Theoretical Predictions for a Two-Dimensional Rhombohedral Phase of Solid C_{60}

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We have calculated the properties of a rhombohedral phase of solid C_{60} using a C tight-binding potential. The solid is formed by layers of hexagonally packed C_{60}, each of them connected to six neighbors by 2 + 2 cycloaddition of double bonds. We predict an equilibrium intermolecular distance of 9.17 Å, in agreement with experimental estimates of 9.2 Å. Rhombohedral C_{60} solid is higher in energy than free C_{60} molecules by 2.1 eV/molecule, and the barrier for dissociation to free C_{60} molecules is estimated to be 1.6 eV/molecule. Our results indicate that the lowest energy conformation of this new phase of solid C_{60} is a semiconductor, but defects in the intermolecular bonding pattern lead to semimetal properties. Results from similar calculations on tetragonal and orthorhombic C_{60} phases are also presented.

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Much attention has been focused on new forms of carbon since the discovery [1] and macroscopic synthesis [2] of C_{60} buckminsterfullerene (BF). Among these new forms of carbon are the experimentally produced graphitic tubules [3]. Recently, new phases of solid C_{60} have been obtained by applying high pressure and temperature to fcc C_{60} [4,5]. One dominant phase appears under x-ray diffraction to be made of layers of hexagonally close-packed C_{60} molecules [4,5]. The observed nearest distance of ~9.8 Å between C_{60} molecules in different layers is suggestive of a weak interaction between layers. However, the in-layer intermolecular distance is only 9.2 Å, much shorter than that of fcc C_{60} solid. The main characteristic of the new C_{60} solids [6], which includes tetragonal and orthorhombic phases [4], is the shortening of intermolecular bonds, indicative of a strong bonding mechanism. A similar bonding feature has also been reported in other compressed fcc C_{60} solids [7–8], in alkali-doped fullerides [9–11], in polymerized C_{60} films [12], and in experiments of surface deposition of C_{60} [13]. In the present work, we first study the structural details and the stability of the new rhombohedral phase of C_{60} solid, and then investigate the conducting properties of the solid in terms of electronic structure calculations. Similar theoretical results on the tetragonal and orthorhombic phases are also presented.

The rhombohedral and tetragonal C_{60} structures studied in this work have been originally proposed by Nuñez-Regueiro *et al.* [4]. Figure 1 depicts one layer of a solid in which C_{60} molecules are hexagonally packed in two dimensions. In this arrangement, C_{60} molecules with identical orientations are positioned at the hexagonal lattice sites, yielding a structure with a threefold rotational axis perpendicular to the layer plane. Each individual molecule is connected to six neighbors by 2 + 2 cycloaddition of "66" bonds [12,14] (the adjoining edge between two six-membered rings in C_{60}). This type of bonding between two 66 bonds belonging to different C_{60} molecules will be abbreviated in this Letter as 66/66. We found that the crystal layer of Fig. 1 belongs to symmetry point group D_{3d} and space group $P\bar{3}m1$. Note also that in this construction the resulting 66/66 bonds are parallel.

We present in this Letter theoretical predictions for the above described solid employing a recently developed tight-binding (TB) carbon-carbon potential [15]. This potential has been shown to correctly predict the geometrical structures, energetics, and electronic energy bands of crystalline linear carbon chains, graphite, and diamond. Application of this TB model to many carbon systems, particularly carbon clusters [14–17], has been very successful. In this work, we perform calculations on the equilibrium geometries and energies, and the electronic density

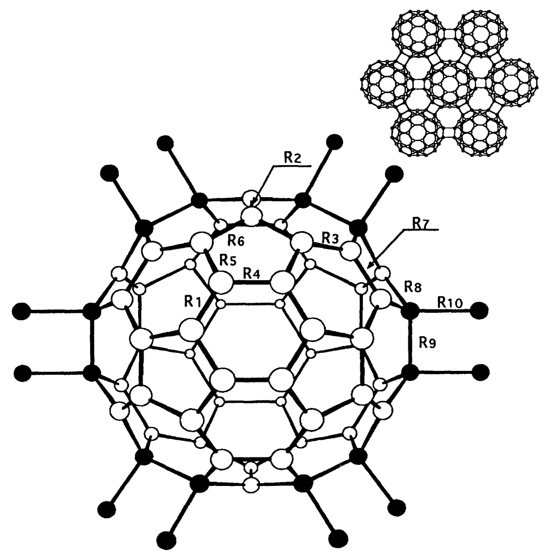

FIG. 1. C_{60} Buckminsterfullerene molecules in a layer of the rhombohedral C_{60} solid (only seven molecules are shown in the inset). The dark atoms are those involved in intermolecular bonding. The predicted equilibrium bond lengths (in Å) from R_1 to R_9 are 1.400, 1.364, 1.392, 1.460, 1.438, 1.478, 1.422, 1.509, and 1.612, respectively.

