PHYSICAL REVIEW B, VOLUME 65, 165417

Bridging C_{60} by silicon: Towards non-Van der Waals C_{60}-based materials

F. Tournus, B. Masenelli, P. Mélinon, X. Blase, and A. Perez
Département de Physique des Matériaux, Université Claude Bernard-Lyon 1, F69622 Villeurbanne, France

M. Pellarin and M. Broyer
Laboratoire de Spectroscopie Ionique et Moléculaire, Université Claude Bernard-Lyon 1, F69622 Villeurbanne, France

A. M. Flank and P. Lagarde
LURE, Centre Universitaire Paris-Sud, F91898 Orsay, France

(Received 26 November 2001; published 5 April 2002)

We report the three-dimensional packing of C_{60} clusters stabilized by the addition of Si. X-ray absorption spectroscopy reveals that Si atoms are in an unusual environment: between two C_{60}, with ten or more carbon neighbors. According to *ab initio* calculations, the cohesive energy is about 2 eV per Si atom, much higher than the Van der Waals binding energy between two C_{60}. Experiment and calculations both indicate a charge transfer from Si to C_{60}. Eventually, the film may have a local decahedral symmetry.

DOI: 10.1103/PhysRevB.65.165417 PACS number(s): 61.48.+c, 61.10.Ht, 61.46.+w, 71.15.−m

I. INTRODUCTION

Endohedrally doped[1] and pristine C_{60} have been extensively studied over the past decade both for their superconducting and molecular semiconducting behaviors. Pristine C_{60} is mainly linked by Van der Waals (VdW) bonding, resulting in a fcc crystal whereas finite size clusters of C_{60} may be icosahedral,[2] decahedral, or close-packed.[3] As the VdW bonding limits the potential applications of such compounds, an outstanding effort has been carried out for the functionalization of these fullerenes. Several chemical routes such as halogenation, cycloaddition and alkylation[4] lead to new stable C_{60} compounds. However, except some studies on silicon heterofullerenes,[5] only a few experiments involving group IV elements have been reported so far.[6,7]

In this paper, we deal with a new and simple way for stabilizing C_{60} packing by addition of silicon atoms between C_{60}. On the basis of both x-ray absorption and *ab initio* calculations, we report on the 3D packing of C_{60} clusters where two C_{60} are linked by a silicon atom. We show that such a compound may have a decahedral symmetry. Silicon transfers electrons towards C_{60} and makes a cohesive energy of up to 2 eV per Si atom. We find that silicon is linked to 10–12 carbon atoms. This is, to our knowledge, the first observation of such an unusual environment with respect to the tetrahedral lattice commonly observed in SiC compounds. These results confirm what was expected from our previous study of a $C_{60}+\mathrm{Si}$ film with Raman spectroscopy.[6]

This paper is organized as follows. In Sec. II, we present briefly the experimental setup used to produce the sample and the analysis protocol. In Sec. III, we show extended x-ray absorption fine structure (EXAFS) results and propose some environments of silicon atoms. In Sec. IV, we study the stability of different structures with *ab initio* calculations and the results are discussed in Sec. V.

II. EXPERIMENT

The sample is a $C_{60}+\mathrm{Si}$ film obtained by deposition of $(C_{60})_n\mathrm{Si}_m$ clusters produced in a sophisticated double-target laser vaporization source, following the low-energy cluster-beam deposition technique described in details elsewhere.[8] Briefly, both targets (a monocrystalline silicon rod and a flat disk obtained by pressing C_{60} powder) are independently vaporized by two Nd:YAG lasers. The resulting plasma is then quenched by a pulsed high pressure helium burst, which ensures the cluster growth in the source chamber, until the cluster/carrier gas mixture is expanded through a conical nozzle. Let us remind the reader that a particularity of this technique is that nonsteady state structures can be obtained. Nascent ionized clusters are characterized in a time-of-flight mass spectrometer.[8] A thin film ($\simeq 100$ nm) is obtained by neutral cluster deposition on a silver-coated ($\simeq 200$ nm) silicon wafer, maintained at room temperature, in ultrahigh vacuum (UHV) conditions. Prior deposition the vacuum is down to 3×10^{-8} Pa. During the cluster deposition, the residual pressure increases up to 2×10^{-7} Pa mainly due to the residual buffer helium gas. The residual pressure due to the reactive components such as O_2, CO, H_2O, and CO_2 is less than 10^{-8} Pa. After deposition, the residual vacuum becomes comparable to the one observed prior deposition. Auger electron spectroscopy and x-ray photoemission spectroscopy measurements do not reveal any significant amount of oxygen in the film. The film stoichiometry (1.2 ± 0.6 silicon atoms per C_{60} molecule) is estimated from both the C_{1s} and the Si_{2p} core levels yield measured by x-ray photoemission spectroscopy. Raman spectroscopy measurements, on similar samples,[6] allow us to ensure that C_{60} molecules were not damaged during the deposition and are still present in the film without noticeable amorphous carbon component. The sample is then transferred in UHV from the deposition chamber to the SA32 station of the LURE synchrotron facility using an appropriate UHV transfer device. The local environment around silicon atoms is probed by EXAFS at the Si K edge, using a standard experimental procedure.[9] Fluorescence-yield spectra are acquired at different temperatures of the sample which is cooled down from room temperature to about 170 K. The latter is below the orientational phase transition temperature ($T\simeq 250$ K) corresponding to a

