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Structure and properties of graphullerene: a semiconducting two-dimensional C_{60} crystal

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Graphullerene is a recently discovered, two-dimensional allotrope of carbon formed from C_{60} molecules. It has been synthesized in the form $(C_{60}Mg_4)_n$ and subsequently transformed into $(C_{60})_n$ by removal of the Mg atoms. Ab initio calculations are employed to examine the structure and properties of this material. Structurally, graphullerene is composed of strained C_{60} molecules. Each of these molecules is connected to six neighbors in a hexagonal network with a total of eight chemical bonds. We find this structure to be meta-stable, owing to the strain produced by the covalent bonding of the molecules. However, the inclusion of Mg atoms transforms the cohesion energy from negative to positive values by forming additional C-Mg bonds, creating an energetically stable material. In the absence of Mg, this allotrope is a pure carbon semiconductor with an indirect band gap. Phonon spectrum calculations confirm the dynamical stability of the material and yield its in- and out-of-plane sound velocities. In addition, symmetry breaking of the C_{60} molecules results in a distribution of bond lengths and creates vibrational modes that serve as a signature of graphullerene.

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INTRODUCTION

Carbon is one of the essential elements in nature, as it participates in most of the complex organic structures that allow life. It can bond within molecules in different electronic configurations: sp, sp^2, and sp^3. As a pure element, carbon has two well-known, extended allotropes: graphite and diamond, each with distinct properties. Diamond is a three-dimensional network of carbon atoms; each atom bonds with its four nearest neighbors within sp^3 hybridization. In contrast, graphite is a layered structure characterized by an sp^2 hybridization between each atom and its three nearest neighbors in a given layer and van der Waals interactions between layers. The recognition that the layered structure of graphite could be cleaved to form a two-dimensional carbon allotrope, graphene, was a significant development in condensed matter physics[1]. However, although carbon is similar to silicon and germanium in its chemical bonding and electronic structure, none of the common allotropes of carbon, diamond, graphite or graphene are semiconductors.

The C_{60} molecule is a carbon ball similar in shape to a football, with an atom in each corner. The carbon ball consists of hexagons and pentagons of carbon atoms, such that each atom bonds to its three nearest neighbors[2] in an sp^2 hybridization. Recently, C_{60} molecules were synthesized with magnesium to create a monolayer of a two-dimensional hexagonal periodic structure $(Mg_4C_{60})_n$[3,4]. Subsequently, it was shown that the magnesium atoms of this two-dimensional crystal could be removed to form a pure allotrope of carbon with a C_{60} molecule occupying each hexagonal lattice point[3]. In this crystal, some of the carbon atoms bond with three nearest neighbors, and some, those that connect two neighboring molecules, have four nearest neighbor bonds. Thus, some carbon atoms in this configuration are in sp^2, and others in sp^3 hybridization states. This two-dimensional structure has been termed graphullerene, and its corresponding three-dimensional van der Waals crystal, graphullerite[3].

Although graphullerene has been synthesized, it has only been partially characterized. Specifically, its structure was deduced indirectly, while its electronic properties have only been probed. A computational study of graphullerene in the absence of Mg was reported[5], indicating that the material is meta-stable.

The role of Mg atoms in stabilizing the structure and their effect on the material properties remain to be determined. In this study, we employ ab initio methods to examine the mechanical and energetic stability, atomic structure, phonon dispersion curve, and band structure of graphullerene.

METHODS

Structure and phonon calculations

The calculations were performed within the plane-wave formulation of density-functional theory (DFT) with ultra-soft pseudopotentials as implemented in the Quantum-Espresso simulation package[6]. The pseudopotential is from the Garrity, Bennett, Rabe, and Vanderbilt data set[7]. The exchange-correlation functional is approximated by the Perdew-Burke-Ernzerhof (PBE) general gradient approximation[8].

Density-functional-perturbation-theory was employed for phonon calculations[9].

Numerical parameters

The numerical parameters were chosen to converge the energy to 10^{-4} Ry per atom. The plane-wave expansion cutoff energies are 40 Ry and 200 Ry for wavefunctions and for density and potential, respectively.