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of states (DOS) of a two-dimensional layer of the rhombohedral C_{60} solid.

Assuming that the diameter of C_{60} in the rhombohedral solid is approximately 7.1 Å, and given that the experimental nearest interlayer molecular separation is 9.8 Å, the resulting nearest distance between carbon atoms belonging to C_{60} molecules from adjacent layers is ~2.7 Å. This clearly suggests that the interlayer interaction is weak, and must be primarily of van der Waals character. However, the shortest distance between carbon atoms on different C_{60} molecules in the same layer is approximately 2.0 Å, close to the range where covalent bonding is dominant. In the present work, the interlayer interaction is neglected, and our calculations are focused on a single layer of the rhombohedral solid, which we term as "hexagonal C_{60} layer" in the following text.

Considering two-dimensional periodic conditions, we choose a unit (or primitive) cell containing 60 atoms. The TB Hellman-Feynman force is determined by a scheme previously discussed [18]. Relaxation of this structure is performed with no volume and no symmetry constraints. Since the TB force scheme yields the electronic energy and force with only one **k** point (**k** equal to zero) in the Brillouin zone (BZ), the effect of the BZ size on the relaxation simulation results is studied with the use of larger unit cells. For 240-atoms unit cells, we already find that the relaxed energy and geometry are well converged. The calculations predict that the equilibrium intermolecular distance d_0 for the hexagonal layer is 9.17 Å, which is in excellent agreement with the experimental value of 9.2 Å [4,5].

The equilibrium geometry of the hexagonal layer is schematically shown in Fig. 1. We find that the relaxed structure preserves the symmetry of point group D_{3d} and of space group $P\bar{3}m1$. The bonds linking adjacent molecules (R_{10}) have a length of 1.64 Å, characteristic of covalent bonding for carbon systems. The individual C_{60} molecules have nine distinct bond lengths (denoted R_1 to R_9) in the 1.36–1.61 Å range (see Fig. 1 caption). This is to be compared with the only two distinct bond-lengths of icosahedral C_{60} predicted to be 1.40 and 1.46 Å by the same TB model [16]. The angle between the R_9 and R_{10} bonds is 90°, much smaller than the sp^3 tetrahedral value in diamond (109.5°). This small angle is consistent with R_9 and R_{10} carbon-carbon bond-lengths longer than those of diamond, for which the TB result is 1.54 Å [15].

The equilibrium energy of the hexagonal layer is predicted to be higher than that of free C_{60} BF molecules by 2.1 eV/molecule. The dissociation energy of the hexagonal layer toward free C_{60} molecules was estimated by constant volume relaxation of the periodic structure with intermolecular distance d stretching from 9.17 Å to 9.8 Å. The energy steadily increases from equilibrium ($d_0 =$ 9.17 Å) until $d = 9.6$ Å, where a sharp energy drop corresponding to bond breaking between adjacent molecules is observed. Relative to the minimum energy at d_0, the height of the energy barrier is found to be 1.6 eV/molecule.

The experimental rhombohedral C_{60} samples were found to dissociate when heated up to a few hundred Kelvin [4,5]. Using the above energy barrier, the temperature T at which the rhombohedral solid reverts to free C_{60} molecules can be roughly estimated. We assume that the intermolecular bond stretching is caused by lattice vibration. For the hexagonal C_{60} layer, the intermolecular stretching can be associated with two acoustic vibrational branches that have wave vectors parallel to the layer. In thermal equilibrium, each branch shares an average potential energy [19] amount of $\frac{1}{2}k_BT$ per lattice site, where k_B is Boltzmann constant. By equating the $k_BT/$(lattice site) energy of the two acoustic branches with the 1.6 eV/molecule energy barrier, we predict a temperature of $T \sim 300$ K. This simplified model gives a reasonable account for the experimental measurement of $T \sim 500$ K [4] in the rhombohedral solid.