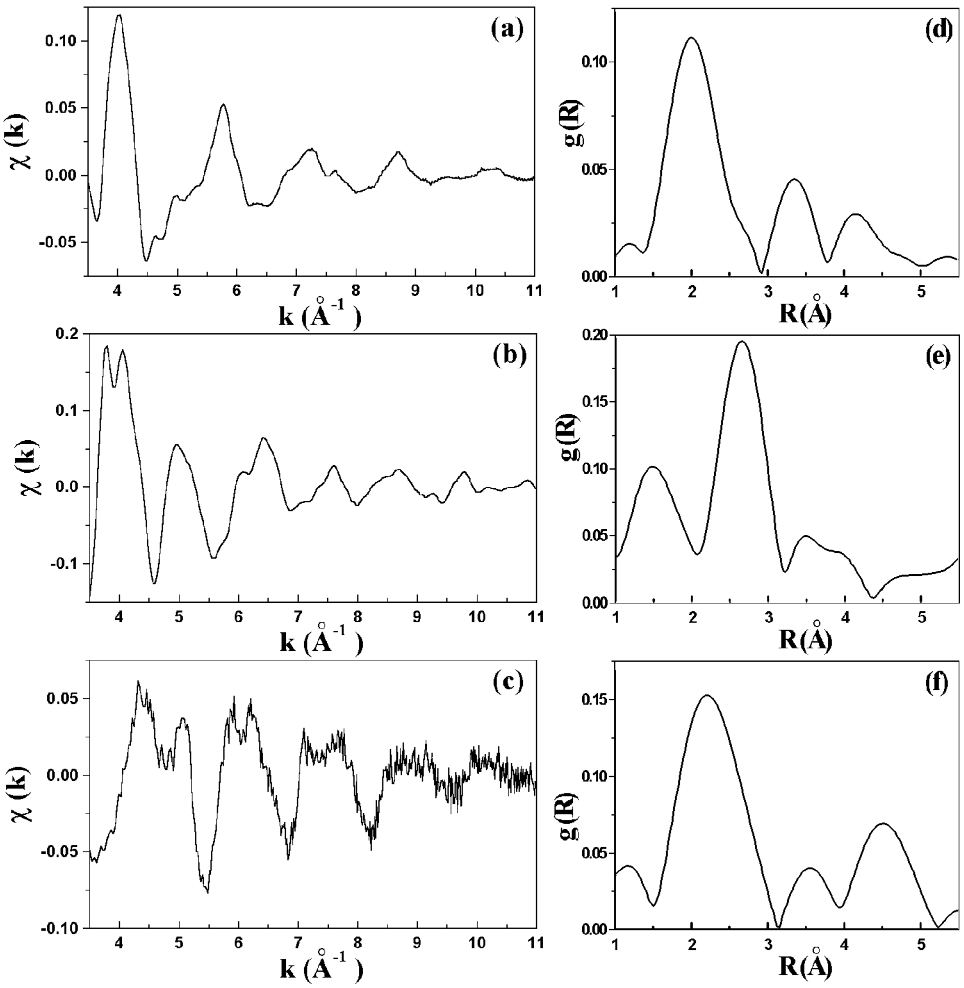

FIG. 1. Experimental EXAFS signals $\chi(k)$ of (a) silicon diamond, (b) 2H-SiC, and (c) the C_{60}+Si film. Pseudoradial distribution functions $g(R)$ of (d) silicon diamond, (e) 2H-SiC, and (f) the C_{60}+Si film.