The band gap calculation with the B3LYP[10] and PBE0[11] exchange-correlation functionals was performed with a norm-conserving pseudopotential and an energy cutoff of 80 Ry.

In all calculations, complete relaxation of both forces and stress is required. The forces and stresses are converged to 10^{-3} a.u. and 0.5 kbar, respectively.

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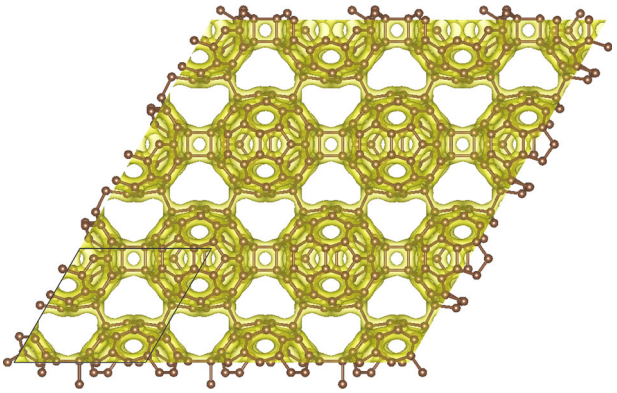

Fig. 1 Two-dimensional projection of the atomic structure of graphullerene together with a high electron density iso-surface. The black lines indicate a primitive unit cell.

RESULTS AND DISCUSSION

Structure

The structure of graphullerene was calculated by constructing a 2D hexagonal unit cell with a C_{60} molecule inside and allowing the crystal structure, including both atomic positions and the lattice parameters, to relax to a minimum energy configuration. The resultant structure and its electronic density are displayed in Fig. 1. This two-dimensional structure consists of parallel, linear C_{60} chains in which each C_{60} unit is connected to its neighbor by two parallel bonds. Each linear chain is then coupled to an adjacent chain by two single bonds emanating from each C_{60} unit. Thus, the structure consists of two pairs of neighboring bonds in addition to four bonds for each C_{60} molecule for a total of eight bonds, all on the same plane. The inter-C_{60} bonds in graphullerene have a high electron density, similar to the bonds within the C_{60} molecule, implying that they are covalent.

To further understand the geometry of the crystal, we calculated the projections of atomic positions on the plane where molecular bonds formed (see Fig. 2a–d). Comparison with results for the C_{60} molecule indicates a strain near the inter-C_{60} bonds,