We next turn our discussion to the electronic properties of the hexagonal C_{60} layer. The electronic band structure energies are calculated using the primitive unit cell (60 atoms). The general form of Bloch sums having quantum index **k**, which reflects the translational symmetry of the lattice, is used for constructing basis functions, where **k** is taken over the BZ parallel to the layer plane. The calculated DOS for the hexagonally packed C_{60} layer is shown in Fig. 2(a). For comparison purposes, the DOS of free C_{60} molecules is presented in Fig. 2(b). An important feature in Fig. 2(a) is the existence at the location of the Fermi level of a band gap of width 1.0 eV which characterizes the solid as a semiconductor or small-gap insulator. The 1.0 eV gap correlates well with the 1.6 eV HOMO (highest occupied molecular orbital)–LUMO (lowest unoccupied molecular orbital) gap in C_{60} [Fig. 2(b)]. Therefore, the formation of 66/66 bonds between C_{60} molecules only slightly narrows the molecular HOMO–LUMO gap.

The TB model overestimates the diamond band gap by ~18% [15], but the 1.0 eV gap predicted herein for the hexagonal C_{60} layer is quite large, and we deem it unlikely to be qualitatively incorrect. However, as discussed below, the presence in the solid of "defect" intermolecular bonding patterns different from the 66/66 scheme described above affects this conclusion. Bonding patterns for connecting C_{60} molecules by 2 + 2 cycloaddition of various types of bonds were described in our previous study of C_{60} dimers [14]. These dimers provide ready candidates to test the effects of different intermolecular bonding patterns on the electronic properties of the rhombohedral C_{60} solid.

We have performed DOS calculations for the C_{60} dimers with 66/66, 56/56, 56/65, and 56/66 intermolecular bonding (labeled as dimers a, b, c, and d, respectively), where 56 and 65 denote the adjacent bond between a five- and a six-membered ring [14]. The DOS of dimer a and hexagonal C_{60} are similar, having band gaps of 1.3 and 1.0 eV, respectively, at roughly the same energy position. However, the DOS of dimers b, c, and d, which all have

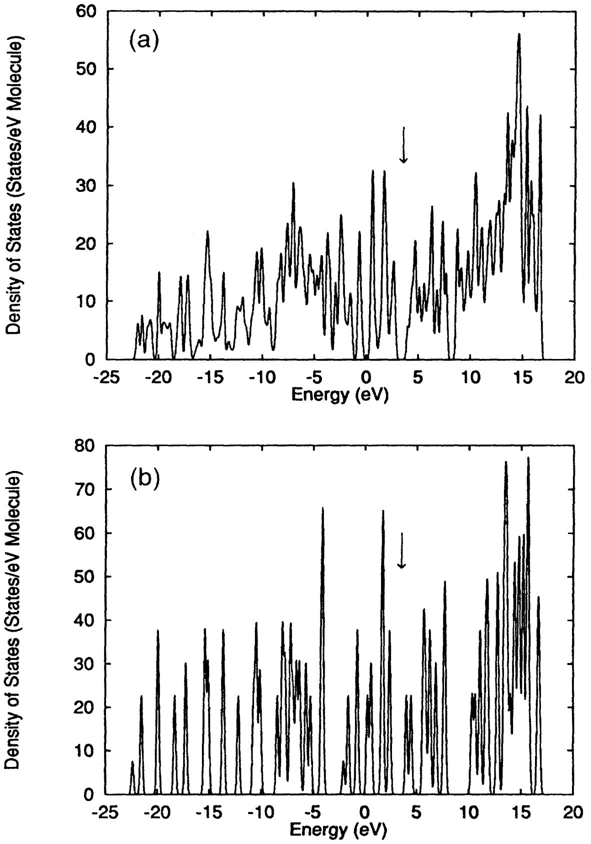

FIG. 2. (a) Electronic DOS of the two-dimensional rhombohedral C_{60} solid studied in this work, compared to that of the C_{60} Buckminsterfullerene molecule (b). The arrows indicate the location of the Fermi level.

56 bonds participating in the intermolecular bonding, are noticeably different from that of the hexagonal C_{60} layer. Particularly, the tails of the HOMO and the LUMO extend into the gap (see Fig. 3 for dimer *b*). Energetically, dimer *a* is found to be more stable than dimers *b*, *c*, and *d* [14], so inclusion of 56 bonding is thermodynamically less favorable than pure 66/66 bonding. Nevertheless, 56 bonding will inevitably occur if a misoriented C_{60} molecule is introduced in the bonding pattern. Our results indicate that this type of defect could lead to a material with semimetal electronic properties.

