

# Electronic structure and properties of rhombohedrally polymerized C<sub>60</sub>

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The valence electronic structure of rhombohedrally polymerized C<sub>60</sub>, synthesized at 6 GPa and 725 °C, has been studied using x-ray emission spectroscopy. The C K $\alpha$  spectrum of the polymer was found to differ from that of the C<sub>60</sub> fullerite especially in the high-energy region. The observed spectra were compared to densities of states, calculated using a tight-binding approximation for three two-dimensional hexagonal C<sub>60</sub> networks, distinguished by the nature of intermolecular bonding. Theoretical spectra of the polymers agree well with experiment and indicate that changes in the valence band of C<sub>60</sub> upon polymerization are mainly due to the formation of intermolecular bonds, and only to a negligible degree due to a distortion of the C<sub>60</sub> cage. Rotation of C<sub>60</sub> within the hexagonal layer changes dramatically the electronic properties of the polymer from a semiconducting behavior for the structure with 66/66 connections to a metallic behavior for a layer containing C<sub>60</sub> molecules that are linked through 56/65 bonds. The occurrence of the latter configuration may explain the observed metalliclike in-plane conductivity of the rhombohedral phase of C<sub>60</sub>. © 2001 American Institute of Physics. [DOI: 10.1063/1.1398079]

## I. INTRODUCTION

The rhombohedral phase of the C<sub>60</sub> fullerene is formed under pressures ranging from 5 to 8 GPa and in the temperature range of 700–1000 °C.<sup>1</sup> The solid is characterized by an anisotropy of bonding. The interaction between polymerized layers has van der Waals character and each C<sub>60</sub> molecule of a layer is bonded to its six neighbors by twelve equatorial atoms.<sup>2,3</sup> The formation of four-membered rings between molecules is evident from <sup>13</sup>C NMR studies on the rhombohedral phase.<sup>4</sup> The C<sub>60</sub> fullerene has two symmetry-independent bonds: one is shared by two hexagons (66-bond, sometimes called a “double” bond) and another separates a hexagon from a pentagon (65-bond, sometimes called a “single” bond). Hence, a cycloaddition of C<sub>60</sub> may develop through 66/66, 66/56, 56/56, and 56/65 intermolecular bonding. For the (C<sub>60</sub>)<sub>2</sub> dimer, the former configuration has been predicted by quantum-chemical calculations to be the most energetically stable.<sup>5,6</sup>

The covalent bonding between C<sub>60</sub> molecules considerably changes the electronic structure and properties of the solid. Density functional (LDA) and tight-binding calculations of the rhombohedral phase and its two-dimensional layer found the fundamental gap to be narrower and the band dispersion to be larger in comparison to bulk C<sub>60</sub> fullerite, a molecular solid.<sup>7,8</sup> The presence of 56-bonding in the hexagonal network was considered to explain semimetal properties of the rhombohedral solid.<sup>8</sup> Furthermore, increase of the  $\pi$  conjugations between C<sub>60</sub> molecules could lead to the tran-

sition in the metallic state.<sup>9</sup> Electrical properties of the rhombohedral polymer were found to be strongly dependent on the temperature of polymerization.<sup>10</sup> In the polymerized plane, the conductivity increases with increasing the preparation temperature up to a metalliclike behavior.

The purpose of the present work is to investigate the electronic structure of rhombohedrally polymerized C<sub>60</sub> using x-ray emission spectroscopy and the tight-binding method. The x-ray emission arises as the result of electron transitions from valence shell to a previously created core vacancy. Due to dipole selection rules and localization of the core orbital, CK $\alpha$  spectrum characterizes the distribution of C 2*p* electrons in the valence band of a compound. Recently, the changes in the valence band of C<sub>60</sub> films upon photopolymerization have been studied by photoelectron spectroscopy using He I (Ref. 11) and Mg K $\alpha$  (Ref. 12) excitations. The valence electronic structure of the polymerized C<sub>60</sub> films was found to be almost the same as that of the pristine films. A shift of the spectrum toward lower binding energies and a broadening of bands was shown to be caused by the increased size of the conjugated  $\pi$ -electron system.<sup>11</sup> The presence of six-coordinated C<sub>60</sub> molecules in the rhombohedral polymer could have a similar effect on the electronic structure. The interpretation of the spectral features and study of the electronic properties of the polymers are performed by considering differently arranged hexagonal networks of C<sub>60</sub> in the calculations.