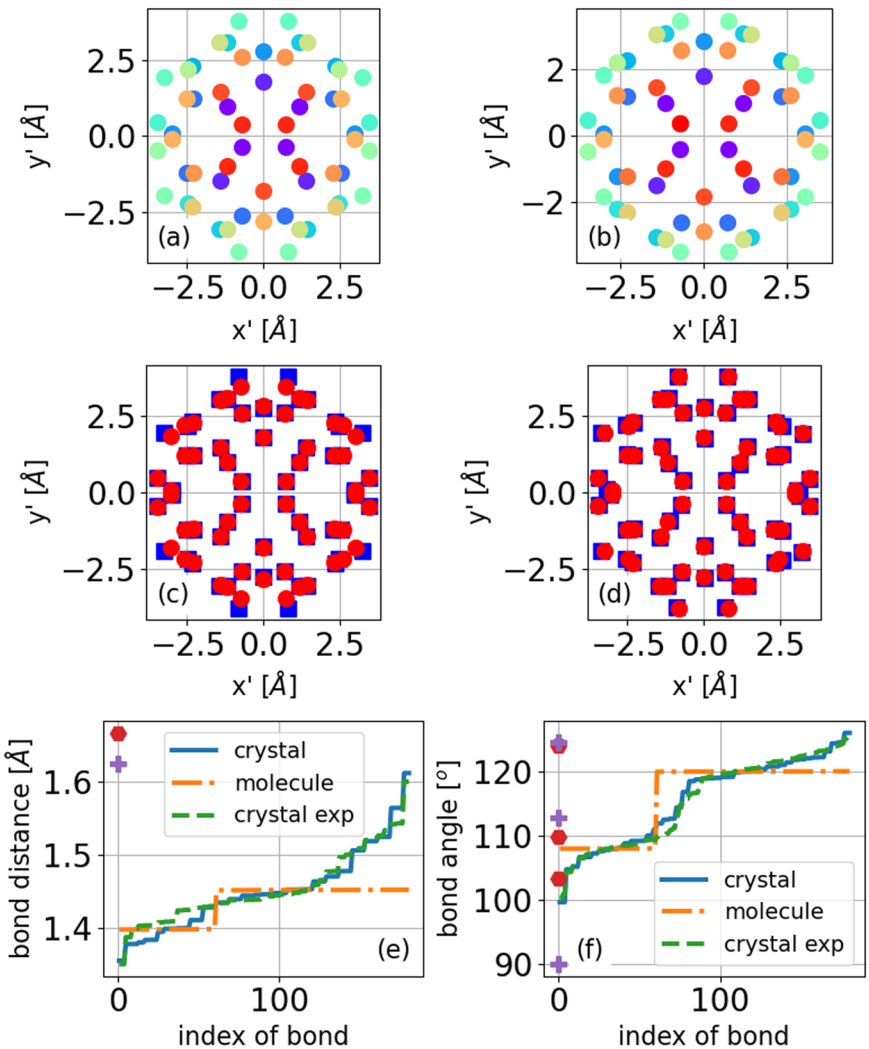

Fig. 2 Analysis of graphullerene structure. Projections of the atomic positions in the crystal (**a**) and in the molecule (**b**) on the plane in which the molecular bonds form, where rainbow colors correspond to the distance from this plane; comparison of calculated projections between the crystal (squares) and the molecule (circles) (**c**) and between experimental positions obtained for Mg_4C_{60} (squares)[3] and calculated positions (circles) (**d**). Distributions of bond lengths (**e**) and angles (**f**) for the crystal and the molecule, where crosses mark the values for dual bonds, and hexagons mark the values for single bonds between the C_{60} molecules.

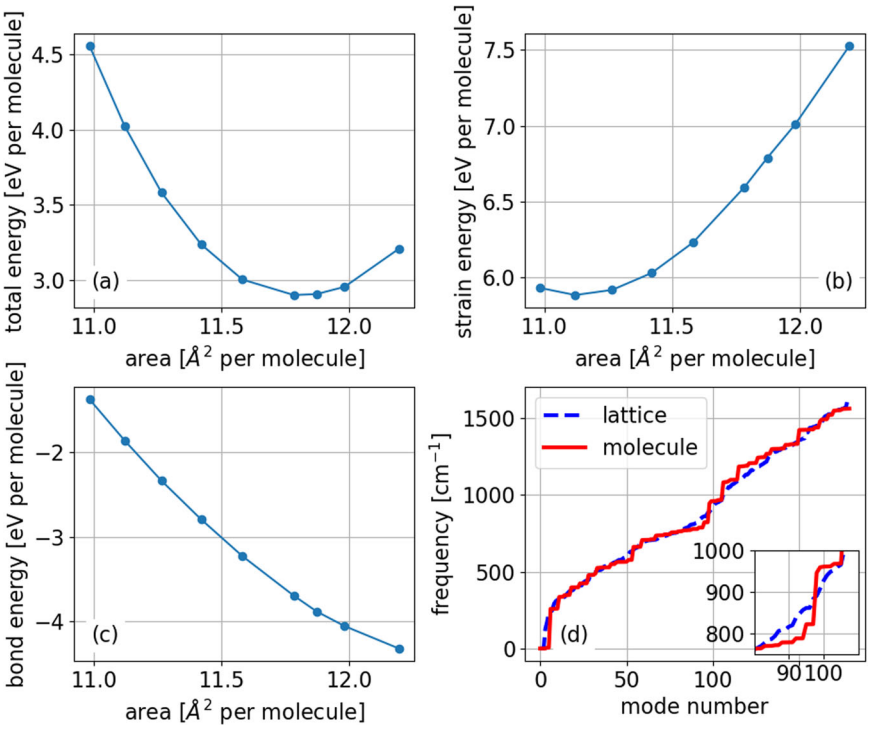

Fig. 3 Energies and frequencies. Total (**a**), strain (**b**), and bond (**c**) energies of graphullerene. The phonon frequencies at the zero wavevector, Γ point, correlate with the molecule's vibrational frequencies shown in (**d**).

