry. Baker attributed the $V_{7,6}$ structure ($C_{2s}$ to the EPR active $R7a$ center [6] although its measured symmetry is $C_{2v}$ (Table SIII, Figs. 5, S2). The number of inequivalent $V_7$ vacancy clusters is 88 and the $V_{7,77}$, corresponds to the chain lying in the $\langle 110 \rangle$ plane. This structure has been attributed to the R11 EPR center [2,6]. It has $C_{2v}$ symmetry as it is expected from EPR experiment (Table SIII and Figs. 4, S2).

5.9. $V_8$ vacancy

The most stable $V_8$ void, the $V_{8,1}$, has $C_{s}$ symmetry (Table SIII and Figs. 2, S2). After relaxation, the orbital 426a′ has a small weight in the vicinity of the vacancy cluster and came from the conduction band. The doubly occupied HOMO orbital 416a′ is in the valence band. Here we obtained one TOG (Fig. 2).

Baker [6] suggested the $V_{8,1}$ structure of Fig. 5 as a relatively stable structure as it is a closed ring. (* indicates that our algorithm did not generate this structure). We obtained $E_{V8}^\# = 3.2476$ eV for this structure, slightly less stable than the 6th most stable we generated. Its relaxed structure does not have TOG. Although $V_{7,6}$ is a parent structure for $V_{8,1}$, our algorithm did not produce it as we used the $M_T = 5$ parameter.

Table 1

<table>
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<tr>
<th>Cluster</th>
<th>$r_1$</th>
<th>$r_2$</th>
<th>$r_3$</th>
<th>$r_4$</th>
<th>$r_5$</th>
<th>$r_6$</th>
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<tbody>
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<td>2.63</td>
<td>2.63</td>
<td>1.93</td>
<td>1.46</td>
<td>1.46</td>
</tr>
<tr>
<td>$V_{6,2}$</td>
<td>2.49</td>
<td>2.61</td>
<td>2.61</td>
<td>1.93</td>
<td>1.46</td>
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<td>2.68</td>
<td>2.58</td>
<td>2.30</td>
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<tr>
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<td>2.46</td>
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<td>3.15</td>
<td>2.19</td>
<td>2.12</td>
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<td>2.13</td>
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<td>1.97</td>
<td>1.58</td>
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<tr>
<td>$V_{6,8}$</td>
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<tr>
<td>$V_{6,9}$</td>
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<td>2.10</td>
<td>1.97</td>
<td>1.58</td>
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<tr>
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<td>1.97</td>
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<td>2.02</td>
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<td>1.59</td>
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<td>$V_{6,13}$</td>
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<td>2.08</td>
<td>1.45</td>
<td>1.57</td>
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</tbody>
</table>

$V_{6,0}$ stands for $V_{8,chain}$. 

V8 chain
In Figs. 4 and S3 we can see the $V_{n\text{-chain}}$ structure of the chain lying in the (110) plane. This structure has been attributed to the KUL11 EPR center [2,6] although it has $C_{3v}$ symmetry contrary to the EPR evidence that supports $C_{2v}$. This structure can not be found in the list of Table SIV for $V_9$ as it has relatively high $E_F = 3.75$ eV. During the relaxation process, we obtained an extra energy level in the gap.

5.10. $V_9$ vacancy

The most stable $V_9$ void has $C_{2v}$ symmetry ($V_{9\text{-}1}$ in Table SIII and Figs. 2, S3) and its relaxed structure has two TOGs. During the relaxation the number of dangling bond states increased by two. The parameters of the TOG are $r_{d1} = 1.97$ (1.54), $r_{d2} = 1.58$ (1.54), $r_{d3} = 1.58$ (1.54) Å. The distances between the surface atoms close to the three different kinds of interior atoms (starting from the symmetry axis) are: $r_4 = 2.09$ (2.52), $r_4 = 2.13$ (2.52), $r_4 = 2.44$ (2.52) Å. This $V_{9\text{-}1}$ void was attributed to the R7a EPR center [2].