reduction of the rotational freedom degrees observed in pristine C_{60}.[10]

III. EXAFS RESULTS

The observation of the Si K edge reveals a shift in our cluster-film towards higher energy, close to the one observed in a SiC crystal. This clearly indicates a charge transfer from silicon towards carbon. The experimental EXAFS signal $\chi(k)$ is obtained from the absorption spectra $\mu(E)$. Figure 1 shows the experimental $\chi(k)$ of the C_{60}+Si sample, to be compared with silicon diamond and silicon carbide. The pseudoradial distribution functions $g(R)$ are also given in Fig. 1. The $\chi(k)$ of the C_{60}+Si sample is remarkably well structured, as evidenced by the oscillations up to 11 Å^{-1} and the features of $g(R)$ up to 5 Å. This implies that the sample is locally well ordered around silicon atoms. The experimental $\chi(k)$ of Fig. 1 corresponds to low temperature measurements ($T=170$ K) but surprisingly it appears that the EXAFS signal does not depend on temperature, in the range of 170 to 300 K, as can be seen in Fig. 2. This point is discussed below.

Another important result is that silicon atoms in the C_{60}+Si sample are obviously not in the same local environment as in silicon diamond or silicon carbide. Instead, we can think of a silicon surrounded by C_{60} molecules, since the C_{60} survive after deposition. The C_{60}+Si $g(R)$ displays three shells. The ones located at 2.2 and 3.5 Å, respectively, are related to the first and second carbon neighbors. As shown below, $g(R)$ can be well fitted assuming the contribution of two C_{60} located on both sides of silicon. The third peak located at 4.5 Å is also unusual. This peak appears in all the data acquisitions and cannot be obtained from the two C_{60} neighbors. This shows that additional C_{60} are needed far from the silicon atom. Such a structure can be obtained with a decahedron made of seven C_{60} molecules (see Fig. 3 and

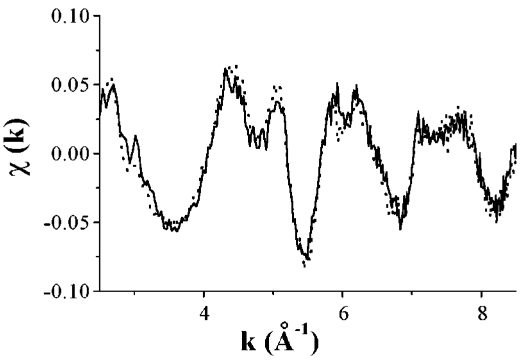

FIG. 2. Experimental EXAFS signals $\chi(k)$ of the C_{60}+Si film at 170 K (solid line) and at 300 K (dotted line).

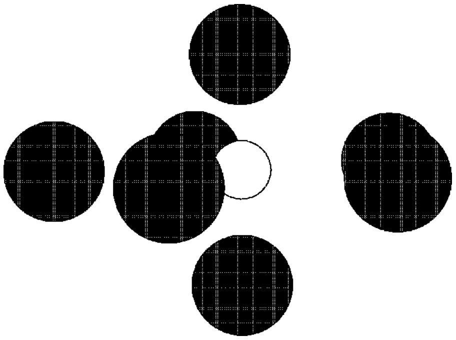

FIG. 3. View of a decahedral cluster of C_{60} (dark balls) with a Si atom (white ball) at its center.

Fig. 6 below): a planar pentagon of C_{60} plus a C_{60} on each side, along the fivefold pentagon axis. If we put a silicon atom at the center of the pentagon, we then have 2 C_{60} close to the silicon and five C_{60} far from it. This structure has already been predicted for C_{60} clusters in gas phase[2] and calculations on $(C_{60})_N$ clusters are in favor of icosahedral or decahedral structures.[3,11] The usual fcc structure of bulk C_{60} is discarded, because doping with Si in interstitial sites[12] is unable to reproduce the EXAFS spectra.