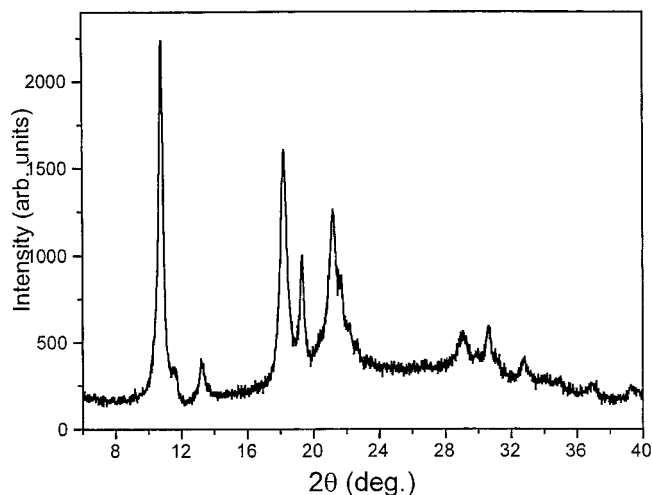


FIG. 1. X-ray diffraction spectrum of rhombohedrally polymerized  $C_{60}$ .

## II. EXPERIMENT

The rhombohedral  $C_{60}$  polymer was prepared in a Toroid-type high-pressure apparatus from fullerene powder of 99.9% purity, produced by Term USA, Berkeley, CA. The fullerite sample was heated rapidly up to 725 °C at a constant pressure of 6 GPa. The details of the sample preparation procedure were published earlier.<sup>13</sup>

The x-ray diffraction pattern of the sample as produced (Fig. 1) indicates the formation of a practically pure rhombohedral phase of  $C_{60}$ , with the lattice parameters  $a = 9.20$  Å and  $c = 24.61$  Å.

The x-ray emission spectra of the  $C_{60}$  molecular solid and the rhombohedrally polymerized  $C_{60}$  were recorded with a "Stearat" spectrometer, using the ammonium biphtalate ( $NH_4AP$ ) single crystal as a crystal-analyzer. This crystal has a nonlinear reflection efficiency, which is corrected by the procedure described elsewhere.<sup>14</sup> The samples were deposited on a copper substrate and cooled down to liquid nitrogen temperature in the vacuum chamber of the x-ray tube with a copper anode ( $U = 6$  kV,  $I = 0.5$  A). The x-ray transition energies, displayed in Fig. 3, were obtained with an absolute accuracy of  $\pm 0.15$  eV and a spectral resolution of 0.4 eV.

## III. THEORY

Three two-dimensional polymers with different intermolecular bonds (Fig. 2) were constructed. Each molecule in polymer I is connected to six neighbors by a  $[2+2]$  cycloaddition of 66-bonds. Hexagonal packing of  $C_{60}$  molecules linked by 65-bonds results in the 65/56 configuration (polymer II), where each pentagon adjacent to a four-membered ring is opposite to a hexagon. Polymer III can be imagined as an insertion of misoriented molecules in polymer I. The central  $C_{60}$  molecule of the fragment depicted in Fig. 2(c) is linked by 65-bonds to 66-bonds of the neighboring molecules. The portion of 66-bonding molecules in the polymerized layer is twice that of the misoriented molecules. A unit cell of polymers I and II contains one molecule, whereas a unit cell of polymer III holds three molecules.

