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Fullerene Networks

Structural and Electronic Properties of Pristine and Ba-Doped Clathrate-Like Carbon Fullerenes

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Open-structure clathrate compounds, particularly those of Group 4 elements, have often been sought after for their potential superconductivity.[1,2] Although only Si, Ge, and Sn clathrates have been synthesized so far, much attention has been paid to the prospective carbon-based clathrate, which has been predicted to be superconducting with a relatively high critical temperature T_c[2] and easily "dopable" with metals and may have potential applications in high-power electronics or field emission.[3,4] Recently, a 3D "clathrate-like" carbon-framework C_{60} fullerene was synthesized from high-pressure high-temperature treatment on a presynthesized 2D C_{60} polymer phase and characterized by single-crystal X-ray diffraction.[5] The crystal has the body-centered orthorhombic space group *Immm*, and the originally spherical C_{60} molecule shows significant deformation into a cuboid (c-C_{60}). The similarity of the cage structure to semiconductor clathrates composed of the same Group 4 element is particularly interesting. Herein we report results of theoretical investigations on the structural and electronic properties of this novel clathrate-like c-C_{60} fullerene obtained from first-principles calculations. Pristine c-C_{60} is shown to be metallic and possesses the electronic band features of a superconductor. It also has the potential capacity of encapsulating metal atoms, which may be exploited to modify the electronic properties.

The optimized crystalline structural parameters at zero pressure (Figure 1, Table 1) are somewhat larger than those determined from experiment.[5] Extensive studies (to be published elsewhere) show the observed structure[5] may not be fully relaxed from the high-pressure state. In addition to eight corner-linked neighbors connected through 16 C–C intermolecular bonds with identical bond lengths of 1.593 Å (Figure 1 a), each c-C_{60} unit is connected to two neighbors along the *b* direction with eight weaker intermolecular C–C bonds (1.755 Å, see C2–C2* in Figure 1 b). Consequently, a c-C_{60} unit is bonded to ten neighbors and consists of 24 sp^3- and 36 sp^2-hybridized C atoms. Two types of open sites, the cuboid cage and the interstitial site surrounded by six c-C_{60} units (only four units in the *ab* plane), are identified in Figures 1 b, c.

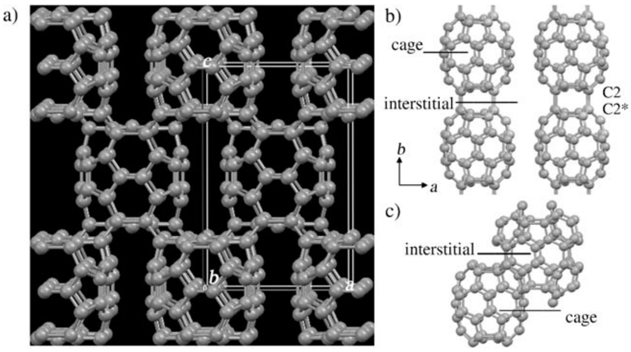

Figure 1. Optimized geometry of the c-C_{60} structure: a) 3D view; b) a single C_{60} layer in the *ab* plane; c) clathrate-like view of the structure.

Table 1: Comparison of calculated structural parameters for pristine c-C_{60}, Ba@C_{60}, and BaC_{60}.

	Lattice constants [Å]			Intermol. bond length [Å]	
	a	*b*	*c*	Corner	*ab* plane
c-C_{60}	8.6523	8.5047	13.1438	1.593	1.755
Ba@C_{60}	8.6746	8.5052	13.1571	1.582	1.753
BaC_{60}	8.6550	9.3367	12.9719	1.656	–

The cage and interstitial sites, with radii of 3.0 and 2.6 Å, respectively, are spacious enough to accommodate alkali and alkaline-earth metal atoms such as Cs and Ba. In this study, we have chosen Ba with an ionic radius of 1.34 Å as the dopant. It is well-known that when Ba is intercalated in the open framework of Si_{46} clathrate, it becomes a superconductor at 9 K.[6,7]

Figure 2 a shows the electronic band structure near the Fermi level E_F for the pristine 3D c-C_{60} polymer along the indicated symmetry lines. The absence of a band gap indicates that c-C_{60} is metallic. This observation agrees with a previous report.[5] Two electronic bands cross the E_F level with large dispersions. The higher-energy band shows rather flat dispersions (almost zero slope) near E_F along the E_1-R-W and T-W directions. The second electronic band also shows flat features at R and E_2. These band features are akin to the "flat-band/steep-band scenario" for superconductivity as proposed by Simon et al.[8,9] It was postulated that the simultaneous occurrence of steep bands crossing E_F and flat bands near E_F is a prerequisite for superconductivity.

