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Theoretical study of the electronic structure of fullerene-cubane cocrystals

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We present a first-principles study of the electronic structure of fullerene-cubane cocrystals, using density-functional theory at the local-density approximation level. The band structure is calculated along high-symmetry lines and compared with that of the fcc fullerene. We also present a study of the effect of possible potassium doping. We find potassium doping to have a similar effect on the density of states in the fullerene-cubane as in the pure fullerene. Charge transfer between the components of the studied materials is also calculated by Bader charge analysis. The possibility of a very small charge transfer between the cubane and the fullerene in the undoped fullerene-cubane cocrystal is discussed.

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I. INTRODUCTION

Cubane[1] (C_8H_8) and fullerene[2] (C_{60}) are high-symmetry carbonaceous cage molecules with remarkable chemical and solid-state properties, which have induced great scientific interest.[3–5] Both materials form polymorphic molecular crystals with variable orientational ordering.[6–9] Recently, it was shown that face-centered-cubic (fcc) C_{60} forms high-symmetry molecular crystals with cubane owing to topological molecular recognition between the convex surface of fullerenes and the concave cubane.[10–12] Static cubane occupies the octahedral voids of the fcc fullerene molecular crystal, such that the carbon-carbon bonds of cubane are parallel with the edges of the cubic fcc unit cell. Since there are exactly as many octahedral sites as fullerenes in the fcc crystal, the two molecules form a cocrystal with both the fullerene and the cubane molecules forming an fcc sublattice. Cubane essentially acts as a bearing between the rotating fullerene molecules. The smooth contact of the rotor and stator molecules significantly decreases the temperature of orientational ordering. These materials have great topochemical importance: at elevated temperatures they transform to high stability covalent derivatives although preserving their crystalline appearance. The size dependent molecular recognition promises selective formation of related structures with higher fullerenes and/or substituted cubanes.

While the octahedral voids of the fcc fullerene are filled up with cubane in the fullerene-cubane cocrystal, the tetrahedral voids are still empty. In principle it may be possible to intercalate the fullerene-cubane crystal with, e.g., alkali atoms by inserting them into the tetrahedral sites (see Fig. 1).

In this work, we examine the electronic properties of the $C_{60}C_8H_8$ cocrystal and compare its band structure with that of fcc C_{60}. We also perform a study of one of the possible intercalated materials, $K_2C_{60}C_8H_8$ with potassium ions at both tetrahedral sites. The band structure in this case is compared with that of K_3C_{60}. For a further comparison, we also calculate the band structure of a fictive material, the K_2C_{60} in which all potassium ions occupy tetrahedral voids, and the octahedral voids are empty. (Bulk quantities of this material are known to be unstable. Since the octahedral void is much larger, it is energetically more favorable for the potassium ions to reorder such that the octahedral voids are occupied, resulting in a material, which is dominated by part K_3C_{60}—with all voids occupied—and part KC_{60}—with only the octahedral voids occupied—instead of bulk K_2C_{60} with empty octahedral voids.) Finally, a Bader charge[13] analysis is also performed on the four multicomponent materials ($C_{60}C_8H_8$, K_2C_{60}, $K_2C_{60}C_8H_8$, and K_3C_{60}) to study the charge transfer between the constituents.

II. METHOD

We used the density-functional theory based VASP (Ref. 14) program in the local-density approximation (LDA) to perform nearly all necessary calculations. For some calculations, the GAUSSIAN 03 (Ref. 15) program was used. In all VASP calculations, the projector augmented wave method was applied using a 400 eV plane-wave cut-off energy. The geometries of the C_{60} and C_8H_8 molecules were first calculated in their isolated geometry within LDA, using GAUSSIAN 03 and employing a 6-31G* basis set. Afterwards, the lattice constants of the fcc crystals were obtained with VASP by

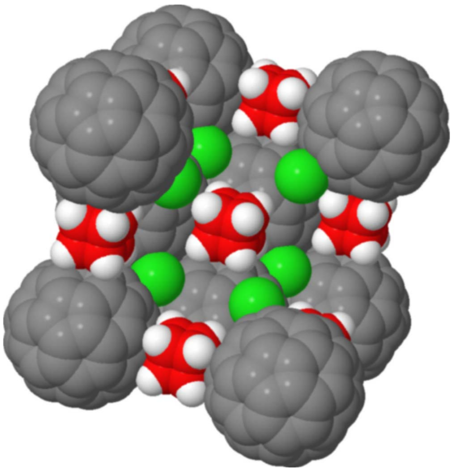

FIG. 1. (Color online) Depiction of the $C_{60}C_8H_8$ cocrystal. The large green orbs are the tetrahedral voids, which may be possible to fill with, e.g., alkali ions.