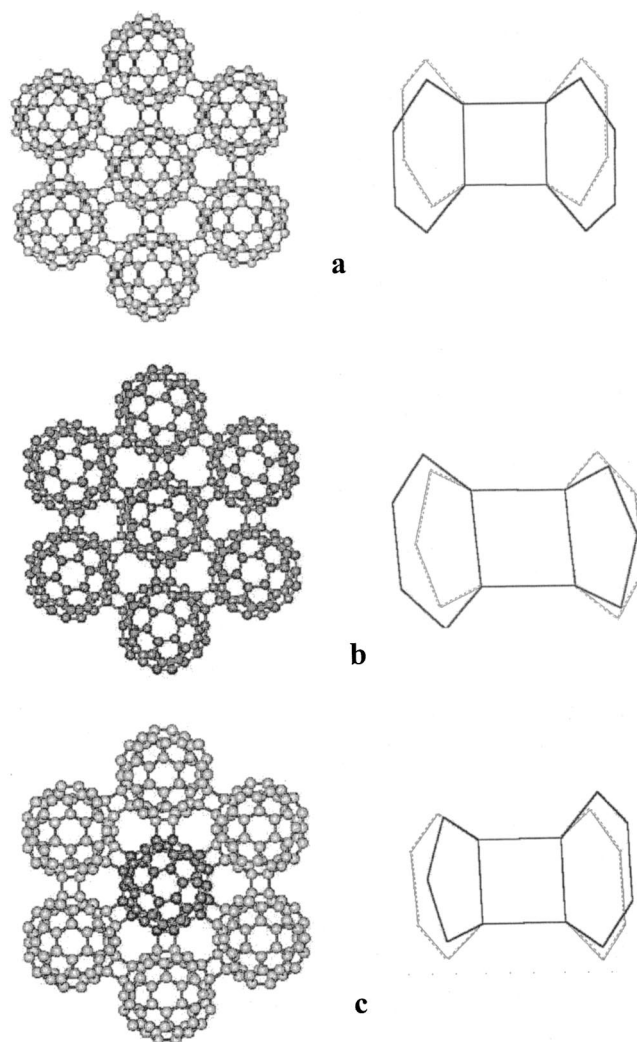


FIG. 2. Structural models describing the bonding within rhombohedrally polymerized  $C_{60}$ . (a) Polymer I with 66/66 bonding, (b) polymer II with 65/56 bonding, and (c) polymer III, characterized by 65 edges of the central molecule being adjacent to 66 edges of neighboring molecules. Changes in the orientation of the fullerenes are emphasized by different levels of shading.

The geometry of the polymer fragments (Fig. 2) was optimized by the molecular mechanic MM+ force field.<sup>15</sup> The relaxed intermolecular bonds in 66/66, 65/56, and 65/66 configurations have a length of 1.582 Å, 1.594 Å, and 1.608 Å, characteristic of covalent bonds in  $sp^3$  hybridized carbon systems. The atomic coordinates of the central molecule in the fragments were used to calculate the electronic band structure of the polymers. For polymer III, the atomic coordinates of the two neighboring 66-bonded molecules were used in addition. The resulting values of a translation vector for polymers I, II, and III are equal to 9.19 Å, 9.17 Å, and 9.26 Å, which is in good agreement with the experimentally determined lattice parameter of 9.2 Å.

The polymers were calculated using an empirical tight-binding Hamiltonian that was especially parameterized to reproduce the features in the x-ray fluorescence spectra of fullerenes.<sup>16</sup> For these calculations, 132  $k$  points were chosen in the irreducible part of the Brillouin zone. The intensity of x-ray transitions was computed as a sum of the squared tran-

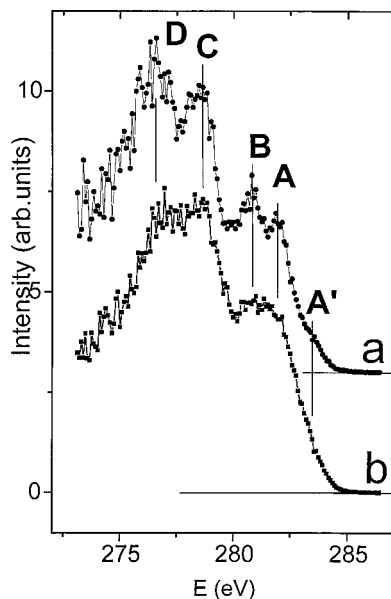


FIG. 3. Observed  $C K\alpha$  spectra of (a) the  $C_{60}$  molecular solid, fullerite, and (b) rhombohedrally polymerized  $C_{60}$ .