The detailed band structure along the Γ-E_1-X_0 direction plotted in Figure 3 a shows two nearly parallel bands that cross the Fermi level and almost intersect near E_F. Parallel electronic bands are highly susceptible to Fermi surface (FS) nesting. FS nesting is a phenomenon that occurs when a piece

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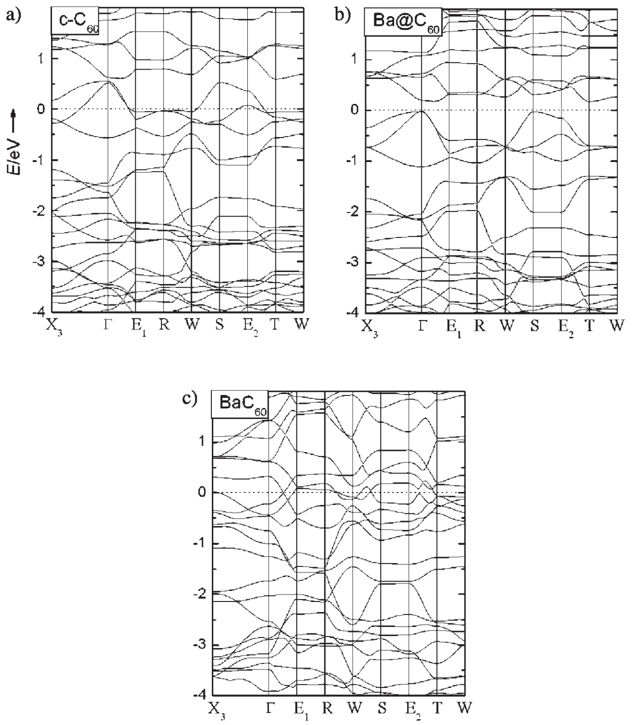

Figure 2. Electronic-energy bands near the E_F level of a) pristine c-C_{60}, b) Ba@C_{60}, and c) BaC_{60}. The dashed lines indicate E_F (or top of the valence band). The points X_3, Γ, R, W, S, T, and W are shown in Figure 3.

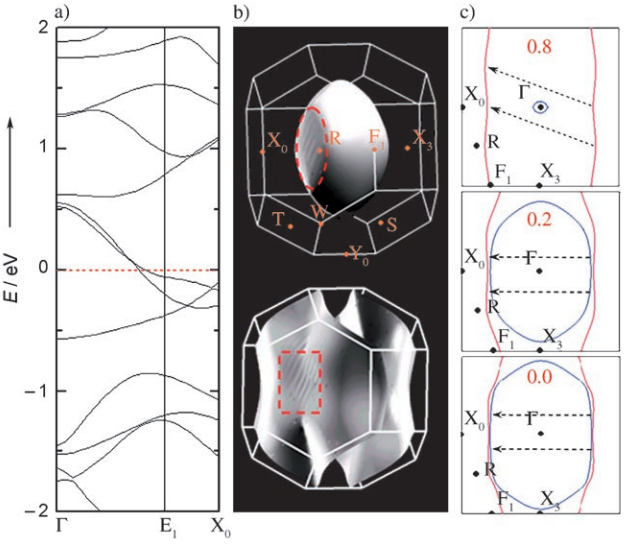

Figure 3. a) The electronic band structure of pristine c-C_{60} along the Γ-E_1-X_0 direction. b) FS for the two bands crossing E_F. c) 2D cross sections of FS at different k_y values (planes perpendicular to Γ-Y_0 and parallel to the Γ-X_0-X_3 plane) in the first BZ. The extrema $k_y = 0.0$ and $k_y = 1.0$ indicate planes cutting though the Γ and Y_0 point, respectively. Arrows indicate possible nesting vectors.

