

Ab-initio study of three dimensional polymers of C₆₀

Federico Zipoli ^(*), Marco Bernasconi ^(*)

*Università degli Studi di Milano-Bicocca, Dipartimento di Scienza dei Materiali,
via R. Cozzi, 53, 20125 Milano^(*)*

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Abstract

I polimeri tri-dimensionali (3D) del C₆₀ rappresentano una nuova forma allotropica del carbonio che negli ultimi anni ha attratto l'interesse della comunità scientifica. Fasi superdure o potenzialmente superconduttrici del polimero 3D del C₆₀ sono state proposte sulla base di calcoli teorici o misure sperimentali ottenute da campioni con bassa cristallinità. Molto recentemente Yamanaka *et al.* (*Phys. Rev. Lett.* **96**, p 76602, 2006) hanno isolato un cristallo singolo del polimero 3D di C₆₀ sintetizzato sottoponendo il polimero 2D ortorombico ad alta pressione (15 GPa) ed alta temperatura (600°C). Diffrazione di raggi X ha permesso di assegnare il gruppo spaziale *Immm*. Questa nuova fase mostra un comportamento non metallico in misure di conducibilità elettriche, un risultato in disaccordo con le previsioni dei calcoli *ab-initio* in diverse strutture di simmetria *Immm* proposte finora. In questo lavoro abbiamo studiato con calcoli *ab-initio* nuove strutture di simmetria *Immm* trovando una fase isolante anti-ferromagnetica compatibile con le misure strutturali ed elettriche di Yamanaka *et al.*

Three-dimensional (3D) C₆₀ polymers represent a new allotropic form of carbon which has been attracting the interest of the scientific community in the last few years because of superhard or potentially superconductive properties envisaged from theoretical calculations and experimental data on poorly crystallized samples of a 3D polymer. Very recently, Yamanaka *et al.* (*Phys. Rev. Lett.* **96**, p 76602, 2006) succeeded in isolating a single crystal of a 3D polymeric phase synthesized by compressing the 2D orthorhombic polymer at 15 GPa and 600°C. X-ray diffraction allows assigning the crystal symmetry of the *Immm* space group. However, the 3D polymer shows a non-metallic behavior in the electrical conductivity measurements which is in contrast with *ab-initio* calculations performed on all the *Immm* 3D polymer proposed so far. In this work we have investigated by *ab-initio* calculations several possible forms of 3D polymer of *Immm* space group and we found an anti-ferromagnetic insulating phase suitable to reproduce the structural and the electrical experimental data by Yamanaka *et al.*

Keywords: Density Functional Theory, polymer, fullerene, C₆₀.

I. Introduction

Fullerenes are cage-like all-carbon molecules which under special conditions, such as exposure to high intensity photon or electron irradiation, ion plasma excitation, pressure, or doping, may form polymeric solids [1]. At normal conditions C_{60} molecules crystallize in a face center cubic (fcc) fullerite structure with a lattice parameter of 14.17 Å and a density of 1.72 g/cm³. The intermolecular forces are due to weak van der Waals interactions which allows free spinning of the C_{60} molecules in the fullerite lattice at normal conditions. Under high pressure and high temperature conditions ($P=1-8$ GPa and $T=350-450^{\circ}\text{C}$) fullerite transforms into one- or two-dimensional polymeric structure via [2+2] cycloaddition reactions between adjacent C_{60} molecules in the (001) (orthorhombic 2D phase) or (111) (rhombohedral 2D phase) planes.

Quite recently, in 1999, Marques and coworkers [2] provided experimental evidence of a polymeric phase of C_{60} obtained by compressing a C_{60} powder up to 13 GPa under non hydrostatic condition at 550°C. The new phase was quenchable at normal conditions. The C_{60} cages are suggested to be covalently bonded to the others neighboring cages forming a 3D network, but the small size of the crystallites of the polycrystalline product prevented a compelling refinement of the crystal structure. Nevertheless later on, different possible 3D polymeric phases have been proposed from the analysis of powder X-ray data all belonging to the body-center orthorhombic (bco) *Immm* space group [3] but with different intermolecular bonding. These structures can be seen as generated from the 2D orthorhombic polymer by introducing “(3+3)” bonding between C_{60} in adjacent planes. Besides [2+2] cycloadditions, common four-sided rings have also been proposed for the in-plane polymerization of the 3D phase [2]. All these bco *Immm* structures (with [2+2] or four-sided rings in plane bindings) have been shown to be metallic by *ab-initio* calculations [4,5].