sition coefficients, corresponding to the contribution of the  $C 2p$ -atomic orbitals (AOs) to the particular molecular orbital (MO). The  $CK\alpha$  intensity profile, shown in Fig. 4, was further convoluted with a 0.5 eV Lorentzian function and plotted in a scale of the one-electron energies of the occupied MOs. Total energies of the polymers were derived using a carbon-carbon interaction potential<sup>17</sup> with somewhat changed parameters.<sup>16</sup>

#### IV. RESULTS AND DISCUSSION

The  $CK\alpha$  spectra of the  $C_{60}$  fullerite and the rhombohedral  $C_{60}$  polymer are displayed side-by-side for comparison in Fig. 3. Due to the reflection peculiarities of the crystal analyzer used, the  $CK\alpha$  intensity can be reliably measured only in the region from 285 eV to 275 eV. The fullerite spectrum exhibits four well-developed maxima, which are in good agreement with spectra recorded on spectrometers with diffraction gratings, using synchrotron radiation.<sup>18,19</sup> The weak intermolecular interactions in fullerite have only a slight effect on the density of states.<sup>20</sup> This permits us to correlate the energy bands to the molecular levels of  $C_{60}$  and, hence, to interpret the  $CK\alpha$  spectrum on the basis of calculations of the free molecule. A detailed analysis of the fullerite spectrum has been performed in Ref. 21. The high-energy maxima A and B correspond to the radially directed  $\pi$ -like MOs, whereas the maxima C and D are mainly formed by  $\sigma$ -like MOs. The shoulder  $A'$  is a nondiagrammatic line caused by the reemission of  $C 1s$  electrons excited into the lowest unoccupied MO (LUMO) of  $C_{60}$ .<sup>19</sup> Formation of covalent intermolecular bonding in the rhombohedral  $C_{60}$  polymer noticeably changes the  $CK\alpha$  spectral profile [Fig. 3(b)]. First, the gaps between the maxima A, B and between the maxima C, D nearly disappear, and the  $CK\alpha$  spectrum of the polymer shows two broad maxima: an intense split maximum around 277.5 eV and a high-energy maximum at 281 eV. Second, all spectral lines move towards the high-