TABLE I. Optimized LDA lattice constants (Å) of the examined fcc structures in the three studied orientations. Experimental values are included for comparison (Refs. 5 and 10).

	C_{60}	$C_{60}C_8H_8$	K_2C_{60}	$K_2C_{60}C_8H_8$	K_3C_{60}
T_h	14.17	14.54	14.16	14.45	14.03
C_{2h}	14.20	14.57	14.64	14.73	14.48
D_{3d}	14.29	14.62	14.42	14.59	14.26
Expt.	14.15	14.74	N/A	N/A	14.24

determining the minimum of the total energy as a function of the lattice constant while neglecting any distortion of the C_8H_8 and C_{60} molecules. A *k*-point set of a $9\times9\times9$ Monkhorst-Pack grid was used for this lattice constant optimization.

Once the optimized geometry was obtained, we calculated the band structure of the fcc crystals along a set of high-symmetry lines within the Brillouin zone. After calculating the fully self-consistent charge density with a *k*-point grid spanning the entire Brillouin zone, we calculated the band structures in 20 *k* points along the high-symmetry lines using this charge density. The full electronic density of states was also calculated with a high *k*-point sampling of $13\times13\times13$. Furthermore, in order to study charge transfer, we determined the Bader charges[13] of all atoms from this charge density using an external utility.[16] The reliability of the charge-transfer results of LDA were tested on small molecules against Hartree-Fock and MP2 calculations with GAUSSIAN 03, this is detailed below.

III. RESULTS

We studied the electronic structure of five fcc crystals: C_{60}, $C_{60}C_8H_8$, K_2C_{60}, $K_2C_{60}C_8H_8$, and K_3C_{60}. Due to the size limitations of VASP, we used the primitive rhombohedral unit cell (one C_{60} per cell) in all cases, neglecting the effects of the neighboring fullerenes having different orientations. In order to examine the possible orientational effects, we performed the calculations on three different orientations. (In the following, we will use a Cartesian coordinate system such that three orthogonal edges of the cubic fcc unit cell lay along the *x*, *y*, and *z* axes.) In the first orientation (which is often used in the literature[17] and is often called the standard orientation of C_{60}), three orthogonal C_2 symmetry axes of the C_{60} coincide with the *x*, *y*, and *z* axes, resulting in a unit cell of overall T_h symmetry. In the second orientation, one of the C_3 symmetry axes of the C_{60} coincides with the *z* axis such that one of the mirror planes containing said C_3 axis coincides with the *yz* plane, resulting in a unit cell of overall C_{2h} symmetry. Finally, in the last orientation, one of the C_3 symmetry axes of the C_{60} coincides with the space diagonal of the cubic fcc unit cell such that one of the mirror planes containing said C_3 axis coincides with the plane formed by the space diagonal and the *z* axis, resulting in a cell of overall D_{3d} symmetry.

In Table I, we list the obtained optimal fcc lattice constants for all three geometries. According to the calculations, the cubane expands the fullerene lattice in all orientations, as expected. The relative expansion shows very small orientational dependence, with values ranging between 2% and 3%. Potassium on the other hand can expand or contract the lattice—both in the case of C_{60} and $C_{60}C_8H_8$—depending on the orientation of the fullerenes. The presence of potassium *atoms* in the voids would always lead to a lattice expansion. However, these are ions, as there is a significant charge transfer between the potassium and the C_{60}, and therefore there is a decent ionic attraction between the potassium and the C_{60}. Depending on the orientation of the fullerenes, this ionic attraction may or may not be sufficient to contract the lattice. Comparing K_3C_{60} with K_2C_{60}, we find that the latter always has a larger lattice constant independent of orientation, despite the fact that less ions are present. This is easy to understand, since the total charge transfer to the C_{60} is larger in K_3C_{60}, hence the ionic attraction is also larger.

Comparing the results with experimental values, the first thing to note is that the calculation overestimates the lattice constant for C_{60} while at the same time it underestimates it for $C_{60}C_8H_8$. In the case of K_3C_{60}, underestimation and overestimation both occur, depending on the orientation used. This clearly shows that orientational effects have an important role in determining the lattice constant of C_{60}-based molecular crystals.

