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Ab initio studies of 5-atom ring carbon and silicon amorphous clusters both pure and with group-V impurities

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We have constructed hydrogen saturated carbon and silicon clusters with *only* 5-atom rings to study their effect on the electronic properties of the corresponding amorphous materials. Using density functional theory and the local density approximation we calculate the electronic structure of pure and contaminated clusters, symmetric and nonsymmetric, with the impurity in the center or in the nearest neighbor position. For the pure cluster we find, by comparison to reference clusters with 6-atom boat-type rings, that the pentagonal clusters have a narrower valence band and that the top of the valence band moves to lower energies. Without the hydrogen contribution the energy gap for the pentagonal carbon cluster is larger than that for the hexagonal one and the gap for both silicon clusters is practically the same, contrary to expectations due only to size. For the impure clusters the carbon gap values decrease as the atomic number of the impurity increases, whereas the effect is opposite for silicon; also, the width of the valence band is larger in all cases than that for the pure clusters.

I. INTRODUCTION

The atomic topology of covalently bonded amorphous semiconductors has been the subject of a long standing controversy. Experimentally, the most one can hope for is to obtain averaged properties like the radial distribution function (RDF) and the electronic density of states (DOS). The presence (or absence) of odd-membered rings is extremely difficult to extract from such quantities as the RDF or the distribution of dihedral angles. Theoretically, realistic structural models are a necessity for proper interpretation of experimental data. For many years it was known that calculating the properties of a continuous random network was a very difficult task and some of the results were in doubt since it was assumed that a given structure would lead to specific properties not necessarily reproduced by other structures. For silicon it was argued that while in the DOS of the crytalline solid the density contributions due to the s orbitals, the p orbitals, and the sp hybridization are easy to observe (since each one gives rise to a prominent peak), the sp peak disappears in the amorphous material. This was observed both experimentally and in computer simulations, and was originally associated with the appearance of 5-atom rings in the structure.[1] It was argued that sp contributions coalesced with p contributions becoming a single broad peak in the DOS of amorphous silicon. Later on a new hypothesis was set forth and it was asserted that the existence of 5-atom rings was not responsible for this occurrence but rather a uniform distribution of the values of the dihedral angles was the cause for the smearing of the sp band and its merging with the p band.[2]

Recently, renewed interest in the atom topology of group-IV semiconductors has appeared, in particular for silicon and carbon in themselves and also for the contrasting influences of 5-atom rings, smaller rings, and bonding in both materials (see works in Ref. 3). The silicon fourfold-coordinated crystalline clathrate structures Si(34) (fcc) and Si(46) (sc) have become relevant for their potential to generate wide band gap silicon semiconductors that have indirect energy gaps near 1.9 eV, 0.7 eV *larger* than the diamondlike structure, which makes them useful from the technological viewpoint (See Adams *et al.*[3(b)]) These structures are formed with a higher proportion of 5-atom rings than the proportion of 6-atom rings, and the Si bond lengths have been found experimentally to be 2.37 Å, slightly larger than the diamondlike structure value of 2.35 Å. It should be borne in mind that it is not possible to construct a crystalline structure with *only* 5-atom rings.[4] Carbon is a more versatile element and its chemistry is richer than that of silicon; nevertheless as far as we know carbon clathrate structures have not been identified experimentally, which could be due to the fact that the C-C bonds are stiffer than the Si-Si bonds and therefore less deformable. Adams *et al.* have found that the theoretical clathrate structures of carbon manifest the opposite effect in the energy gap than the clathrate structures in silicon; i.e., the band gap for carbon in these structures is *smaller* than the band gap in diamond.

Clathrate structures have not been doped with substitu-

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tional impurities, as far as we know, neither experimentally nor theoretically, and this could be a very relevant feature if these crystalline materials were to be used extensively as wide band gap semiconductors. That is why we decided to study the effect of group-V impurities in clusters with *only* 5-atom rings.

Another important calculated feature is the reported presence (Clark *et al.*[3(e)]) of a larger concentration of 5-atom rings for amorphous silicon than that for amorphous carbon, which again indicates the existence of a more rigid structure for carbon than that for silicon. They also find that fivefold overcoordination of atoms is possible in amorphous silicon but not in amorphous carbon (see also Godwin[5] for a very complete report of computer simulations of amorphous carbon). The calculations of Saito and Oshiyama[3(d)] show that for the structure of the crystalline tetrahedrally coordinated clathrate Si(46), which contains 87% of 5-atom rings and 13% of 6-atom rings, the electronic structure is remarkably different from that of the diamondlike tetrahedral silicon lattice, which contains 100% of 6-atom rings. The top of the valence band moves to lower energies, making it narrower and the band gap larger than that of diamondlike silicon; moreover, a new gap is reported to appear within the valence band for the clathrate silicon.