with little effect on the atoms far from these bonds (Fig. 2c). A comparison to the experimental data shows good agreement, as shown in Fig. 2e, f, even though experimental values were obtained from the related Mg_4C_{60} compound. Because the structure of Mg_4C_{60} is not closely packed, magnesium atoms are intercalated between molecules[4] and do not significantly affect interatomic separations.

An analysis of bond lengths in graphullerene found the inter-C_{60} bonds to be the longest, with single bond distances being the greatest (Fig. 2e). Within the C_{60} molecule, the most extended bonds were those between atoms partaking in intermolecular bonding, a reflection of the strain in the molecule. Between molecules, the shortest distance was 1.62 Å, compared with the experimental value of 1.57 Å that was obtained without magnesium[3]. An analysis of the bond angles found that angles between inter-molecular bonds were within the range of the bond angles within molecules, except for the right angle (Fig. 2f) formed by the dual bonds connecting adjacent C_{60} units (see Fig. 1). However, the formation of graphullerene distorts the highly symmetric structure of C_{60}, resulting in a distribution of both bond lengths and angles (see Fig. 2e, f).

Material stability

To study the stability of graphullerene, we first calculated the cold potential energy curve, which is the system's total energy as a function of the unit cell area. This curve was obtained by applying isotropic two-dimensional stress to the system. The results are presented in Fig. 3a and show that a minimum in the energy curve is present, indicating a mechanically-stable structure without external forces (the equivalent of zero pressure in bulk materials).

The total energy, defined relative to that of free C_{60} molecules, is positive throughout indicating that the minimum in the energy curve corresponds to an energetically meta-stable state. It can be decomposed into two terms: strain energy (Fig. 3b), which is the energy of a strained molecule less the energy of a molecule in a vacuum at equilibrium, and the remaining energy, which is the bond energy (Fig. 3c). The strain energy has a minimum where strain transforms from compression to tension (~11.1 Å^2), and tension energy increases as unit cell area increases. In contrast, the bond energy decreases because molecules move further from each other as the unit cell area increases. Thus, these two terms have opposite trends in the tension region and combine to form the system's total energy with a minimum. As shown in Fig. 2c, this local minimum, corresponding to the stable structure, is in the tension region, corresponding to the tension strain of atoms near bonds.

Table 1. Strain, bonding, and cohesion energies per C_{60} molecule.

Strain energy	Bonding energy	Cohesion energy
6.53 eV per molecule	−3.67 eV per molecule	−2.86 eV per molecule

We calculated the phonon spectrum of graphullerene at the minimum energy configuration and found only positive (real) frequencies, as shown in Fig. 3d. Thus, we can confirm that the graphullerene structure is a local minimum of the Born–Oppenheimer potential energy surface.

Some of the degeneracy in the vibrational frequencies of the C_{60} molecule is removed in the graphullerene structure due to the symmetry breaking, causing the material to present additional frequencies (Fig. 3d). This result agrees with the reported measurement of the Raman spectrum, in which the splitting of some modes is observed[3].

The cohesion energy, a measure of stability, is negative, as shown in Table 1, due to the large strain energy, which is larger than the bonding energy. The negative value indicates that the graphullerene structure is energetically meta-stable with respect to C_{60} molecules. The bond energy is approximately 0.92 eV per bond, of the order of magnitude for covalent bonding, in agreement with the results for the electron density.