5.11. $V_{10}$ vacancy

$V_{10\text{-}1}$ ($T_d$) is particularly stable. It has four TOGs in the relaxed structure (Table SIII and Figs. 2, S3).

5.12. $V_{11}$ vacancy

The most stable $V_{11\text{-}1}$ void ($C_{3v}$) has four TOGs in the relaxed structure. (Table SIV and Figs. 2, S3). One TOG has the same axis of rotation as the void and the other three TOGs can be transformed by the three-fold axis. Jakoubovskii and Stesmans [2] attributed the $V_{11\text{-}1}$ void of Fig. 5 to the R7 EPR center. Although this structure has one TOG, its formation energy per vacancy at 2.9021 eV is less stable than our 10 most stable $V_{11}$ structures.

5.13. $V_{13}$ vacancy

The most stable $V_{13\text{-}1}$ void has $C_s$ symmetry and 1 + 1 + 2 = 4 TOGs in the relaxed structure ($V_{13\text{-}3}$ in Table SIV and Figs. 2, S2). However, Jakoubovskii and Stesmans [2] and Baker [6] attributed the $V_{13\text{-}3}$ void of Fig. 5 to the R8 EPR center. It has $C_{2v}$ symmetry and its formation energy per vacancy (2.93 eV) is higher than the formation energies of the $V_{13\text{-}1}$ structures listed in Table SIV.

5.14. $V_{14}$ vacancy

Especially stable is the lowest energy $V_{14\text{-}1}$ ($D_{3d}$) with six equivalent TOGs in the relaxed structure (Table SIV and Figs. 2, S3).

5.15. Trends in vacancy cluster geometries

We have noticed trends among the distances marked by the identical notation (Table 1). These regularities point to the possibility of rich chemistry and physics of vacancy clusters given their unusual CC contacts. Most remarkable are the CC contacts that appear to represent a new kind of bonding in the tetrahedra of graphitization.

The parameters of the TOG are in the ranges $r_{d1} = 2.01 \pm 0.11$ Å, $r_{d2} = 1.525 \pm 0.075$ Å, $r_{d3} = 1.525 \pm 0.075$ Å, and $r_{d4} = 1.525 \pm 0.075$ Å. Clearly, the first neighbor contact distances of 2.01 ± 0.11 Å found in the TOGs are highly unusual and not found as an equilibrium carbon–carbon bond distance in any of the over 500,000 organic molecular structures in the CSD [40]. As pointed out above many of the contact distances are stabilized only by the surrounding dangling orbitals of the carbon network and the multicenter bonding that they provide.

Some second neighbor distances also show trends that are summarized below. In the most stable vacancy clusters for example only the vacancies $V_1, V_{2\text{-}1}, V_{3\text{-}1}, V_{4\text{-}1}, V_{5\text{-}1}, V_{7\text{-}1}$ and $V_{8\text{-}1}$ have vacancy atoms with at least three cut bonds. The chain-like structures $V_{2\text{-}1}, V_{3\text{-}1}, V_{4\text{-}1}, V_{5\text{-}1}, V_{6\text{-}1}, V_{7\text{-}1}, V_{7\text{-}7}$ belong to the family defined by the following characteristics: $r_4 = 2.515 \pm 0.025$ Å, $r_{2\text{-}1} = 2.59 \pm 0.04$ Å. For $V_{8\text{-}24}$ we obtained a slightly smaller $r_1$, but the $r_2 = r_3$ value is in the same range. The exception of $V_{8\text{-}1}$, can be explained by the limited size of the supercell. In other structures there are special relative positions between the surface atoms of the voids leading to $r_1, r_2$ and $r_3$ distances outside of the abovementioned ranges. Similar remarks can be made for the $r_4$ distances as well. There are some exceptions due to insufficient supercell size, e.g. for $V_{13\text{-}1}$. Most of them are in the range $r_4 = 2.1 \pm 0.09$ Å, which makes these contacts approach values where multicenter bonding contributes to the stability of the structure.