On the diamondlike lattices the DOS for the valence band has three prominent areas that consist mainly of *s*-like states, sp-like states, and *p*-like states, in order of increasing energy. That is, for carbon one expects to find $2s$ and $2p$ states at the band extremes, plus some $2sp$ hybridization in the middle of the band, whereas for silicon one has $3s$ and $3p$ states with some $3sp$ component.[6] Due to the symmetry of the 6-atom rings in crystalline lattices, the *s* states can form antibonding states having a node on each bond, whereas with the pentagonal rings this cannot happen. Therefore, it is expected that in pentagonal structures the *s* states of the fivefold rings would have a lower energy than the corresponding *s* states of the sixfold rings, thereby possibly creating a gap in the middle of the valence band, separating *s* and *p* states for both silicon and carbon (Saito and Oshiyama.[3(d)]) A similar argument is invoked for the lowering of the top of the valence band in pentagonal structures compared to the value of the crystalline structures.

In 1998, however, Mélinon *et al.*[3(f)] measured the valence band spectrum of the clathrate Si(34) by photoemission spectroscopy and found that for this mainly pentagonal structure no new gaps are created but a merging of the *s*-like and the sp-like subbands appears. They conclude that this merging agrees with the original propositions of Joannopoulos and Cohen[1] and is the signature of the existence of fivefold rings, although in Ref. 1 the merging of the sp and *p* subbands was invoked.

It is clear then that the influence of 5-atom ring topology on amorphous semiconductors is not well known, although there are indications that they affect the properties and electronic structure of silicon and carbon, sometimes perhaps in opposite ways, like the size of the energy gap. In order to better understand the role of fivefold atom rings on the electronic properties of both *a*-Si and *a*-C, pure and contaminated with group-V impurities, we constructed clusters with 17 atoms of either Si or C arranged in a pentagonal structure with a central atom and 16 nearest and second neighbors, saturated with hydrogens, and with the inclusion of substitutional impurities as is described in the next section. Reference clusters that contain 21 silicons or carbons with 6-atom rings and no impurities were used in order to cancel out size and surface effects as well as possible. We studied their electronic structure with an *ab initio* density functional technique. The study of clusters can shed new light on these problems since it allows the analysis of particular properties, specific restrictions, or geometries that may elucidate the role of the different factors that are relevant to the electronic structure of these materials.[7]

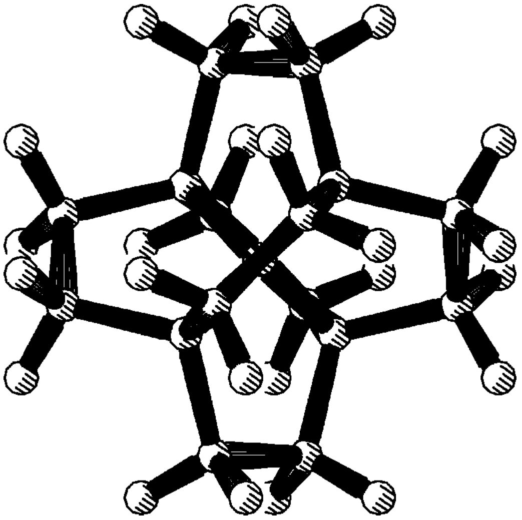

FIG. 1. Cluster with a central atom that is a common vertex for 6 pentagons tetrahedrally arranged. The central atom has 4 NN and 12 2N. The cluster has the symmetry of the T_d point group with 6 degrees of freedom.

II. THE CLUSTERS

All the clusters were constructed using the Builder Module within the INSIGHTII graphical user interface of MSI.[8] The basic pure cluster of carbon or silicon atoms has 5-atom planar rings and fourfold coordination with 17 host atoms and 24 hydrogen saturators for a total of 41 atoms. These clusters have the symmetry of the T_d point group with six degrees of freedom. A schematic representation of the starting clusters is shown in Fig. 1 where it can be seen that there is a central atom that is a common vertex for 6 pentagons tetrahedrally arranged, with four nearest neighbors, NN, and twelve second neighbors, 2N. The interior angles of the pentagons are one of 109.47° at the common vertex, two of 106.84° closest to the previous angle, and the remaining two of 108.425°, for a total of 540°. A regular pentagon would have had five angles of 108°. The interatomic distances are all 1.54 Å for carbon and 2.35 Å for silicon before energy optimization. The clusters were hydrogenated and the H atoms placed at a distance of 1.07 Å for carbon and 1.48 Å for silicon, without altering the tetrahedral symmetry.