Electronic and vibrational properties

The electronic structure of graphullerene is important for applications as it is the first pure carbon two-dimensional semiconductor to be discovered. The electronic band structure of graphullerene was calculated using the PBE functional. We found that it exhibits an indirect band gap of 0.7 eV (Fig. 4a) and a direct band gap of 0.78 eV, which are desirable for many applications. However, a band gap of 2.1 eV is obtained using the B3LYP[10] functional. Common DFT functionals underestimate the band gap of carbon allotropes, for example, diamond[12]. Thus, to the carbon allotropes that present insulator (diamond), metallic (graphite), and semi-metallic (graphene) phases, there is added a semiconducting phase, graphullerene, with mixed sp^2 and sp^3 hybridization states.

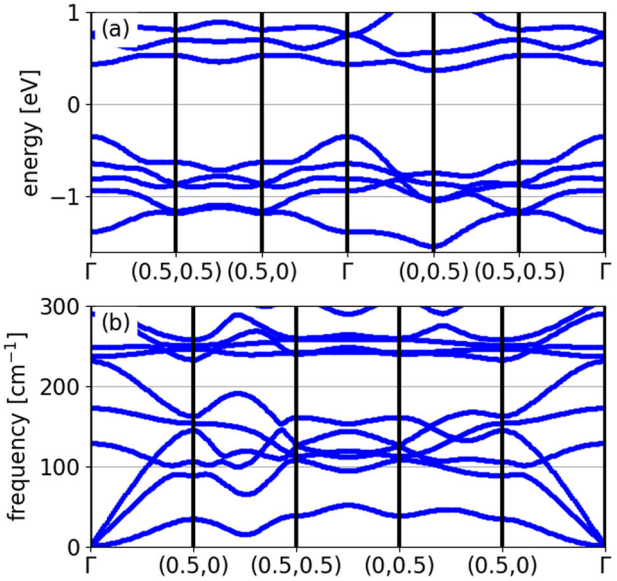

Fig. 4 Band structure and phonon frequencies. Graphullerene band structure wherein energy is relative to Fermi energy (**a**) and the lower region of the phonon dispersion relation (**b**).

We calculated the vibrational phonon spectrum, and the low-frequency section containing the acoustic branches is presented in Fig. 4b. As in all two-dimensional materials, the phonon spectrum contains two linear, Debye-like branches, which correspond to the material's in-plane sound waves, and one parabolic branch, which corresponds to its out-of-plane sound waves. The highest frequency of the crystal (not shown) is 1620 cm^{-1}, and is slightly larger than the highest vibrational frequency of the molecule (see Fig. 3d)[13,14]. In this highest frequency mode, the significant motion is that of atoms about the bonds with the shortest length (1.35 Å). Short bond lengths correspond to stronger bonds and, thus, higher frequencies. We note that this mode does not appear in the molecule without the expanded bond length distribution.

In-plane sound velocities were calculated and found to have a small anisotropy (see Table 2). Compared to graphene, in-plane sound velocities are lower[15], reflecting softer chemical bonds. In addition, out-of-plane sound velocities were zero, as the transverse acoustic branches were parabolic with zero group velocity in the long-wavelength limit.

In graphullerene, a frequency gap appears in the upper part of the phonon spectrum (Fig. 5c). Phonon band gaps are phenomena that can affect the material's properties[16–19]. The highest frequencies belong to graphullerene phonon modes that differ significantly from the vibrational modes of the molecule. These modes involve displacements of only specific atoms with the shortest bond distances and, thus, the highest frequencies. These specific atoms are indicated in Fig. 5a, b. The shortest bond distance is 1.35 Å (for a comparison to other bond distances, see Fig. 2e). The displacements of the atoms are in the bond directions, and thus the shortest bonds are those most affected. Furthermore, these short bond length atoms are neighbors of the atoms that bond with neighboring molecules and have the largest bond length. Thus, the short bond length is compensation.

Table 2. In-plane sound velocities.

Wave type	Longtitudinal: Single bond direction	Transverse: Single bond direction	Longtitudinal: Double bond direction	Transverse: Double bond direction
Sound velocity (km per s)	11.0	7.1	9.9	6.8

Graphullerene with Mg

To examine the role of Mg atoms in graphullerene, we modeled $(C_{60}\ Mg_4)_n$ similar to $(C_{60})_n$ above. The structure of graphullerene

Table 3. Strain, bonding, and cohesion energies of graphullerene with four Mg atoms per C_{60} molecule.