More recently, Yamanaka *et al.* [6] succeeded in isolating a single crystal ($0.3 \times 0.2 \times 0.2$ mm³) of a 3D polymeric phase synthesized by compressing the 2D orthorhombic polymer at 15 GPa and 600°C. Measurements of the electrical conductivity σ as a function of the temperature shows the behavior $\ln \sigma \propto T^{-1/4}$ typical of the variable range hopping between localized states within the band gap of insulating material. Similar electrical behavior has been reported on polycrystalline 3D polymers by Burgos *et al.* [7]. Structural refinement from single crystal X-ray diffraction pattern by Yamanaka *et al.* [6] still assigned a body-center orthorhombic *Immm* space group. The internal structure consists of C_{60} molecules linked via “(3+3)” bonds only between adjacent planes with no in plane bonding. However, *ab-initio* calculation revealed

a metallic character of this phase as well for both the experimental geometry and the theoretically optimized structure which is inconsistent with the conductivity measurements.

Aiming of resolving this inconsistency, in this work we explore by *ab-initio* calculations several modifications of the 3D polymeric phase proposed in Ref. [6], which, given the large uncertainty in the crystal structure refining, might still be consistent with experimental diffraction pattern. Indeed, we have found an insulating anti-ferromagnetic phase suitable to reproduce both the electronic and structural experimental data by Yamanaka *et al.* [6].

II. Computational details

Calculations of structural and electronic properties have been performed in the framework of density functional theory (DFT), with generalized gradient correction (PBE) [8], as implemented in the code PWSCF [9]. Ultrasoft pseudopotential [10] and plane wave expansion of the Kohn-Sham orbitals up to a kinetic cutoff of 30 Ry have been used. Geometry optimization and band structure calculations have been performed by integration over Monkhorst-Pack (MP) meshes in the irreducible part of the Brillouin Zone (4x4x4) [11]. All the structures considered belong to the bcc *Immm* space group with a single C₆₀ per unit cell. Geometry optimization has been repeated at several volumes and the resulting energies fitted by a Murnaghan [12] equation of state. The b/a and c/a ratio have been optimized at fixed volume such as to reproduce a diagonal stress tensor (with residual anisotropy in the diagonal components lower than 2 kbar).

III. Results

We started our investigation by computing the equation of state of the structure proposed experimentally by Yamanaka *et al.* [6], that we will hereafter refer to as structure A (Fig. 1). An enlargement of the “(3+3)” binding configuration is shown in Fig. 2. For this type of linkage we follow the notation introduced in Ref. [3].

Starting from structure A and by topological considerations, we propose three new structures, all of *Immm* symmetry with “(3+3)” bonds between adjacent planes. The first we considered is produced by [2+2] cycloaddition along *b* direction and “(4+4)” bonds (Fig. 4) along *a* direction (structure B, Fig. 3). The “(4+4)” binding is in fact a [8+8] cycloaddition reaction in the organic nomenclature which we refer as “(4+4)” to highlight the number of atoms involved in the linkage. The second structure we considered is formed by “(4+4)” bonds in both *a* and *b* directions (structure C, see Fig. 5). Finally, we considered a structure in

which in plane binding takes place only along a via “(4+4)” linking (structure D, see Fig. 6). A similar structure (D’) has been obtained in Ref. [6] by *ab-initio* optimization of structure A at the experimental lattice parameters. This latter phase differs from ours because of the presence of the “(4+4)” bonds along b instead of along a , with a consequent rotation by 90° of the “(4+4)” linkage.