The basic reference pure clusters of carbon or silicon have 6-atom boat-type rings that are found in amorphous solids, the coordination number is 4, and they also have tetrahedral symmetry.[7] These clusters have the symmetry of the T_d point group with eight degrees of freedom. The clusters (Fig. 2) have a central atom, 4 NN, 12 2N, and 4 third neighbors, 3N,

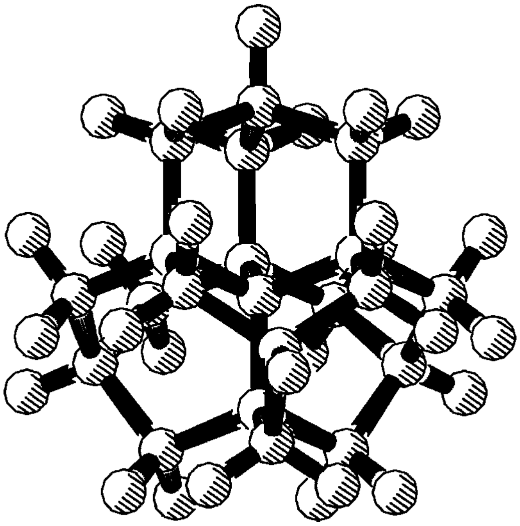

FIG. 2. Cluster with 6-atom boat-type rings. The central atom has 4 NN, 12 2N, and 4 3N. The cluster has the symmetry of the T_d point group with 8 degrees of freedom.

for a total of 21 atoms. All interior angles of the 6-atom rings are 109.47° and the interatomic distances are also 1.54 Å for carbon and 2.35 Å for silicon. The clusters were hydrogenated and 28 H atoms were placed at a distance of 1.07 Å for carbon and 1.48 Å for silicon, without altering the tetrahedral symmetry. The total number of atoms is 49.

When group V impurities were substituted in the pentagonal clusters they were put either at the center or in a NN position; the impure clusters are then identified by the number of atoms of the different species, the type of the substitutional impurity and its position. For example, a cluster $X_{16}I_{1,c}$ indicates that X is the host atom, i.e., C or Si, and I represents the impurity atom, i.e., N, P, or As located in the central position. In the second case we replace one of the host NN atoms by a group V impurity atom; these will in turn be denoted as $X_{16}I_{1,\mathrm{NN}}$. The geometry optimizations were carried out for X_{17},$X_{16}I_{1,c}$, and $X_{16}I_{1,\mathrm{NN}}$, maintaining the 2N atoms and the hydrogens fixed and using the DMOL program within the *ab initio* density-functional theory (DFT) local-density analysis (LDA) self-consistent approximation for unrestricted spins. All clusters were analyzed in two ways: first, maintaining symmetry (tetrahedral or C_{3v}) and then without symmetry restrictions.

III. METHOD

We use the DFT approach of Hohenberg and Kohn[9] and Kohn and Sham[10] implemented in the DMOL comercial code,[11] which treats the electronic structure of molecules or clusters by solving the Kohn-Sham self-consistency equations within local- or nonlocal-density approximations; in our work we used the local-density approximation (LDA) of Vosko, Wilk, and Nusair (VWN).[12] DMOL calculates the solutions to the DFT equations variationally and self-consistently, and these solutions provide the molecular wave functions and electron densities that can be used to evaluate the energetics and the electronic and magnetic properties of the system. In this paper we report the results of the density of states calculations that are necessary to study the possible appearance of new gaps, the behavior of the forbidden energy gap, the width of the valence band, the position of the Fermi level, and the impurity levels and their implication for the shallowness or for the depth of the impurity energy levels in the clusters.

DMOL employs a real space method with numerical basis functions centered on the atoms, and this allows the handling of systems larger than those that would be possible with other *ab initio* techniques for comparable computational costs. This code also allows the calculation of the electronic properties both for spin restricted and spin unrestricted systems. The electron gas exchange-correlation energy in DMOL is based on the work of von Barth and Hedin;[13] the exchange energy is spin independent and the correlation contributions depend upon whether the computation is spin restricted or spin unrestricted.[11]

The solutions of the Kohn-Sham equations generate interatomic forces and the evaluation of the energy gradients provides a convenient method for determining the equilibrium geometry of the system, free or subject to constraints. In fact DMOL includes a suite of algorithms for geometry optimization that locates both the minima and transition states on a potential energy surface. The core of the program is the so-called eigenvector following algorithm (EF), proposed by Baker.[14] It can optimize in Cartesian coordinates or in a set of nonredundant internal coordinates that are generated automatically from the Cartesian coordinates used as input. It can also handle fixed constraints on distances, bond angles, and dihedral angles. The process is iterative, with repeated calculations of energies, gradients, and calculations, or estimations, of Hessians in every optimization cycle until convergence is attained.