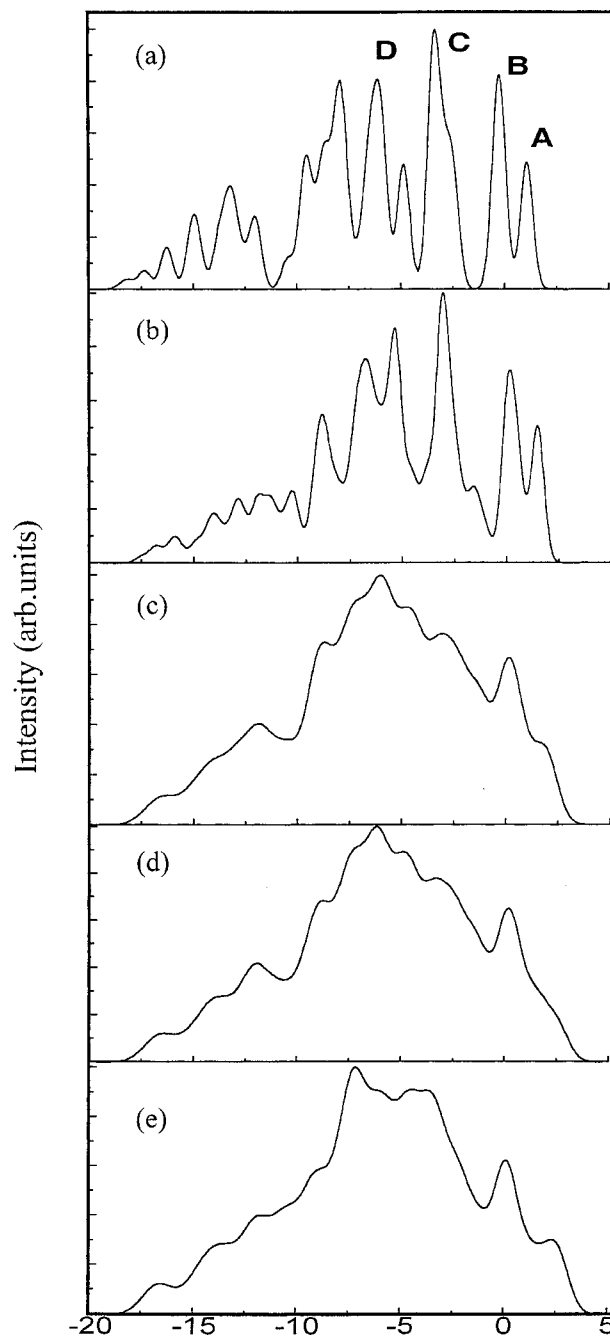


FIG. 4. Calculated  $C K\alpha$  emission spectra for (a) the icosahedral  $C_{60}$  molecule, (b) the distorted  $C_{60}$  cage taken from the 66/66 layer, (c) polymer I, (d) polymer III, and (e) polymer II. The spectral lines were convoluted with a 0.5 eV Lorentzian function.

energy region with respect to the molecular solid. The observed effects may be caused by a distortion of the  $C_{60}$  cage in the polymer and/or by the formation of new intermolecular bonds.

Figure 4 demonstrates the change of the theoretical  $CK\alpha$  spectrum of the free  $C_{60}$  molecule due to polymerization. Maxima in the spectrum of the icosahedral molecule [Fig. 4(a)] were labeled in accordance with those in the experimental spectrum of fullerite. The calculated spectrum, plotted for a distorted  $C_{60}$  that is isolated from 66/66 layer, keeps the basic maxima [Fig. 4(b)]. Splitting of MOs that were initially degenerate in the icosahedral  $C_{60}$  results in a broad-

ening and a shift of the spectral maxima. The main effect of the interactions between  $C_{60}$  molecules in the polymer is on the  $CK\alpha$  profile [Figs. 4(c)–4(e)]. Compared to the theoretical spectra of  $C_{60}$ , those of polymerized  $C_{60}$  are characterized by a significant broadening of the high-energy maxima A and B and their shift towards the Fermi level. Furthermore, one can see an increase in the electronic density of states between the maxima. These tendencies are observed in all theoretical spectra, although the spectra of polymers I and III, which are similar in appearance, differ from the spectrum of polymer II in the intensities and positions of the features. Therefore, to decide which is the most preferable arrangement of a hexagonally polymerized  $C_{60}$  layer, based only on a comparison between theoretical and experimental  $CK\alpha$  spectra, seems not to be feasible. Actually, the electronic density of states in the vicinity of the Fermi level<sup>8</sup> is much more sensitive to the local structure than the distribution of  $C2p$  valence electrons in the solid.

The energy band dispersion of the calculated polymers along high-symmetry lines in the Brillouin zone of the hexagonal lattice is shown in Fig. 5. The polymer I has an indirect 0.81 eV gap between the top of the valence band (marked as  $T$  point) and the bottom of the conduction band ( $K$  point). A previous calculation of the 66/66 layer with different atomic positions, based on the same quantum-chemical scheme, had provided the gap value of 0.57 eV,<sup>16</sup> thus demonstrating the strong effect of geometry on the width of the fundamental gap. Nevertheless, the basic features in the density of states in a wide energy interval are practically the same for both structures. The character of the band dispersion near the Fermi level is also similar. In particular, the highest occupied and lowest unoccupied bands are doubly degenerate in the  $\Gamma$  point.

Significant changes in the electronic band structure of hexagonal layer occur when  $C_{60}$  molecules are connected by 56-bonds [Fig. 5(b)]. The conduction and valence bands meet at the  $K$  point, indicating metallic properties of polymer II. Compared to the 66/66 configuration, the electronic structure of polymer II is characterized by increasing the width of the lowest branch of the conduction band and shifting the top of the valence band towards the higher energy. Both of these effects reveal an enhancement of the intermolecular overlap of  $\pi$ -type states. To analyze the possible reasons for such an enhancement, the electron density associated with the LUMO was drawn for the fragments of polymer I, II (Fig. 6). Let us focus our attention on the charge distribution within the cavity in-between the linked molecules. The  $\pi$ -electron overlap is negative in polymer I, whereas it is positive in polymer II. We conclude that it is the interaction within the  $C_{60}$  layer across the intermolecular space, which most likely enhances the electron conductivity in the two-dimensional layer of polymer II. Two basic differences in the molecular arrangement within the layer of polymers I, II seem to play a major role in their properties. First, the  $C_{60}$  unit cell in polymer I belongs to the  $D_{3d}$  symmetry, whereas that of polymer II is of  $S_6$  symmetry; thus also the symmetry of the wave functions is different. Actually, as seen in Fig. 6, the LUMO shown for the three-molecule fragment of polymer I has one node and that of polymer II has three nodes. The second