The equation of state (EOS) of all these structures are reported in Fig. 7. The equilibrium lattice parameters are reported in Table I. All the EOS have been calculated by enforcing a non magnetic solution of the electronic problem (non spin polarization). Best agreement with experimental data on the lattice parameter in Ref. [6] is obtained for structure C. The overall overestimation of the equilibrium volume with respect to experiments might be partially due to the neglect of the van der Waals interaction in our DFT calculations. The electronic density of states (DOS) of our new structure B, C, and D (Fig. 8) show that all these phases are metallic as found for structure A in Ref. [6]. By visualizing the Kohn-Sham orbitals we recognize that the high density of states at the Fermi level is mainly due to π states localized on the atoms close to the “(3+3)” links which due to the geometry constraints experience a frustration in the π -conjugation. By removing the constraint of a non-magnetic solution and allowing the occurrence of spin polarization within a PBE-LSD calculation, we have found indeed an anti-ferromagnetic solution which allows turning the system from metallic to insulating.

In structure C, for instance, the anti-ferromagnetic solution corresponds to an insulating system with the opening of a band gap of 0.5 eV (Fig. 9) and an energy gain of 3 meV/atom with respect to the non-magnetic solution. The absolute magnetization of the system is $3.8 \mu_B/\text{cell}$ large. The spin polarization is localized on twelve atoms of the cage, six on the upper face and six on the lower face (Fig. 10) which are three-fold coordinated. Because of (3+3) bonds (Fig. 2) which turn the hybridization of the neighboring atoms from sp^2 to sp^3 there is a frustration in the π -conjugation, as mentioned above the spin polarized solution allows the occurrence of singly occupied orbitals which could not couple effectively with neighboring orbitals due to the geometric frustration.

So far the spin polarized calculations have been restricted to structure C whose theoretical equilibrium density shows the best agreement with the experimental density of Ref. [6]. However, we might expect an anti-ferromagnetic solution also for other structures (A, B and D), which similarly to the structure C, experience a frustration in the π -conjugation due to the presence of “(3+3)” bonding.

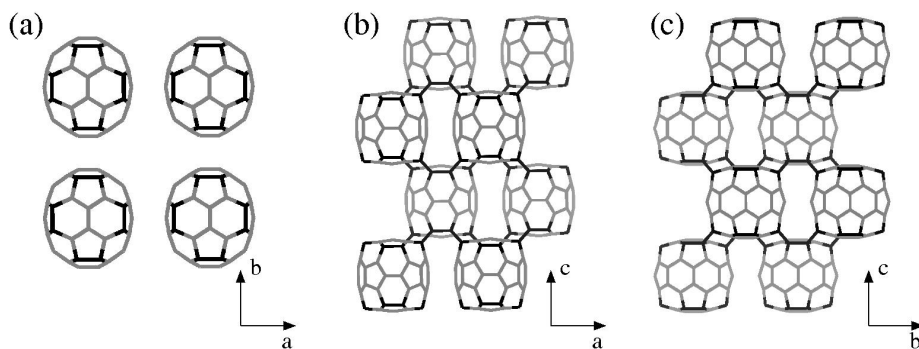


Figure 1: View of the (a) (001), (b) (010) and (c) (100) planes of 3D polymeric structure A (see text) proposed in Ref. [6]. A C_{60} molecule linked by “(3+3)” bonds to eight nearest neighbor cages (Fig. 2). There is no covalent bonding in the a, b plane. The atoms depicted in gray are three-fold coordinated (44 atoms) and the black one are four-fold coordinated (16 atoms).

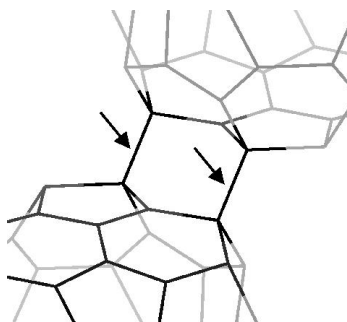


Figure 2: The “(3+3)” bonds [3] between two cages on different planes which are linked by two covalent bonds (indicated by two arrows) throughout the $\langle 111 \rangle$ directions.