Recent calculations in silicon[15] have shown that the energy gap value changes only marginally when using different approximations at the local level. We assume that the same occurs for carbon and since we are concerned here with tendencies, and not with the absolute values of the gaps, we used the VWN approximation throughout. We also used a double numerical basis set that includes d polarization of the atoms (DND) and the frozen inner core orbital approximation; a medium grid was used for the numerical calculations since we were looking for consistent trends of the properties of these clusters as a function of concentration. The self-consistent field density parameter that specifies the minimum degree of convergence for the LDA density was set at 10^{-6}.

IV. RESULTS AND DISCUSSION

The pentagonal and hexagonal clusters used in this work emphasize characteristics that are expected to occur in both amorphous carbon and silicon, in order to study their influence on the electronic properties of a-C and a-Si. We analyze the influence of 5-atom rings in these amorphous materials because there are features that should depend on them. All pentagonal clusters were geometry optimized, subject to the constraints mentioned in Sec. II, and in order to investigate the minimum energy configuration of the disordered clusters (no symmetry) these were deformed before geometry optimization either by displacing the central atom in X_{17} and $X_{16}I_{1,c}$, or displacing the NN where the impurity was located in $X_{16}I_{1,\mathrm{NN}}$. For all of them, pure and impure, sym-

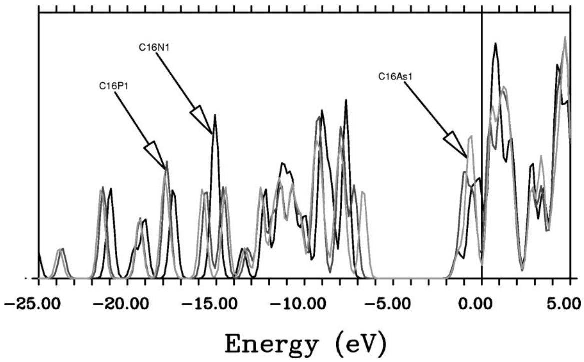

FIG. 3. Density of states (DOS) curves for the symmetric carbon clusters with N, P, or As as a central impurity.

metric and nonsymmetric, we studied the density of states curves, the variation of the top of the valence band, the changes in the gap size, the valence band width, the possible existence of new gaps, and the depth of the impurity levels. The pure reference clusters were also geometry optimized subject to the constraints of Sec. II.

In order to obtain global information of the electronic properties of the clusters it is necessary to construct the DOS for each one of them. To understand the DOS curves and the calculation of energy gaps, activation energies, and depths of the donor states, we have to identify adequately the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) as well as the impurity levels. The definition of an energy gap is very clear in the pure clusters, since it is simply the energy difference between the HOMO and the LUMO. However, when looking at the experimental results it becomes apparent that for impure materials there are other parameters that enter into consideration. Thus it is common to refer to the impurity levels as states localized within the energy gap and then one has to be careful with the HOMO and LUMO interpretation since in these circumnstances the HOMO would be the highest occupied *impurity* level and the LUMO the lowest unoccupied *impurity* level, which in general are very close to one another and do not represent the quantities measured experimentally. Since the unrestricted spin option of DMOL was used α and β orbitals were obtained for the same spatial molecular orbitals, so we averaged the energy values of the same orbitals for the symmetric clusters and averaged pair levels for the highest position in the valence band for the lowest positions in the conduction band and the two levels associated with the impurities, to give a single value for the gap, for the impurity levels and for the depth of the donor states.

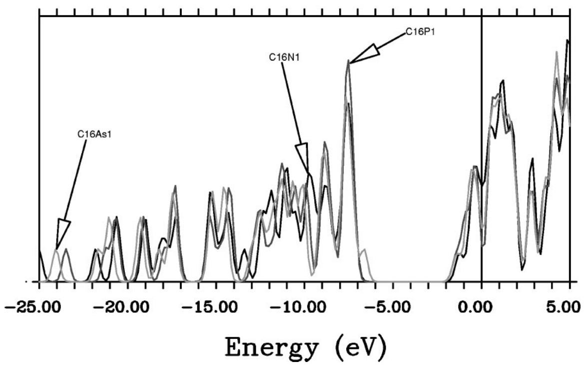

FIG. 4. Density of states (DOS) curves for the symmetric carbon clusters with N, P, or As as a nearest neighbor impurity.