Even within the decahedron structure, there is an infinite number of configurations, corresponding to the different possible orientations of the C_{60}. Thus, trying to fit the experimental EXAFS signal, we restrict our investigations to a limited number of configurations corresponding to the highest symmetry positions. Our calculations are done with a C_{60} defined by its two C-C bond lengths: 1.40 Å for the hexagon-hexagon (HH) edges, and 1.45 Å for the pentagon-hexagon edges. EXAFS simulations are done with the *ab initio* self-consistent real space multiple-scattering code FEFF8,[13] using self-consistent scattering potentials. Except $d_{SiC_{60}}$ (the distance, center to center, between Si and the nearest C_{60}), $d'_{SiC_{60}}$ (the distance, center to center, between Si and the 5 C_{60}), and an edge-energy shift ΔE_0, no adjustable parameter is used. In particular, we use neither Debye-Waller factors, nor any amplitude reduction factor S_0^2. For each configuration, the distances and ΔE_0 are hand optimized. The simulation is robust since a good fit is obtained with these only adjustable parameters.

The results of EXAFS simulations $[\chi(k)$ and $g(R)]$ for some selected configurations are given in Fig. 4. The edge configuration corresponds to the two nearest C_{60} facing the silicon atom with a HH edge (four nearest neighbors, the closest distance between Si and C, $d_{SiC}=2.55$ Å, i.e., $d_{SiC_{60}}=5.93$ Å) and the five other C_{60} facing the silicon atom with a pentagonal face [the closest distance between Si

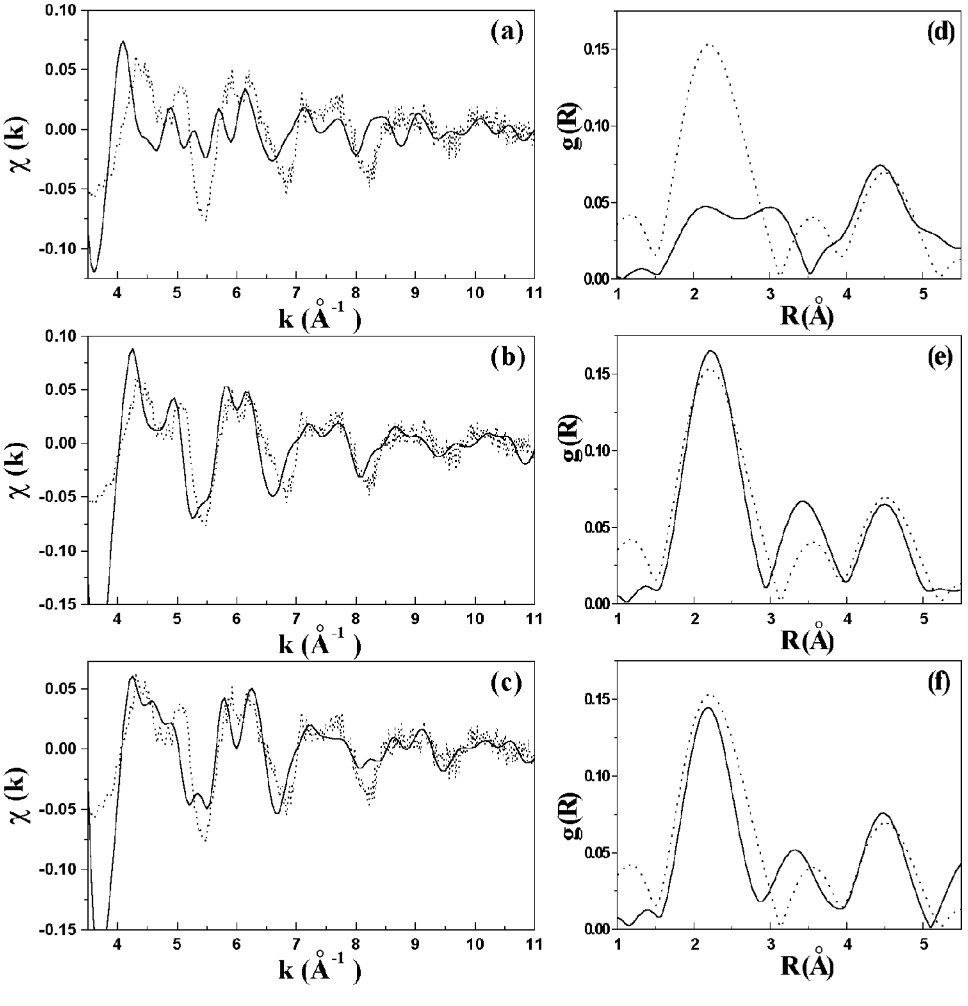

FIG. 4. Solid line: simulated (a) $\chi k)$ and (d) $g(R)$ for the edge-configuration, simulated (b) $\chi(k)$ and (e) $g(R)$ for the hexagon-configuration, and simulated (c) $\chi(k)$ and (f) $g(R)$ for the pentagon configuration. Dotted line: experimental (a)–(c) $\chi(k)$, and (d)–(f) $g(R)$, for the $C_{60}+$Si film.