In Fig. 2, we show the electronic band structures of the examined materials in the T_h arrangement along high-symmetry lines in the fcc Brillouin zone. Note that, due to the icosahedral symmetry of the fullerene, the *W* points in

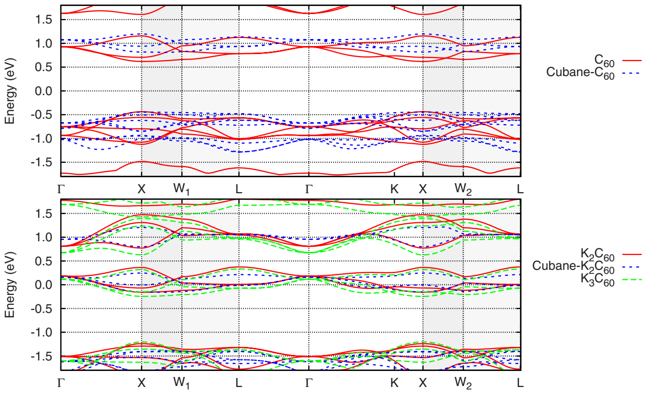

FIG. 2. (Color online) Electronic band structures of the studied materials in the T_h orientation with the Fermi levels shifted to 0 eV. The upper panel shows C_{60} (solid red online) and $C_{60}C_8H_8$ (short dashed blue online); the lower panel shows K_2C_{60} (solid red online), $K_2C_{60}C_8H_8$ (short dashed blue online), and K_3C_{60} (long dashed green online).

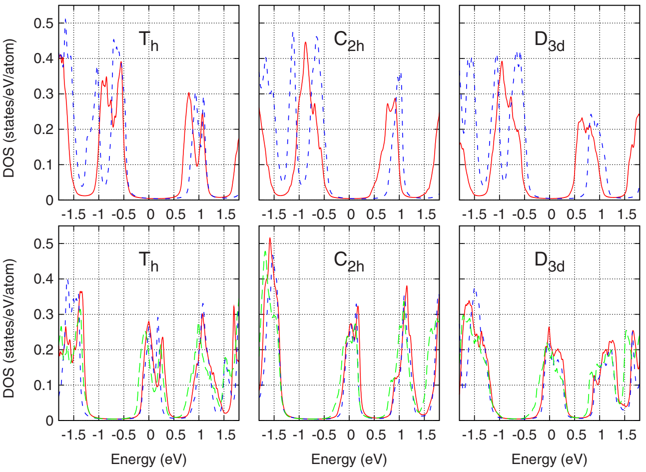

FIG. 3. (Color online) Electronic density of states of the studied materials with the Fermi levels shifted to 0 eV. The upper panel shows C$_{60}$ (solid red online) and C$_{60}$C$_8$H$_8$ (short dashed blue online); the lower panel shows K$_2$C$_{60}$ (solid red online), K$_2$C$_{60}$C$_8$H$_8$ (short dashed blue online), and K$_3$C$_{60}$ (long dashed green online).

the fcc Brillouin zone are not all symmetry equivalent and the bands are different near the two inequivalent W points, which will be labeled as W_1 and W_2. This fact is not well known in the literature and only one W point was previously considered in calculations (see below). In the other two orientations, the overall symmetry is further lowered, resulting in further splitting between originally equivalent high-symmetry points. Therefore, instead of calculating just the band structures, we calculated the full electronic density of states as well. This is plotted in Fig. 3 for all three orientations.

Note that the electronic band structure of the high-symmetry T_h arrangement has been extensively studied in the literature, both for C$_{60}$ (Refs. 18 and 19) and for K$_3$C$_{60}$.[20–22] Our results for these band structures agree well with previous calculations, including that the band gap of C$_{60}$ is located at the X point. As mentioned above, only one of the W points (W_1) was considered in the calculations in the papers cited above.

When comparing the results on C$_{60}$ and C$_{60}$C$_8$H$_8$, it can be seen that the lattice expanding effect of the cubane molecule is visible on the band structure and the density of states as well: the bands are narrower in energy than in the case of C$_{60}$, which agrees well with the reduced interaction between fullerenes, caused by the increased nearest-neighbor distance. The same thing can be seen when comparing K$_2$C$_{60}$C$_8$H$_8$ and K$_2$C$_{60}$: the bands in the former are more compact than in the latter. Interestingly, the lattice expanding (or contracting) effect of the potassium ions is not very well visible on the band structures.

However, the charge transfer from the potassium to C$_{60}$ is very much visible on the band structures. Electrons are removed from the potassium ions and are transferred to the fullerenes, resulting in a downshift of some higher-lying bands of C$_{60}$, making both K$_3$C$_{60}$ and K$_2$C$_{60}$C$_8$H$_8$ metallic. The exact magnitude of the charge transfer is possible to obtain by Bader charge analysis, this is detailed below.