6. Concluding remarks

We have obtained the structures and properties of $V_n$ multi-vacancy voids in diamond in the range of $n = 1$ through 14. Most of these structures are novel and are described for the first time. Several of these voids are different from the corresponding multi-vacancy voids in silicon. We have traced these differences to the tendency of carbon to form π-bonds in the “tetrahedron of graphitization” allowing the adjacent dangling bonds to turn towards each other and “heal.”

The tendency to form π-bonds is a sign of a certain degree of graphitization around some of these voids, which in turn removes the non-bonding dangling orbitals from the middle of the gap lending both stability and, perhaps, reduced reactivity to these voids. This was a surprising result and we speculate that if this tendency is maintained for larger voids, the characteristics of such voids and pores for chemical storage may be favorable. The tendency of local “graphitization” around parts of the vacancy cluster appears already at an unexpectedly small size. We have identified a noncontiguous vacancy cluster of three monovacancies, $V_{3\text{-}10b}$. We found that this motif goes hand in hand with similar local graphitization tendencies in all vacancy clusters studied. Each tetrahedron of graphitization (TOG) produced an extra energy level in the gap. It is possible, even likely, that in large vacancy clusters such tendencies for graphitization on the atomic scale may lead to the formation of larger graphitic regions significantly affecting their properties as gas storage or electrode materials. The multi-vacancy voids studied in this paper were generated by a novel generational algorithm that proceeds to spawn generation $n+1$ from the list of the most stable structures in generation $n$. A key point in the algorithm is to determine and eliminate equivalent structures, which is done by comparing the eigenvalues of a modified adjacency matrix of the contiguous atoms of the vacancy. This novel method permits a significant reduction of the number of inequivalent vacancy clusters to consider for any given $n$. This allowed us to describe all possible vacancy clusters up to $V_7$ for the first time. We also obtained the optimized geometries by tight binding DFT for all possible vacancy clusters up to $V_7$.

An advantageous feature of the generational algorithm is that it is fully reproducible because five integers contain all the information necessary to define a member of the new generation. Using this algorithm combined with tight binding DFT, we determined the most stable contiguous vacancy clusters for $V_8$ through $V_{14}$. For the most stable structures we identified the surface states and their symmetries. These can be used in devising more sophisticated calculations for determining the measured electronic transitions.

We also investigated structures suggested by other groups [2,6,24] based on EPR experiments for vacancy clusters with $n = 2, 3, 4, 5, 7, 9,$ and 11. Most of these structures were found to be higher in energy than the most stable vacancy clusters generated by our algorithm, in some cases significantly higher. Note that our calculations, being of the TB kind, is limited to spin = 0 states. There is controversy in the literature concerning the identities of these structures (see Figs. 2–5). It seems that if the identification of these structures with EPR signals is correct in the literature, then the more stable structures obtained in...
this work should also exist in the $S = 0$ state. For possible existing structures see, for example, those highly stable structures in Figs. 2 and 3 which are not are visible by EPR.

One of the interesting features of this study is the high frequency of neighboring C–C distances in the unusual range of 1.8 to 2.6. There are no molecular examples of such distances either as intramolecular bond distances or intermolecular contact distances in the Cambridge Structural Database (CSD), as most C–C contacts are found below 1.6 and above 3.2. It is clear that the environment surrounding vacancies in diamond is entirely unique and different from other carbon systems owing to the presence of dangling radicals whose relaxation is hindered due to the scaffold of the surrounding covalent network. Whether these unusual contacts have all the features of ordinary chemical bonds remains to be seen. They appear to be more variable than ordinary electron pair bonds, but variability is not unusual for multielectron multicenter delocalized bonding.

Acknowledgement

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.diamond.2010.05.001.

References