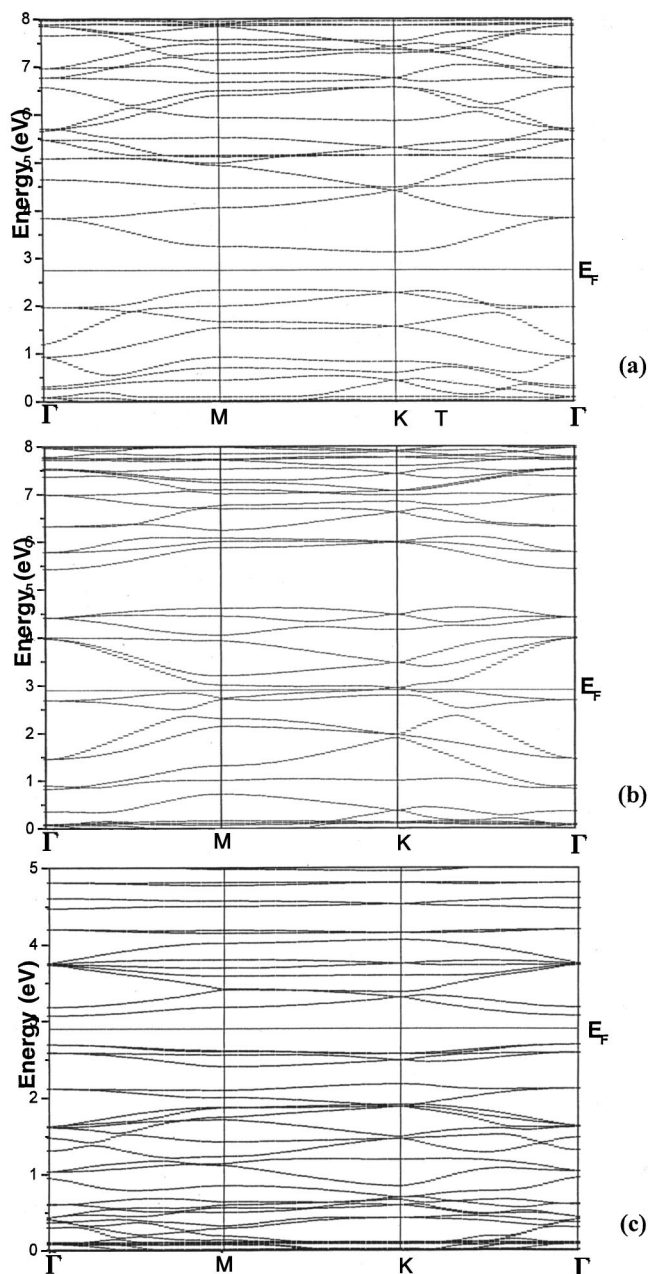


FIG. 5. Electronic band structure of (a) polymer I, (b) polymer II, and (c) polymer III.

difference distinguishing between the polymers is the position of the nearest threefold coordinated atoms within the neighboring molecules. These atoms form vertices of pentagons or hexagons in polymers I and II. In polymer I, such atoms are much further separated from the equator of the central  $C_{60}$  than in polymer II. Consequently, the radially directed  $\pi$ -type orbitals interact more effectively in polymer II.