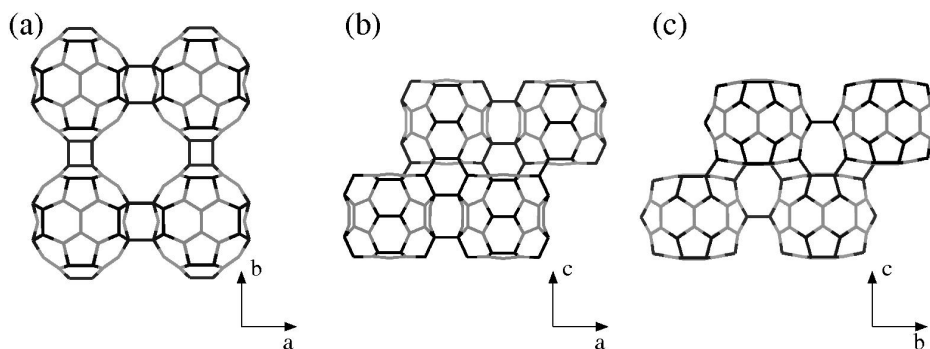


Figure 3: View of the (a) (001), (b) (010) and (c) (100) planes of 3D polymeric structure B (see text). Adjacent planes are linked by “(3+3)” bonding. In the a , b plane C_{60} are linked by “(4+4)” bonds and [2+2] cycloadditions in the a and b directions, respectively. The atoms depicted in gray are three-fold coordinated (32 atoms) and the black one are four-fold coordinated (28 atoms).

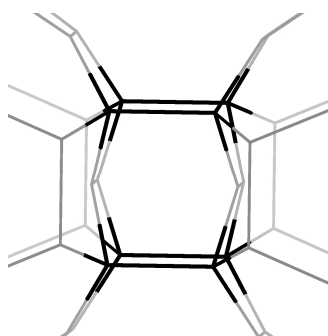


Figure 4: The “(4+4)” bonding between two adjacent cages in the a , b plane. Four covalent inter-cage bonds are formed. The four inter-cage bonds in structure C are 1.66 Å and 1.75 Å along the a and b directions, respectively. In structure B and D the four inter-cage bond distances are in the range 1.6-1.8 Å.

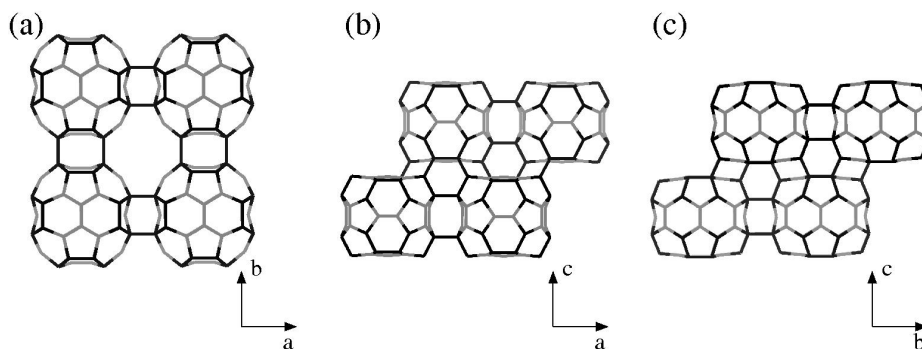


Figure 5: View of the (a) (001), (b) (010) and (c) (100) planes of 3D polymeric structure C (see text). Adjacent planes are linked by “(3+3)” bonding. In the a, b plane C_{60} are linked by “(4+4)” bonding in both a and b directions. The atoms depicted in gray are three-fold coordinated (28 atoms) and the black one are four-fold coordinated (32 atoms).