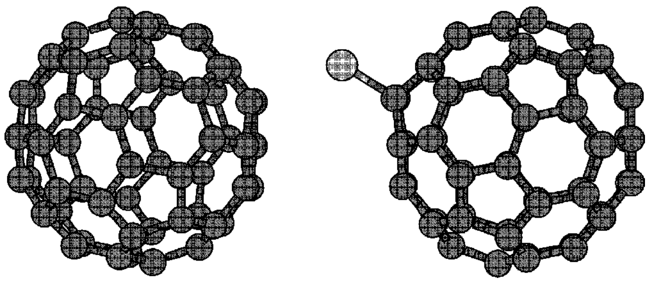

FIG. 5. View of the HH-edge structure obtained by relaxation of the hexagon-configuration (see text). The silicon atom is in light gray.

and C in the (Oy,Oz) plane is $d'_{\mathrm{SiC}}=4.86$ Å]. The hexagon-configuration is the same apart from the two nearest C_{60} facing in this case the silicon atom with a hexagonal face (12 nearest neighbors, $d_{\mathrm{SiC}}=2.54$ Å, i.e., $d_{\mathrm{SiC}_{60}}=5.35$ Å). The pentagon configuration is the same apart from the two nearest C_{60} facing in this case the silicon atom with a pentagonal face (10 nearest neighbors, $d_{\mathrm{SiC}}=2.52$ Å, i.e., $d_{\mathrm{SiC}_{60}}=5.53$ Å). The value of ΔE_0 is 4 eV for the hexagon-configuration and 3 eV for the pentagon-configuration.[14,15] All these configurations are close to the “ideal” C_{60} decahedron, where the C_{60}-C_{60} distance, center to center, is taken to be the one in the fcc crystal (10.02 Å), corresponding to $d_{\mathrm{SiC}_{60}}=5.27$ Å.

We note that the simulations results do not depend on the precise orientation of the faces of each C_{60}, i.e., the rotation angle on the bond axis. For example, concerning the pentagon configuration, we obtain practically the same $\chi(k)$ whenever the pentagonal faces are eclipsed or staggered. Thus, EXAFS is unable to give the precise orientational order, if there is one. However, if we cannot claim that C_{60} are totally frozen, we expect that the only rotation axis is the C_{60}-Si-C_{60} bond axis. A rotation on another axis strongly disturbs the geometry and consequently the EXAFS signal. As mentioned previously, since this latter does not change for temperatures between 170 and 290 K, it shows that C_{60} are not freely rotating. This “freezing” is due to the presence of silicon in the film, because at room temperature fullerenes are free to rotate and orientationally disordered in pristine C_{60}.[10] Moreover, the freezing must be quite efficient since the Debye-Waller attenuation hardly changes with increasing temperature. In addition, we cannot expect EXAFS to give the configuration of the five C_{60} farther away. Indeed, there is only a slight difference in $\chi(k)$, depending on whether the five C_{60} face the Si atom with a pentagonal or a hexagonal face.[16]

We can see (Fig. 4) that the edge configuration gives an EXAFS signal very different from the experimental one, whereas the two other configurations are in quite good agreement, the $\chi(k)$ of the hexagon-configuration being slightly closer to the experimental one.[17] The conclusion is the following: silicon atom has 10–12 nearest carbon neighbors,