It is worth to note here that the bands at the Fermi level are similarly flat in these two materials, suggesting that we may find a good candidate for superconductivity among intercalated fullerene-cubane cocrystals, similar to, e.g., K$_3$C$_{60}$ among intercalated fullerenes. It is known that the T_C critical temperature of superconducting A_3C$_{60}$—where A is an alkali ion—increases with the increasing ionic radius of the alkali ions. This effect is due to the increased lattice expansion of the intercalated fullerene, which leads to flattened bands and therefore an increased density of states at the Fermi level. The largest experimental lattice constant attained in fcc A_3C$_{60}$ is 14.55 Å in RbCs$_2$C$_{60}$.[23] For C$_{60}$C$_8$H$_8$, the experimental lattice constant is even larger, which suggests that through proper intercalation, an even higher density of states could be achieved at the Fermi level than in RbCs$_2$C$_{60}$ and perhaps lead to a higher T_C in the end. However, it is an open question whether superconductivity will be possible in A_2C$_{60}$C$_8$H$_8$ given that the fullerene ions only have two extra electrons as opposed to the three in A_3C$_{60}$. In fact, it may be possible that A_2C$_{60}$C$_8$H$_8$ is an insulator. It is known that in A_2C$_{60}$ and A_4C$_{60}$, Mott-Hubbard transition occurs, leading to an insulating state.[24–26] [We must also mention that C$_{60}^{2-}$ is known to suffer a Jahn-Teller distortion due to the presence of the extra charge, which in itself leads to a splitting of the lowest unoccupied molecular orbital (LUMO) bands of the fullerene.[27] This splitting however is smaller than the energy width of the fullerene bands in the fcc lattice,[28] and therefore the Jahn-Teller distortion in itself does not lead to a semiconducting band structure. Hence, while the Jahn-Teller distortion of the fullerene can be expected to appear in A_2C$_{60}$C$_8$H$_8$ as well, it will not be relevant to the question of metallicity, and therefore Jahn-Teller distortion in this respect can be neglected. The Hubbard interaction on the other hand should be taken into account in the case of A_2C$_{60}$C$_8$H$_8$, which we neglect in the present study due to the limitations of the applied method.] Currently it is an open question whether there is a Mott-Hubbard transition in A_2C$_{60}$C$_8$H$_8$, but it is more likely than not. Hence we expect a gap to open in the band structure of K$_2$C$_{60}$C$_8$H$_8$ due to the Hubbard interaction. And if that is indeed the case, then in order to arrive at a metallic state it is necessary to have C$_{60}^{3-}$ in the sample. Since the cubane fills the octahedral void, this is only possible to achieve by using two different dopant ions, one alkali (A) and one alkali-earth (Ae) ion per fullerene: AeAC$_{60}$C$_8$H$_8$. This will lead to triple negative fullerene ions, for which no Mott-Hubbard transition should take place. We expect that AeAC$_{60}$C$_8$H$_8$ will be metallic, and based on the calculations on A_2C$_{60}$C$_8$H$_8$, we expect that it will have a high density of states at the Fermi level and may be a good candidate for superconductivity. It is of course an open question whether intercalated fullerene-cubanes can give a higher T_C value than the highest T_C achieved in intercalated fullerenes to date, T_C=40 K in Cs$_3$C$_{60}$ under a pressure of 12 kbar.[29]

Finally, let us summarize our results on the magnitude of the charge transfer in the examined materials. We calculated the Bader charges of all atoms and determined the charge transfer between the components. This is summarized in Table II.

It can be seen that the magnitude of the charge transferred from the potassium to the fullerene in K$_3$C$_{60}$ and K$_2$C$_{60}$ agrees with the expectations for alkali intercalation. However, a somewhat unexpected result based on the band struc-

TABLE II. Charge transfer between the components of the examined materials based on Bader charge analysis.