Strain energy	Bonding energy	Cohesion energy
7.89 eV per molecule	−11.52 eV per molecule	3.60 eV per molecule

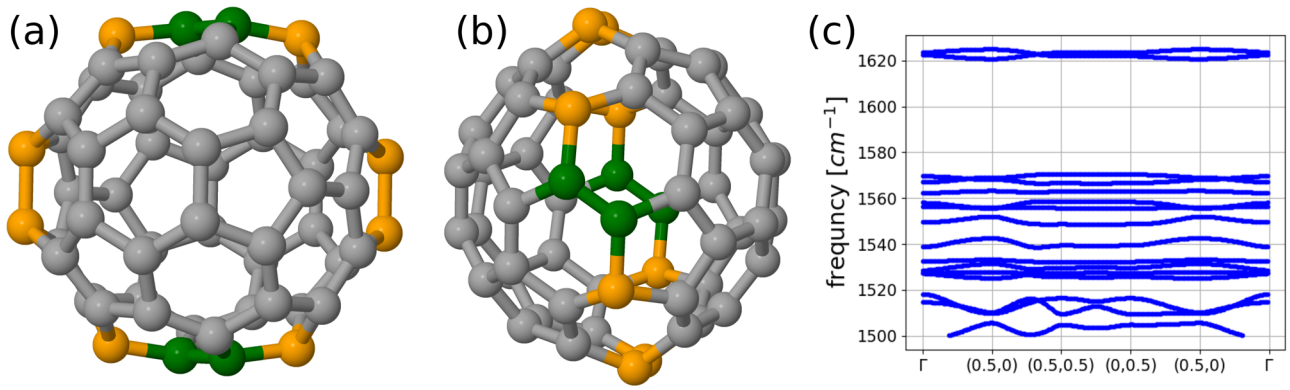

Fig. 5 Phonon modes. a, **b** visualization of the highest frequency Phonon mode in two different orientations and (**c**) the upper part of the phonon spectrum. The orange atoms in (**a**) and (**b**) bond with neighboring molecules, and the green atoms are the atoms that move.

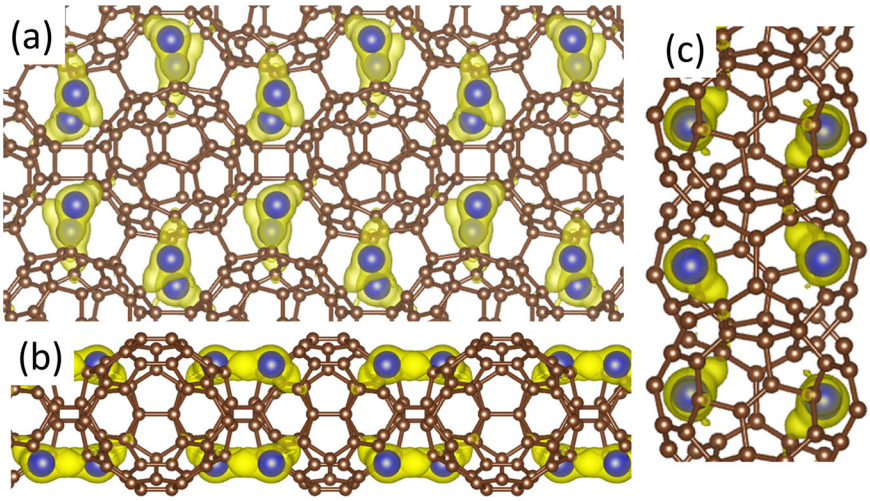

Fig. 6 The electronic density difference between graphullerene with and without Mg atoms. The large and small spheres are Mg and C atoms, respectively, shown with a high-density difference iso-surface. **a**, **b** and **c** are top and side views.