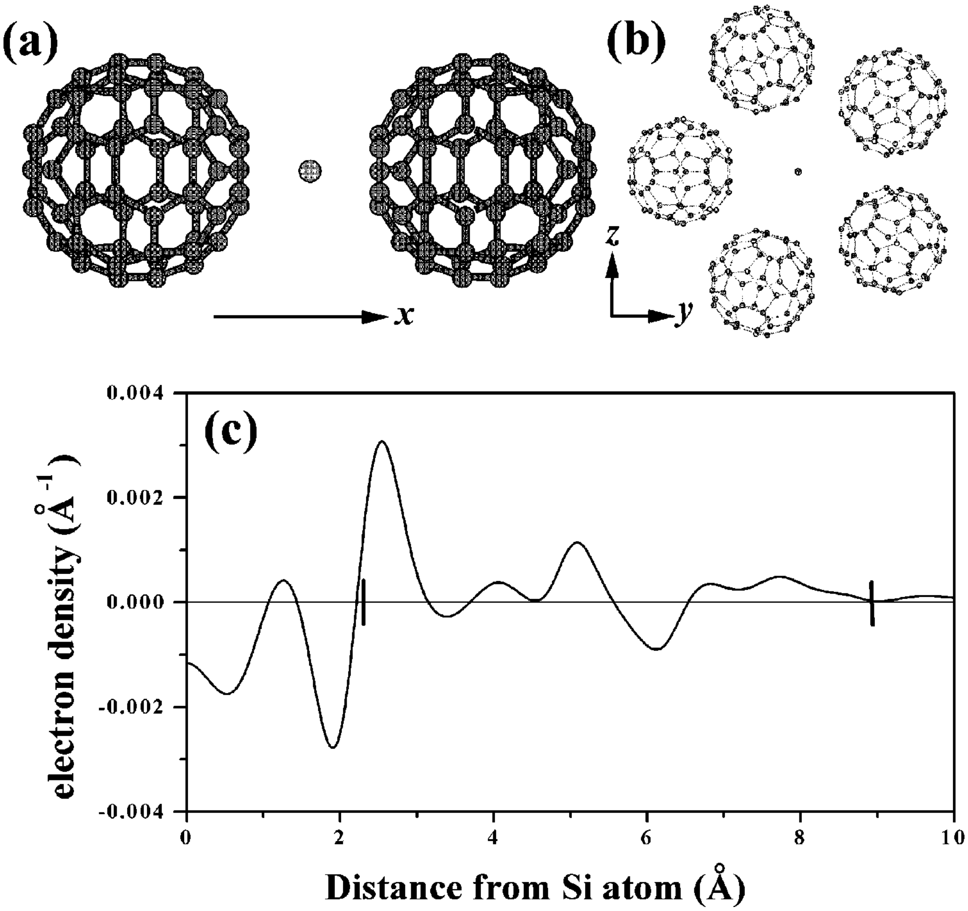

FIG. 6. View of (a) the two nearest C_{60} of the relaxed pentagon-configuration, and (b) of the pentagon of the 5 far C_{60} in the (Oy,Oz) plane. The two views are represented separately for clarity. Difference electron-density profile (c) for the relaxed pentagon-configuration. The two markers correspond to the limits of the C_{60}.

which is quite unusual in SiC compounds, the distance $d_{\mathrm{SiC}} \simeq 2.53$ Å being very different from the well known covalent SiC bonding one (1.88 Å).

IV. CALCULATIONS

To study the stability and electronic properties, we perform *ab initio* calculations, within the local density approximation to the density functional theory (DFT-LDA) (Ref. 18) on two C_{60} molecules with a Si atom. The role of the five surrounding C_{60} is neglected and will be discussed in a forthcoming paper. We adopt a pseudopotential approach[19] and a pseudo-atomic-orbitals (PAO) expansion of the wave functions[20] using the SIESTA code.[21] Structural relaxation is obtained by minimization of the total energy, using a conjugate gradient method. Upon relaxation, the pentagonal structure is found to be stable with only a slight deformation of the C_{60}. The mean distance between Si and the carbon atoms of the pentagonal faces is $d_{\mathrm{SiC}} = 2.59$ Å. This value is in good agreement with the results of the EXAFS simulations. The cohesive energy of the relaxed structure, compared to two relaxed C_{60} molecules plus a silicon atom infinitely far from one another, is about 2 eV, much more than the 0.28 eV VdW binding energy.[22] This configuration is metastable, since the structure obtained by relaxation of the hexagon configuration is about 1 eV more stable. This structure (called the HH edge) is very different from the input one, the Si atom being above a HH edge (see Fig. 5), with a Si-C distance $d_{\mathrm{SiC}} \simeq 1.95$ Å close to the one in bulk SiC (1.88 Å). It is the same result as with a Si atom and a single C_{60}. The initial hexagon-configuration is not even metastable and, according to our calculations, there is no energy barrier for the Si to move away from its initial position, on the middle of the C_{60}-C_{60} bond axis, to its relaxed position, above a HH edge.