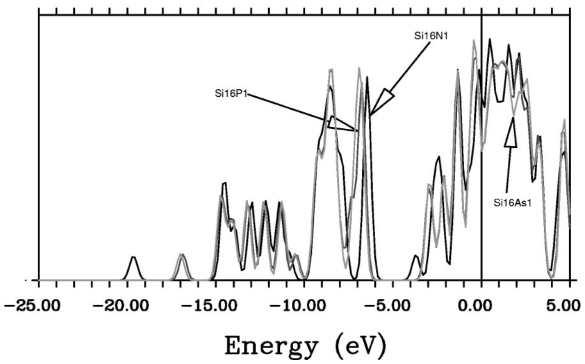

FIG. 5. Density of states (DOS) curves for the symmetric silicon clusters with N, P, or As as a central impurity.

A. Density of States

In Figs. 3–6 the total density of states for the impure C_{17} and Si_{17} are shown. Since the calculations give discrete energy levels (finite cluster), we have fitted Gaussians to them with a halfwidth of 0.2 eV. The graphs represent the symmetric clusters since the DOS curves are practically indistinguishable from the nonsymmetric ones. It can be seen that *N* generates deeper levels than P or As in all the clusters, as expected, since nitrogen has strong tendencies to become threefold coordinated.[7] The levels of phosphorus and arsenic are closer to the conduction band than the nitrogen levels. This is analyzed in the next subsection.

B. Energy Levels

In Tables I–IV the average values for the pertinent energy levels are given, together with the depth of the impurity levels. In most cases the results obtained for clusters with or without symmetry are qualitatively the same, which indicates the relevance of the short range order over the symmetry of the clusters.

For the pentagonal carbon clusters with the impurity at the center, both symmetric and nonsymmetric, it can be seen (Table I) that the top of the valence band, the HOMO, increases systematically in energy as the atomic number of the impurity increases; the value for the pure cluster being sur-

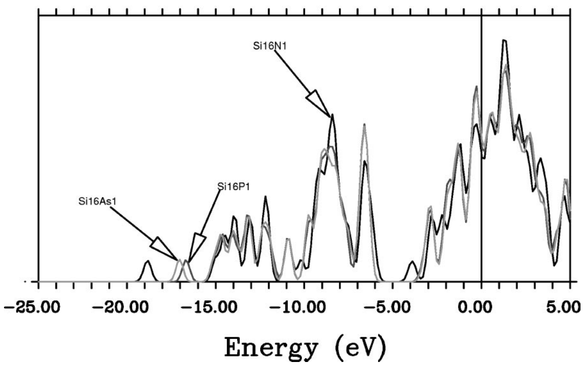

FIG. 6. Density of states (DOS) curves for the symmetric silicon clusters with N, P, or As as a nearest neighbor impurity.

TABLE I. Energy levels (eV) for the carbon clusters pure and with an impurity in the center.

	T_d Symmetry			No Symmetry		
Cluster	HOMO	LUMO	Impurity Depth	HOMO	LUMO	Impurity Depth
C_{17}	−6.96	−0.85		−6.94	−0.84	
$C_{16}N_{1,c}$	−7.56	−0.58	0.76	−7.56	−0.66	0.68
$C_{16}P_{1,c}$	−7.19	−0.97	0.31	−7.18	−1.00	0.28
$C_{16}As_{1,c}$	−6.69	−0.75	0.56	−6.68	−0.79	0.52

TABLE III. Energy levels (eV) for the silicon clusters pure and with an impurity in the center.

	T_d Symmetry			No Symmetry		
Cluster	HOMO	LUMO	Impurity Depth	HOMO	LUMO	Impurity Depth
Si_{17}	−6.46	−2.84		−6.51	−2.93	
$Si_{16}N_{1,c}$	−6.35	−2.70	0.99	−6.33	−2.73	0.83
$Si_{16}P_{1,c}$	−6.63	−2.76	0.23	−6.61	−2.95	0.13
$Si_{16}As_{1,c}$	−6.70	−2.82	0.11	−6.68	−2.92	0.10

passed only by the value for the As contaminated clusters. On the other hand, the bottom of the conduction band, the LUMO, does not present this systematic variation; it has its smallest value for the P contaminated clusters followed by the pure, the As and the N contaminated clusters. For the carbon clusters with the impurity at the NN position it can be seen (Table II) that the top of the valence band for the symmetric case does not show a systematic behavior with the atomic number of the impurities, neither does the bottom of the conduction band. For the nonsymmetric case the systematic behavior appears for the HOMO, which increases with the atomic number of the impurity, while the LUMO does not show it.