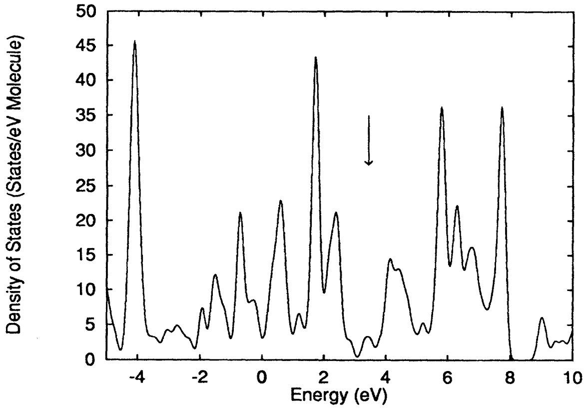

FIG. 3. Electronic DOS of C_{60} dimer *b*, which fuses two C_{60} molecules by 2 + 2 cycloaddition of 56 bonds (see text). Only the energy portion near the Fermi level (see arrow) is shown. Note that there is negligible mixing of HOMO and LUMO at the Fermi level.

We also performed similar geometry relaxations and electronic band structure calculations for a layer of the tetragonal and a linear chain of the orthorhombic C_{60} solids. Figure 4 shows the structural construction with 2 + 2 cycloaddition of 66 bonds for the tetragonal layer, and for the chain phase when the intermolecular bonds formed along the *y* (or *x*) direction are disconnected. The binding energies *E*, the intermolecular distances *d*, and the electronic band gaps *Eg* for these solids and for the hexagonal layer are presented in Table I. The intermolecular bond lengths (*R*) of $\sim$9.1 Å are in good agreement with the experimental observations [4,5]. The common features of these materials are that they have higher energy *E* than that of free C_{60} molecules, they have shortened intermolecular bonds which are of covalent character, and they all behave like semiconductors.

The elastic constants c_{11} and c_{12} of the hexagonal C_{60} layer are predicted (using the hexagonal cell parameter c_0 of 24.6 Å from Refs. [4] and [5]) to be 2.1 and 0.2 Mbar, respectively. This yields an elastic modulus $M = (c_{11} + c_{12})/2$ (the two-dimensional analog of the bulk modulus [20]) of 1.1 Mbar. *M* is much larger than the bulk modulus of fcc C_{60} solid (0.14 Mbar) [21,22], but comparable to that obtained for most of the hypothetical

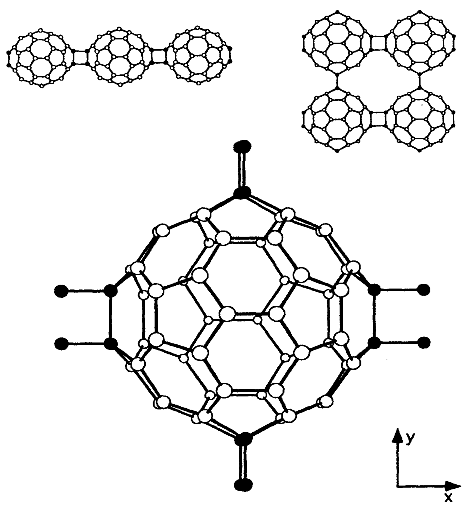

FIG. 4. The structure of the two-dimensional tetragonal C_{60} solid (right inset) and that of the C_{60} chain phase (left inset). In the chain case, no intermolecular bonds exist along the *y* direction.

TABLE I. Binding energies E with respect to C_{60}, intermolecular center-center distances d, intermolecular bond-lengths R of 2 + 2 cycloadditon, and electronic band gaps E_g for the C_{60} phases studied in this work.

	E (eV)	d (Å)	R (Å)	E_g (eV)
Rhombohedral	2.1	9.17	1.64	1.0
Tetragonal	0.9	9.06 (x) 9.13 (y)	1.64 (x) 1.64 (y)	1.2
Orthorhombic (linear chain)	0.4	9.11	1.64	1.2

Schwarzite structures (~1.0 Mbar) [23]. Again, these results are consistent with the formation of covalent bonds between molecules in the two-dimensional layer.

In summary, we have carried out calculations on the structure, stability, and electronic properties of the recently observed rhombohedral, tetragonal, and orthorhombic C_{60} solids using a tight-binding potential model. The calculated nearest neighbor intermolecular distance of 9.1–9.2 Å for these materials agrees well with experiment, and the intermolecular bonds are of covalent character. The C_{60} solids are predicted to be less stable than free C_{60} molecules, and to dissociate at a temperature of a few hundred Kelvin. Our calculated electronic DOS indicates that the new materials have semiconducting or semimetal properties depending on the intermolecular connection pattern present in the layered or chained lattice. Defects arising from the presence of single bonds in the 2 + 2 cycloadditions (56 bonding) seem to affect the electronic properties of the rhombohedral solid by smearing out the C_{60} HOMO–LUMO gap.

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