V. DISCUSSION

From the present results, the configuration compatible with the EXAFS results is the pentagonal one, ruling out the hexagonal one. It still remains to understand why the HH-edge configuration is not observed experimentally. Further researches on the growth mechanism and the nucleation process could provide an explanation. At this stage, let us note that if Si is inserted between two C_{60} in preformed $(C_{60})_N$ free clusters it is not amazing to have a decahedral environment.[3] In addition, in a decahedral cluster of C_{60} we can expect two molecules to face each other with a pentagonal face. Indeed, Gunnarson *et al.*[23] pointed out that for two C_{60} this configuration must be the most stable one. Although this orientation is not observed in fcc C_{60} crystal (it is forbidden by symmetry), it could stabilize a decahedral cluster of C_{60}. Si can then be inserted between two C_{60} leading to the pentagon configuration. This scenario can explain the structure of the film, if the clusters do not fragment upon impact on the substrate. The film obtained by cluster deposition could then locally have a decahedral symmetry and it questions the existence of a quasicrystalline phase. Since the film is composed by "covalent" atoms, this quasicrystal could be regarded as the dual of the Frank Kasper phase.[24] If the free clusters structures are not preserved upon deposition there is no straightforward explanation for the observed structure. However, the film growth is not epitaxial and does not lead to crystalline C_{60}. The film also differs from usual amorphous nanogranular C_{60} films because it is clearly locally ordered around silicon atoms. The growth of C_{60} and C_{60}+Si films on Au(111) is currently under investigation using scanning tunneling microscopy.

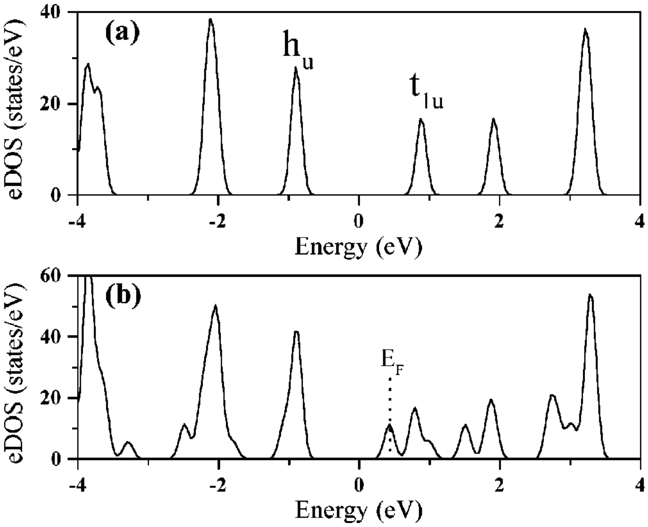

FIG. 7. EDOS of (a) C_{60}, and (b) of the C_{60}+Si film. The curves are shifted so that the C_{60} HOMO h_u coincides with the corresponding peak of C_{60}+Si. E_F indicates the Fermi level in (b).

Figure 6 gives some views of the relaxed pentagon-configuration, in a decahedral environment, and shows the difference-electron-density profile,[25] along the C_{60}-Si-C_{60} axis, integrated on perpendicular planes. The electronic depletion near the silicon atom shows that there is a charge transfer from the silicon atom to the C_{60} molecules. The electronic density of states (EDOS) of the relaxed pentagon-configuration and the one of C_{60}, for comparison, are given in Fig. 7. It indicates again a charge transfer from Si to C_{60} because the C_{60} LUMO (t_{1u}) is now partially occupied. This transfer is in agreement with the edge energy-shift experimentally observed (Sec. III). There are also some electronic levels splittings coming from both the symmetry lowering and the chemical hybridization.

In conclusion, we report the formation of an unusual Si-C bonding with silicon having ten or more carbon neighbors, in agreement with our previous Raman study.[6] *Ab initio* calculations show that this bonding stabilizes the structure, with a gain in energy of 2 eV per silicon atom and a charge transfer from Si to C_{60}. Moreover, EXAFS spectroscopy suggests that Si is embedded in C_{60} clusters having a decahedral symmetry. Works are in progress to detail the growth mechanism of the film, as well as its electronic, structural and conductive properties.

ACKNOWLEDGMENTS

The authors are indebted to the "Structure et dynamique des systèmes complexes" (SESC) project supported by Région Rhônes-Alpes and CNRS for use of computer time and to E. Artacho for guidance in using the SIESTA code.

[1] A.F. Hebard, M.J. Rosseinsky, R.C. Haddon, D.W. Murphy, S.H. Glarum, T.T.M. Palstra, A.P. Ramirez, and A.R. Kortan, Nature (London) **350**, 600 (1991).