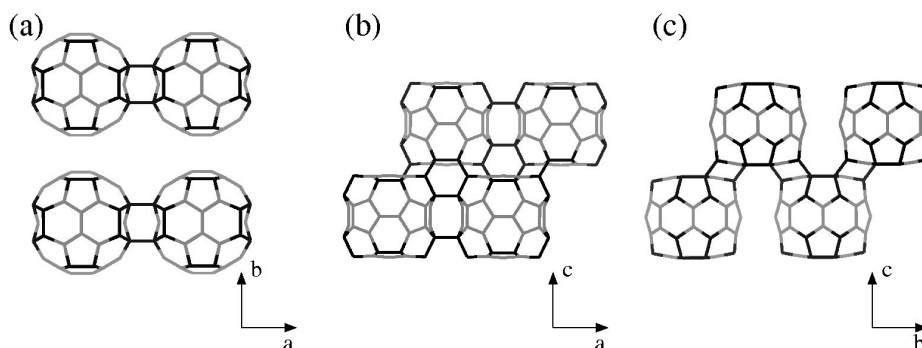


Figure 6: View of the (a) (001), (b) (010) and (c) (100) planes of 3D polymeric structure D (see text). Adjacent planes are linked by “(3+3)” bonding. In the a, b plane C_{60} are linked by “(4+4)” bonding in the a direction. There is no covalent bonding in the b direction. The atoms depicted in gray are three-fold coordinated (36 atoms) and the black one are four-fold coordinated (24 atoms).

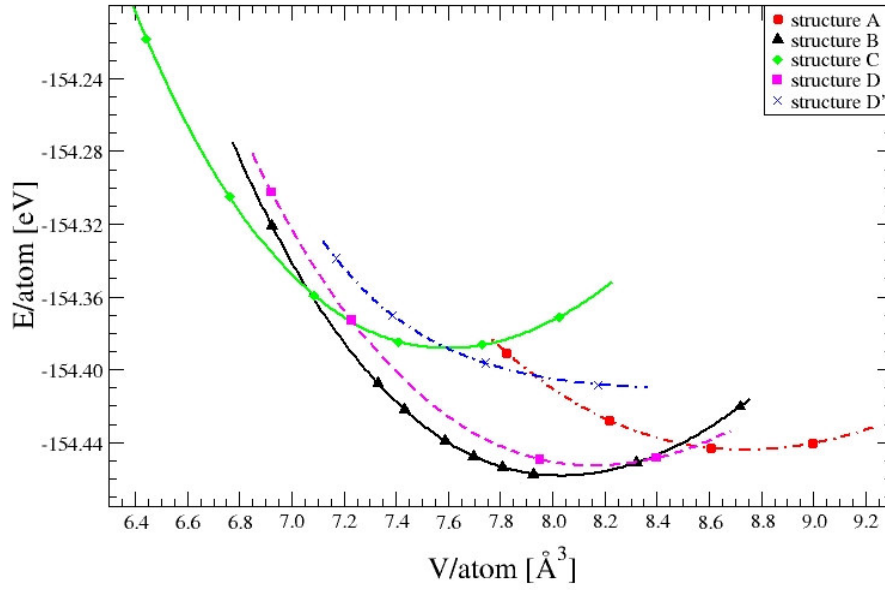


Figure 7: Equation of state (EOS) of different structures A (Fig. 1), B (Fig. 3), C (Fig. 5) and D (Fig. 6) and D' described in the text. The system is enforced to be non-magnetic for all structures (non spin polarization allowed).

Structure	a [Å]	b [Å]	c [Å]	$V_{eq}[\text{Å}^3/\text{atom}]$
A	8.62 (7.86)	9.24 (8.59)	12.96 (12.73)	8.60 (7.16)
B	8.03	9.08	13.22	8.03
C	8.15	8.49	13.18	7.60
D	8.04	9.10	13.03	7.94
C ^{exp}	8.00	8.30	12.93	7.16

Table I: Theoretical equilibrium lattice parameters of the investigated structures. C^{exp} refers to the theoretical lattice parameter at the experimental density of the quenched structure in Ref. [6].