Polymer III contains  $C_{60}$  cages of the two orientations present in polymers I and II. According to the band structure calculation, this polymer is a semiconductor. A direct band gap at the  $\Gamma$  point is about 0.38 eV wide. The insertion of “misoriented”  $C_{60}$  molecules into the 66/66 layer in a ratio of 1:2 narrows the gap to practically half its value. The rather

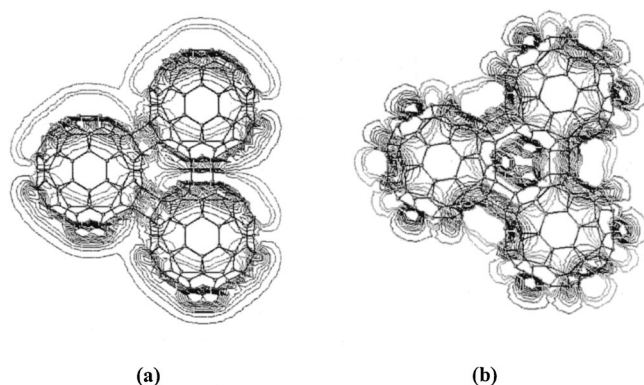


FIG. 6. Electronic charge density associated with crystal states derived from the lowest unoccupied molecular orbitals for fragments of (a) polymer I with 66/66 connections, and (b) polymer II with 65/56 connections within the layer.

small band dispersion near the top of the valence and bottom of the conduction band reflects a smaller degree of interaction within the  $\pi$  electron system in the 65/66 configuration than in the other geometries considered. Furthermore, we can also see an increased separation between the top of the valence and bottom of the conduction bands near the  $K$  point in the Brillouin zone of polymer III. The relative position of atoms belonging to 66-connected molecules of polymer I and 65-connected molecules of polymer II, distinctly different from polymer III, and the longer intermolecular bonds in polymer III decrease the  $\pi$ -like orbital overlap through the cavities. Inspection of Figs. 5(a) and 5(b) reveals that the upper branches of the valence band of polymer II are located at a higher energy than those of polymer I. The appearance of these  $\pi$ -states in the electronic structure of polymer III explains the observed band gap narrowing in comparison to the 66/66 configuration. The large spacing between the top four occupied bands and deeper lying bands supports our interpretation that the  $\pi$ -states are rather localized in comparison to the other bands. Polymer III is also less stable than the other polymers and may be considered as an intermediate structure between the more stable configurations of polymers I and II.

## V. SUMMARY

Our study of the electronic structure of rhombohedrally polymerized C<sub>60</sub> using x-ray emission spectroscopy revealed changes in the density of occupied C 2*p*-states with respect to fullerite, the C<sub>60</sub>-based molecular solid. Upon polymerization, the main features of the CK $\alpha$  spectrum were found to broaden and shift towards higher binding energies. To interpret the experimental results, we calculated the electronic spectra of hexagonal C<sub>60</sub> layers using an empirical tight-binding approach. The calculations considered three configurations, with neighboring molecules connected by 66/66, 65/56, and 65/66 bonds. Comparison between the calculated spectra revealed that the differences between the polymer phase and a free C<sub>60</sub> molecule are similar to the differences between the experimental spectra of polymerized C<sub>60</sub> and the molecular solid. The intermolecular interactions in the poly-

mer were found to play a primary role in determining the electronic structure and properties of rhombohedrally polymerized C<sub>60</sub>. Insertion of misoriented C<sub>60</sub> molecules in the 66/66 layer reduces the fundamental gap by one half, and the gap disappears completely in the polymer containing molecules connected by 65/56 intermolecular bonds. The formation of a specific bond between neighboring C<sub>60</sub> molecules is primarily caused by the geometric configuration in the pristine solid. At the onset of the polymerization process in an ordered layer, the 66-bond of one molecule faces a hexagon of the neighboring molecule. Furthermore, the 66/66 configuration is energetically preferable. Thus, formation of a 66/66 connected layer is favored both on kinetic and energetic grounds. Under particular conditions, however, which may involve temperature gradients or imperfect packing, polymers might form that involve other configurations. Our produced samples of rhombohedrally polymerized C<sub>60</sub> have a polycrystalline structure that may be caused by spatially varying intermolecular connections. Our electronic structure calculations of the different polymers indicate that the occurrence of regions containing 65/56 bonded molecules within a 66/66 connected hexagonal layer may cause variations of in-plane conductivity.

## ACKNOWLEDGMENTS

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