For the carbon clusters with central impurities the impurity levels are closest to the LUMO in the order $C_{16}P_{1,c}$, $C_{16}As_{1,c}$, and $C_{16}N_{1,c}$; see Table I. The impurity levels for the carbon cluster with NN impurities are again closest to the LUMO in the P cluster, followed by the As cluster and finally the N cluster; see Table II.

For the pentagonal silicon clusters with the impurity at the center Table III shows that the HOMO, for both symmetric and nonsymmetric cases, decreases systematically in energy as the atomic number of the impurity increases. The LUMO presents this same systematic variation for the symmetric clusters, but for the nonsymmetric ones the P cluster LUMO is now slightly lower in energy than the As one. For the silicon clusters with the impurity at the NN position it can be seen (Table IV) that again the top of the valence band decreases systematically in energy as the atomic number of the impurity increases, but for both cases, symmetric and nonsymmetric, the HOMO for the P and As clusters has practically the same value. The LUMO essentially does not change for these impure clusters.

As for the impurity levels in the silicon clusters we find that for the central impurities, they are closest to the LUMO in the As cluster, followed by the P cluster and finally the N cluster. The position of the nitrogen levels indicates that this element may not be a dopant in these clusters; see Table III. The impurity levels for the clusters with the impurities in a NN position are such that they are closest to the LUMO in the As cluster, followed by the P cluster and finally the N cluster, which again seems not to be a dopant in this type of pentagonal structures; see Table IV.

C. The energy gaps and the width of the valence bands

It is well known that gap values are underestimated by DFT since this approach works well for the ground state but needs improvement to adequately describe the excited states (conduction band); nevertheless, it is possible to speak of trends in the behavior of these values. The energy gap for both pure and impure clusters has been discussed above in the introduction to this section. For the pure clusters we take the energy gap as the difference between the averaged HOMO and LUMO values. For the impure ones we define the energy gap in the following way: the energy of the highest molecular orbital below which the number of electrons is equal to the pure case corresponds to the new HOMO or the top of the valence band, E_v; having done this we account for the impurity levels as mentioned above, and the next molecular orbital is defined as the new LUMO or bottom of the conduction band with energy E_c. The energy gap, E_g, is then equal to the difference $E_g = E_c - E_v$. Tables V and VI list the values of the gap for all the pentagonal clusters. It can be seen that nonsymmetric clusters have slightly smaller values for the gap than the corresponding symmetric ones.

From Table V it is clear that for the carbon clusters, the impurity gap is only smaller than the pure gap for the arsenic contaminated cluster; for nitrogen and phosphorus the gap is larger (except for the P nonsymmetric NN substitution, where there is a very slight difference). The gap for these carbon clusters *decreases* systematically as the atomic number of the impurity increases, being largest for nitrogen and smallest for arsenic.

TABLE II. Energy levels (eV) for the carbon clusters with an impurity in the NN position.

	C_{3v} Symmetry			No Symmetry		
Cluster	HOMO	LUMO	Impurity Depth	HOMO	LUMO	Impurity Depth
$C_{16}N_{1,NN}$	−7.17	−0.53	0.71	−7.20	−0.66	0.61
$C_{16}P_{1,NN}$	−7.24	−0.90	0.49	−7.14	−1.05	0.39
$C_{16}As_{1,NN}$	−6.65	−0.73	0.65	−6.69	−0.85	0.57

TABLE IV. Energy levels (eV) for the silicon clusters with an impurity in the NN position.

	C_{3v} Symmetry			No Symmetry		
	HOMO	LUMO	Impurity Depth	HOMO	LUMO	Impurity Depth
$Si_{16}N_{1,NN}$	−6.14	−2.88	1.03	−6.11	−2.88	1.02
$Si_{16}P_{1,NN}$	−6.41	−2.87	0.35	−6.39	−2.91	0.28
$Si_{16}As_{1,NN}$	−6.42	−2.88	0.27	−6.39	−2.90	0.27

TABLE V. Gap values (eV) for carbon clusters.

Impurity in the center			Impurity in the NN Position		
Cluster	T_d Sym.	No Sym.	Cluster	C_{3v} Sym.	No Sym.
C_{17}	6.11	6.10			
$C_{16}N_{1,c}$	6.99	6.91	$C_{16}N_{1,NN}$	6.64	6.54
$C_{16}P_{1,c}$	6.22	6.18	$C_{16}P_{1,NN}$	6.34	6.10
$C_{16}As_{1,c}$	5.94	5.89	$C_{16}As_{1,NN}$	5.91	5.84

TABLE VII. Valence band width (eV) for carbon clusters.