[2] T.P. Martin, U. Näher, H. Schaber, and U. Zimmermann, Phys. Rev. Lett. **70**, 3079 (1993).

[3] J.P.K. Doye, A. Dullweber, and D.J. Wales, Chem. Phys. Lett. **269**, 408 (1997); J. García-Rodeja, C. Rey, and L.J. Gallego, Phys. Rev. B **56**, 6466 (1997).

[4] R. Taylor and D.R.M. Walton, Nature (London) **363**, 685 (1993).

[5] C. Ray, M. Pellarin, J.L. Lermé, J.L. Vialle, M. Broyer, X. Blase, P. Mélinon, P. Kéghélian, and A. Perez, Phys. Rev. Lett. **80**, 5365 (1998); I.M.L. Billas, C. Massobrio, M. Boero, M. Parrinello, W. Branz, F. Tast, N. Malinowski, M. Heinebrodt, and T.P. Martin, J. Chem. Phys. **111**, 6787 (1999).

[6] P. Mélinon, F. Tournus, B. Masenelli, A. Perez, M. Pellarin, J. Lermé, M. Broyer, and B. Champagnon, Eur. Phys. J. D **16**, 337 (2001).

[7] F. Tast, N. Malinowski, I.M.L. Billas, M. Heinebrodt, W. Branz, and T.P. Martin, J. Chem. Phys. **107**, 6980 (1997).

[8] M. Pellarin, C. Ray, J. Lermé, J.L. Vialle, M. Broyer, and P. Mélinon, J. Chem. Phys. **112**, 8436 (2000).

[9] The x-ray beam is monochromatized by an InSb (111) double-crystal monochromator (0.7 eV resolution), and energy calibration is done using Si (111) K edge. Absorption spectra are recorded, collecting the fluorescence emission as a function of the photon energy.

[10] P.A. Heiney, J.E. Fischer, A.R. McGhie, W.J. Romanow, A.M. Denenstein, J.P. McCauley, Jr., A.B. Smith, III, and D.E. Cox, Phys. Rev. Lett. **66**, 2911 (1991).

[11] For large N, close-packed structures are the most stable ones (Ref. 3).

[12] A.M. Rao and P.C. Eklund, Mater. Sci. Forum **232**, 173 (1996).

[13] A.L. Ankudinov, B. Ravel, J.J. Rehr, and S.D. Conradson, Phys. Rev. B **58**, 7565 (1998).

[14] For the edge configuration, no good agreement with the experimental EXAFS signal can be obtained, so we take $\Delta E_0 = 0$, and the result of simulation is given Fig. 4 to show that this configuration is not the right one.

[15] A positive ΔE_0 corresponds to a shift of the edge energy to a lower value.

[16] On the other hand, an edge configuration for the 5 far C_{60} cannot reproduce the peak around 4.5 Å.

[17] We have to compare the $\chi(k)$ rather than the $g(R)$, because it depends on the way the Fourier transformation is made. Moreover, intensity of $g(R)$ peaks depends on the way $\chi(k)$ is extracted from $\mu(E)$, leading to an uncertainty of about 15%.

[18] P. Hohenberg and W. Kohn, Phys. Rev. **136**, 864 (1964); W. Kohn and L.J. Sham, *ibid.* **140**, 1133 (1965).

[19] N. Troullier and J.L. Martins, Phys. Rev. B **43**, 1993 (1991); L. Kleinman and D.M. Bylander, Phys. Rev. Lett. **48**, 1425 (1982).

[20] D. Sánchez-Portal, E. Artacho, and J.M. Soler, J. Phys.: Condens. Matter **8**, 3859 (1996), and references therein. While a DZP basis has been adopted for Si, a DZ basis was found to be accurate enough for C atoms.

[21] D. Sánchez-Portal, P. Ordejón, E. Artacho, and J.M. Soler, Int. J. Quantum Chem. **65**, 453 (1997).

[22] L.A. Girifalco, J. Phys. Chem. **96**, 858 (1992).

[23] O. Gunnarsson, S. Satpathy, O. Jepsen, and O.K. Andersen, Phys. Rev. Lett. **67**, 3002 (1991).

[24] F.C. Frank and J. Kasper, Acta Crystallogr. **11**, 184 (1959).

[25] That is, the electron density of the relaxed structure (C_{60}-Si-C_{60}), minus the one of C_{60}-C_{60}+Si, at the same positions.