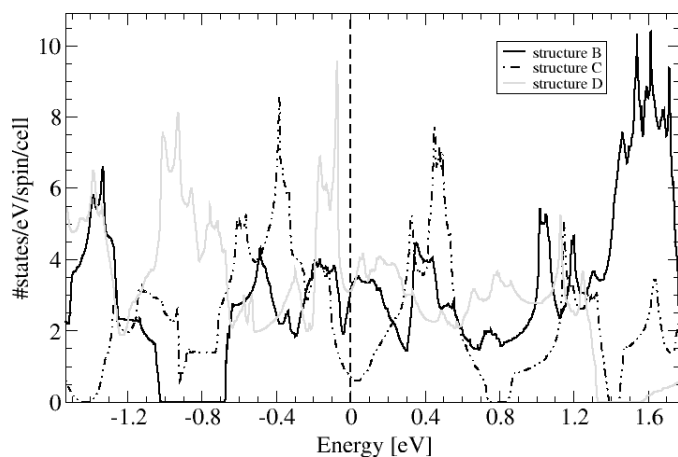


Figure 8: Electronic density of state (DOS) of structure B (Fig. 3), C (Fig. 5) and D (Fig. 6) at the theoretical equilibrium volume.

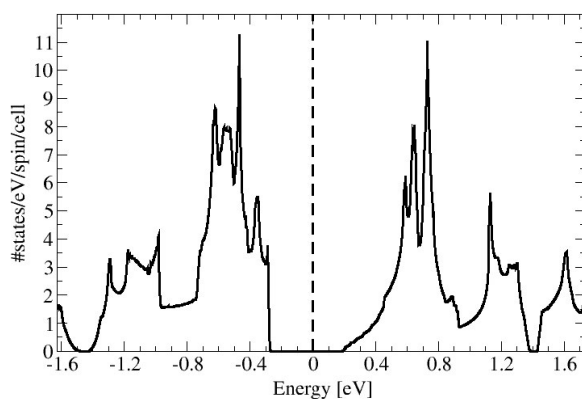


Figure 9: Electronic density of state (DOS) of structure C (Fig. 5) at the theoretical equilibrium volume computed allowing the magnetization of the system (LSD calculation). In its anti-ferromagnetic ground state the spin polarization (LSD calculation) induces the opening of an energy gap of about 0.5 eV with an energy gain of 3 meV/atom.

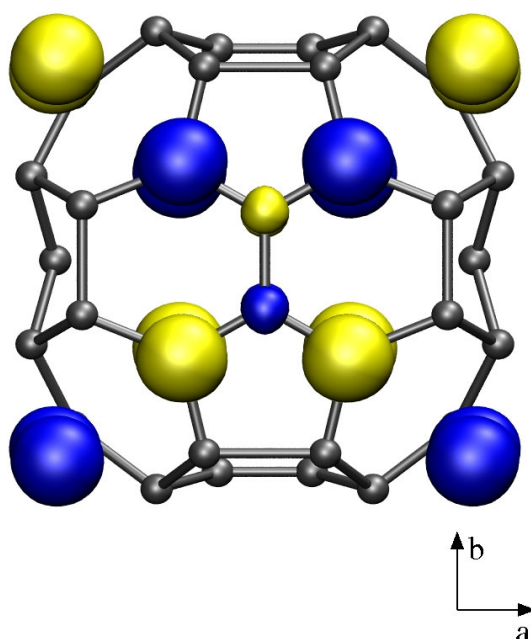


Figure 10: Spin density of structure C (Fig. 5). In its anti-ferromagnetic ground state the absolute magnetization is $3.8 \mu_B/\text{cell}$. The light gray and dark orbitals indicate excess of spin up and down electron, respectively.

IV. Conclusions

Stimulated by a recent experimental work on a 3D non-metallic polymeric form of C_{60} , we have investigated the structural and the electric properties of several 3D polymeric structures with the constraint of the $Immm$ symmetry identified experimentally. We found that the structure with the best agreement with experimental lattice parameters is made of C_{60} cages with “(4+4)” bonds in plane and “(3+3)” bonds between cages of nearest planes along $\langle 111 \rangle$ directions (structure C). This structure is an anti-ferromagnetic insulator, with an absolute magnetization of $3.8 \mu_B/\text{cell}$ and an energy gap of 0.5 eV.

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