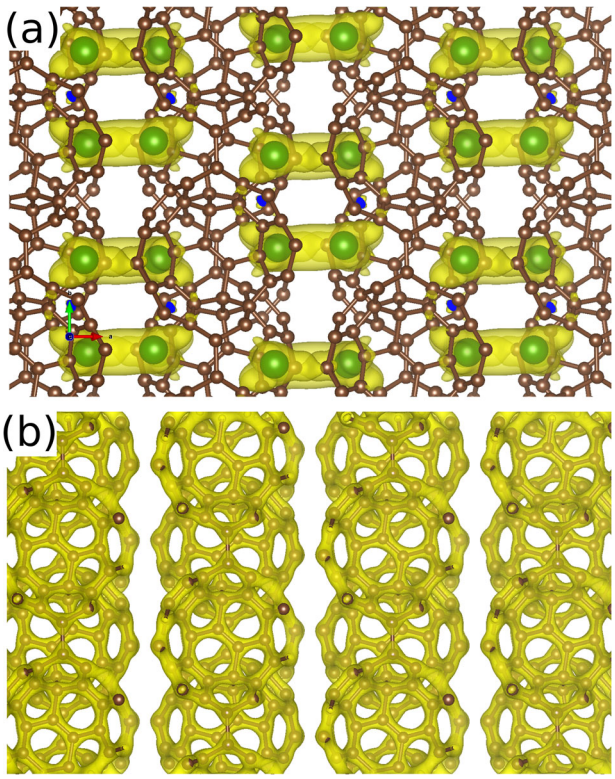

Fig. 7 Electron density of bulk graphullerene. **a** Electron density difference between the crystal with and without Mg; **b** The electron density of the crystal without Mg.

with Mg was formed in a 128-atom rectangular unit cell with two C_{60} molecules and 8 Mg atoms initially placed as reported experimentally[4], which was then allowed to relax.

The large strain caused by the bonds between the C_{60} molecules makes the cohesion energy of $(C_{60})_n$ negative, as we showed above, and thus the graphullerene structure is hard to achieve in practice. Incorporating Mg atoms stabilizes the structure with positive cohesion energy (Table 3). The strain energy is similar with and without Mg atoms; thus, the positive cohesion energy in $(C_{60}Mg_4)_n$ results from additional, strong bonding. This bonding is achieved through C-Mg bonds, as shown in Fig. 6, where it can be seen that the additional electronic density is located between an Mg atom and two C_{60} spheres. Thus, the Mg atoms function as bridges that bind the C_{60} spheres even more strongly.

The incorporation of Mg atoms also affects the electronic structure. We find that the band gap is smaller and obtained to be 0.49, 1.35, and 1.56 eV with PBE, B3LYP, and PBE0 exchange-correlation functionals, respectively.

In passing, we note that introducing Mg atoms also creates bonding between adjacent layers of graphullerene in the bulk beyond the van der Waals interactions between the layers in the absence of Mg. Fig. 7 illustrates these bonds.

To conclude, we have demonstrated that the recently discovered two-dimensional allotrope of carbon, graphullerene, is a meta-stable semiconductor whose structure consists of strained C_{60} molecules bound covalently with their neighbors. We have determined the bond lengths and vibrational spectrum of graphullerene, contrasted them with that of isolated C_{60} molecules, and identified a vibrational signature of graphullerene. We have exposed the role of Mg atoms. The cohesion energy changes from negative to positive with the inclusion of Mg atoms that form additional bonds with the carbon atoms, bridging the C_{60} molecules and thus making the structure energetically stable with respect to C_{60} molecules and Mg atoms. This observation agrees with the experience that the $(C_{60})_n$ structure is first synthesized with Mg atoms that are subsequently removed. The inclusion of Mg atoms also reduces the electronic band gap. Our results agree with the reported experimental observations and extend them to establish a more robust basis for further pursuing technological applications of this class of materials and developing synthetic routes.

DATA AVAILABILITY

All data generated or analyzed during this study are included in this published article.

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AUTHOR CONTRIBUTIONS

Conceptualization: G.M.; Methodology: U.A. and G.M.; Formal analysis and investigation: U.A.; Writing—original draft preparation: U.A.; Writing—review and editing: G.M.

COMPETING INTERESTS

The authors declare no competing interests.

ADDITIONAL INFORMATION

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