Impurity in the center			Impurity in the NN Position		
Cluster	T_d Sym.	No Sym.	Cluster	C_{3v} Sym.	No Sym.
C_{17}	15.22	15.26			
$C_{16}N_{1,c}$	17.58	18.32	$C_{16}N_{1,NN}$	17.89	17.91
$C_{16}P_{1,c}$	16.52	16.52	$C_{16}P_{1,NN}$	16.28	16.49
$C_{16}As_{1,c}$	17.18	17.18	$C_{16}As_{1,NN}$	17.44	17.44

The trend for the silicon clusters is opposite to the one observed for the carbon clusters, as can be seen in Table VI; i.e., the gap *increases* systematically as the atomic number of the impurity increases, except for the C_{3v} symmetric P and As clusters for which the values of the gap are practically the same.

To calculate the width of the valence bands E_{vb} of the clusters we first find the lowest energy levels E_{lv} of this band and then obtain its value as $E_{vb}=E_v-E_{lv}$, where E_v was defined above; Tables VII and VIII. Another subject of relevance is the possible splitting of the valence band into two bands due to the pentagonal structure of the 5-atom rings as oppossed to the hexagonal structure of crystalline diamond-like structures. In a previous publication,[7] we dealt with the effect of nitrogen as an impurity within three different types of carbon clusters: one with 21 carbon atoms and sixfold boat-type rings, one with 57 carbon atoms and both six- and fivefold atom rings, and one with 59 carbon atoms and only sixfold chair-type rings. Looking at the value of the gap and the width of the valence band of the 21 carbon atom cluster, the closest in number to those we are analyzing here, we found[7] that $E_g=5.42$ eV and $E_{vb}=16.52$ eV. For the reference 21 silicon atom cluster we obtain $E_g=3.36$ eV and $E_{vb}=9.45$ eV. If we assume that the difference in the total number of electrons manifests itself in the height of the DOS curves and not in a significant alteration of the distribution of the energy levels, then it is clear that our results (Tables VII and VIII) indicate that, in fact, for the pure clusters, 5-atom rings tend to contract the valence band, and that this effect is more pronounced for carbon than for silicon. For the impure clusters the results given in Tables VII and VIII show that the width increase and that the largest change occur for the N clusters. The P clusters have the smallest bandwidth of all the impure ones.

Finally, since our calculations for these clusters necessarily give a discrete set of energy levels, it is difficult to identify a tendency towards a splitting of the valence band in spite of the broadening of the levels with 0.2 eV Gaussians. For the pure clusters, both 5 atom and 6 atom, we decided to make a direct comparison of the partial density of states; i.e., the density of states due only to the carbons or the silicons, excluding the hydrogen saturators. The reason for this is to subtract the influence of hydrogen as much as possible. In Figs. 7 and 8 we show the partial density of states of the 5-atom ring clusters with the reference clusters C_{21} and Si_{21}, which are clusters that contain *only* 6-atom boat-type rings, 21 atoms of carbon or silicon, and 28 hydrogen saturators. One can see that there is a noticeable difference in the electronic structure of corresponding clusters; thus, C_{17} has a lower top, a higher bottom, a narrower valence band, and a larger energy gap than the C_{21} cluster. For Si_{17} the top of the valence band is lower in energy than that of the Si_{21} cluster, but the bottom of this band practically does not move, leading nevertheless to a narrower valence band; the energy gaps in Si_{17} and Si_{21} are practically the same.

V. CONCLUSIONS

The clusters that we have constructed are by necessity amorphous, since they contain *only* 5-atom rings and it is not possible to construct a crystalline solid with this type of rings alone. Assuming that the difference in the number of atoms of the $C(Si)_{21}$ and $C(Si)_{17}$ pure clusters is not as important as the difference in the type of atomic rings, we find, from the partial density of states, that the width of the valence band for the $C(Si)_{17}$ is smaller than the width for the $C(Si)_{21}$, in agreement with theoretical and experimental results reported in the literature;[3] also, the top of the valence band of the $C(Si)_{17}$ clusters moves to lower energies with respect to the top of the $C(Si)_{21}$ clusters in agreement with published results.[3] We also find that for carbon the bottom of the valence band moves to higher energies accentuating the narrowing of the band, whereas for silicon it stays practically the same. The energy gap of C_{17} is considerably larger than the gap of C_{21}, whereas the gaps for Si_{17} and Si_{21} are quite similar.