of the FS is brought into contact with another portion through a wave vector $\boldsymbol{q}$. It has been shown very recently that electronic instabilities as a result of FS nestings create hot zones that enhance electron–phonon coupling.[10,11,12] To investigate this possibility, 3D Fermi surfaces were calculated and analyzed. The lower-energy band, shown in the top panel of Figure 3b, has two opposing flat faces perpendicular to the Γ-E_1-X_0 direction. The higher-energy band, although a little ragged, also possesses two fairly flat surfaces perpendicular to Γ-E_1-X_0. Consequently, "intraband" FS nestings of the opposing faces of either band are quite likely to occur. There are signs favoring "interband" FS nestings connecting the flat portions of the two electronic bands. To investigate further, 2D cross sections of the FS perpendicular to the Γ-Y_0 ($0k_y0$) direction and parallel to the Γ-X_0-X_3 plane in the first Brillouin zone (BZ) at three k_y values are shown in Figure 3c. Possible nesting vectors are indicated by arrows. It was found that "intraband" nestings can occur in both the top portion of the higher-energy band (red line at $k_y = 0.8$) and the middle portion of the lower-energy band (blue line at $k_y = 0.2$ and 0.0). At $k_y = 0.2$ to 0.0, the Fermi surfaces of the two electronic bands are almost parallel, indicating possible "interband" nestings. Analyses of the electronic band structure and the Fermi surface of pristine c-C_{60} reveal 1) the simultaneous occurrence of steep and flat bands near E_F and 2) evidences for FS nestings that may enhance electron–phonon coupling. These features are characteristics of a potential superconductor.[9]

We now turn to the studies of the two Ba-doped compounds. There are two possible doping sites: inside the cuboid cage (Ba@C_{60}) and at the interstitial channel site (BaC_{60}). Doping at either site was found to be exothermic and therefore energetically favorable. The formation energies at ambient pressure (difference between the sum of the total energies of the pristine c-C_{60} and body-centered cubic (bcc) Ba metal and the doped compound) are 6.26 and 9.28 eV per Ba atom for Ba@C_{60} and BaC_{60}, respectively. In both doped systems the closest Ba−C separations are nearly the same (3.09 Å). It was also found that Ba doping inside the c-C_{60} cages does not affect the structure of the carbon framework. In contrast, when Ba is doped into the interstitial sites, the unit cell is strongly perturbed (see Table 1) and the volume increases by 8.4 %. The resulting volume, however, is still 4 % smaller than the sum of the volumes of pristine c-C_{60} and bcc Ba. Therefore, Ba doping of c-C_{60} into either the cage or interstitial sites should be thermodynamically favorable at high pressures.

The electronic band structure of Ba@C_{60} (Figure 2b) shows a strong resemblance to that of pristine c-C_{60}, apart from a rigid shift of E_F to higher energy. This observation suggests that the interaction between the encapsulated Ba atoms and the c-C_{60} framework is ionic. Bader analysis[13] shows that the Ba atom transfers 0.96 e to the host framework. Consequently, filling of the framework empty bands with the additional electrons resulted in the opening of an indirect band gap of 0.195 eV between Γ and T. Thus, encapsulation of Ba in the cage sites converts metallic c-C_{60} into a narrow-gap semiconductor. In contrast, Ba intercalation in the interstitial sites (BaC_{60}) is not a simple electron-transfer process; it has dramatic effects on both the structure (Table 1) and electronic properties (Figure 2c). The character and dispersion of the electronic bands in the vicinity of E_F are modified signifi-

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cantly. The calculated charge transfer from Ba is 0.87 *e*, which is smaller than that at the cage site. The contribution of the Ba orbital at E_F is small and the doped compound remains metallic.

In conclusion, theoretical calculations on the recently characterized 3D c-C_{60} fullerene confirm that it is metallic. The electronic band structure reveals "steep-band/flat-band" features near E_F. The observation of nearly parallel bands that cross E_F indicates the possibility of FS nesting, which may lead to electronic instability and the enhancement of electron–phonon coupling. These features are indicative of possible superconducting behavior in pristine c-C_{60}. Recent experiments have shown that, although pristine c-C_{60} is indeed a weak metal, no superconductivity was found at least down to 4 K.[14] Perhaps the experimental measurement should be extended to a lower temperature. Doping of Ba into the c-C_{60} cages leads to an unusual metal–semiconductor transition. The change in electronic properties with Ba doping suggests that c-C_{60} may potentially be an important electronic material for technological applications. Although metal-doped C_{60} has not been realized, the theoretical results reported here show that enclathrations of Ba atoms in the cage and interstitial sites are energetically favorable and should be achievable experimentally.

Methods Section

All calculations were performed within a generalized-gradient approximation (GGA)[15] implemented in the VASP code.[16] The projector augmented wave (PAW) pseudopotentials[17] from the standard pseudopotential library supplied with VASP were used. Plane-wave basis functions were generated from the $2s^22p^2$ valence electrons for C and $5s^25p^66s^2$ for Ba with an energy cutoff of 900 eV. A $4\times4\times4$ Monkhorst–Pack[18] *k*-point mesh was used in the sampling of the BZ. The Fermi surface was sampled with a $24\times24\times24$ *k* mesh.

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