The symmetric and nonsymmetric clusters, pure and impure, behave qualitatively in the same manner, emphasising the preponderance of short range order over symmetry. The gap values for the nonsymmetric clusters are consistently

TABLE VI. Gap values (eV) for silicon clusters.

Impurity in the center			Impurity in the NN Position		
Cluster	T_d Sym.	No Sym.	Cluster	C_{3v} Sym.	No Sym.
Si_{17}	3.62	3.58			
$Si_{16}N_{1,c}$	3.65	3.60	$Si_{16}N_{1,NN}$	3.26	3.21
$Si_{16}P_{1,c}$	3.87	3.66	$Si_{16}P_{1,NN}$	3.55	3.48
$Si_{16}As_{1,c}$	3.88	3.76	$Si_{16}As_{1,NN}$	3.54	3.50

TABLE VIII. Valence band width (eV) for silicon clusters.

Impurity in the center			Impurity in the NN Position		
Cluster	T_d Sym.	No Sym.	Cluster	C_{3v} Sym.	No Sym.
Si_{17}	9.04	9.02			
$Si_{16}N_{1,c}$	13.41	13.41	$Si_{16}N_{1,NN}$	12.80	12.75
$Si_{16}P_{1,c}$	10.28	10.23	$Si_{16}P_{1,NN}$	10.34	10.36
$Si_{16}As_{1,c}$	10.35	10.31	$Si_{16}As_{1,NN}$	10.69	10.66

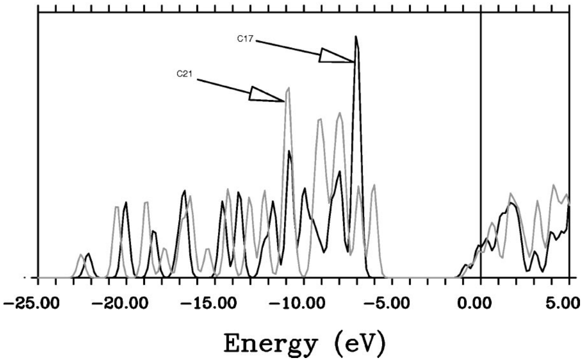

FIG. 7. Density of states for the C_{17} and C_{21} symmetric clusters where the hydrogen contributions have been removed. The effect of the 5-atom rings can be noticed in the width of the valence band, and in the displacements of the top and bottom of this band.

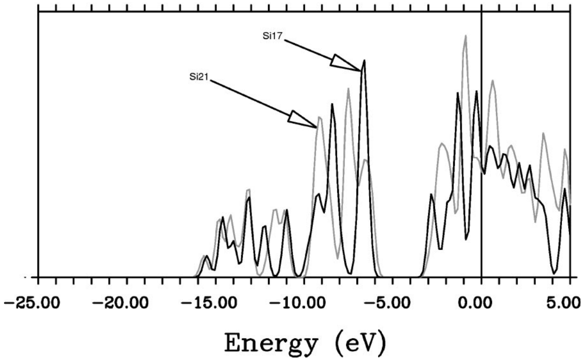

FIG. 8. Density of states for the Si_{17} and Si_{21} symmetric clusters where the hydrogen contributions have been removed. The effect of the 5-atom rings can be noticed in the width of the valence band, and in the displacements of the top and bottom of this band.

smaller than those corresponding to the symmetric ones. The gap values for the contaminated carbon clusters decrease as the atomic number of the impurity increases, whereas for the contaminated silicon clusters the behavior is opposite. The depth of the impurity levels in carbon suggests that for the pentagonal structures at most P is a dopant, whereas for silicon both P and As could be dopants. The fact that silicon and carbon behave in opposite ways may be due to the fact that the C-C bond is more rigid than the Si-Si bond. The width of the valence band is larger for all contaminated clusters, either in the central position or in the NN position, and the behavior is very similar in both cases; i.e., wider for N, narrower for P, and intermediate for As, but always larger than the pure value.

No clear sign of additional gaps caused by the 5-atom ring topology can be observed in the DOS graphs reported above and the smearing of the sp area in the DOS (either towards the p region or the s region), as a signature of 5-atom rings cannot be discerned in our results. Since this is most likely due to the finite size of the clusters, we have undertaken additional studies of larger clusters with pentagonal structures. It should be borne in mind that most of the published conclusions (except Ref. 1) refer to studies of the electronic structures of the *crystalline* clathrate phases for both silicon and carbon,[3] and that the clusters treated here are *amorphous*.

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