	C_{60}	C_8H_8	K_2 or K_3
T_h $C_{60}C_8H_8$	$-0.04e^-$	$+0.04e^-$	N/A
C_{2h} $C_{60}C_8H_8$	$-0.02e^-$	$+0.02e^-$	N/A
D_{3d} $C_{60}C_8H_8$	$-0.07e^-$	$+0.07e^-$	N/A
T_h $C_{60}K_2$	$+1.63e^-$	N/A	$-1.63e^-$
C_{2h} $C_{60}K_2$	$+1.62e^-$	N/A	$-1.62e^-$
D_{3d} $C_{60}K_2$	$+1.62e^-$	N/A	$-1.62e^-$
T_h $K_2C_{60}C_8H_8$	$+1.60e^-$	$+0.07e^-$	$-1.67e^-$
C_{2h} $K_2C_{60}C_8H_8$	$+1.57e^-$	$+0.06e^-$	$-1.63e^-$
D_{3d} $K_2C_{60}C_8H_8$	$+1.55e^-$	$+0.10e^-$	$-1.65e^-$
T_h $C_{60}K_3$	$+2.49e^-$	N/A	$-2.49e^-$
C_{2h} $C_{60}K_3$	$+2.52e^-$	N/A	$-2.52e^-$
D_{3d} $C_{60}K_3$	$+2.48e^-$	N/A	$-2.48e^-$

tures is that the cubane molecule also participates in the charge transfer, albeit with a much smaller magnitude. In the case of $C_{60}C_8H_8$, the cubane takes away some electrons from the fullerene. This is extremely surprising, given the well-known high electronegativity of fullerene.[5,30] However, this charge transfer is very small, on the order of $0.0025e^-/\mathrm{CH}$ pair for the C_8H_8 and on the order of $0.0005e^-/\mathrm{atom}$ for the C_{60}. To examine the reliability of this result, we have calculated the Fermi levels of an isolated C_8H_8 and an isolated C_{60} molecule; the results were -5.73 and -5.68 eV, respectively, which is perfectly consistent with a small electron transfer from the C_{60} to the C_8H_8.

At first, one may suspect that this charge-transfer result reflects the error of the Bader charge analysis within the applied method, given the well-known high electronegativity of C_{60}. However, the same method was successfully applied to double walled carbon nanotubes with success recently and a similar charge transfer magnitude of roughly $0.001e^-/\mathrm{atom}$ was obtained.[31,32] Following those calculations, charge transfer between the layers of double walled nanotubes was in fact measured with photoemission spectroscopy; both the direction and the order of magnitude (measured values are about a factor of 4 larger) for the charge transfer agreed well with the calculations.[33,34] This suggests that it might in fact be possible that the calculated charge transfer between the constituents of $C_{60}C_8H_8$ is not an error, especially since the Fermi-level calculations confirm the direction of the charge transfer found in the Bader charge analysis. Experimental studies should be able to decide this question. We mention that this small charge transfer does not have any noticeable effect on the band structures (i.e., $C_{60}C_8H_8$ has a semiconducting band structure), which is possible to explain if we consider a small hybridization between the orbitals of the cubane and the orbitals of the fullerene. Such a small hybridization would allow for a small charge transfer between the constituents without yielding a metallic band structure, this is what happens in semiconducting double walled carbon nanotubes as well.[31,32]

Note that the cubane participates in the charge transfer in the case of $K_2C_{60}C_8H_8$ as well, but in this case it is more negatively charged due to the overwhelming amount of electrons removed from the potassium. In the case of this material, the magnitude of the charge on the cubane is twice as much as in $C_{60}C_8H_8$, but it is so much smaller than the extra charge on the fullerene, that it is likely not possible to detect this small charge transfer onto the cubane in $K_2C_{60}C_8H_8$.

IV. DISCUSSION

Orientational effects in C_{60} are known to have importance and have been extensively studied in the literature.[19,21,35] Fullerenes freely rotate at room temperature both in C_{60} and $C_{60}C_8H_8$, this effect however is neglected in our calculations due to the limitations of the applied method. In order to consider the effects of this rotation, a very large supercell would need to be taken into account with every fullerene molecule having a different random orientation. This would require thousands of atoms in the supercell, which is beyond the capabilities of the VASP code.

In order to make some estimates regarding these neglected effects, we performed calculations on three different orientations, as detailed above. We have found that the band structure is strongly dependent on the orientation. In particular, the high-symmetry points in the fcc Brillouin zone are no longer equivalent due to the lowered symmetry, and the energies in these inequivalent points are no longer identical. For example, in the T_h arrangement, there are two inequivalent W points in the Brillouin zone and the bands along the XW_1 and XW_2 lines are significantly different, as evidenced by Fig. 2. In the other geometries, this effect is even more pronounced due to the further lowered symmetry. For example in the D_{3d} arrangement, only the X points remain all equivalent and there are two inequivalent points of L, W, and K as well. In the lower-symmetry orientations we therefore expect the specific orientation to have a significant effect on the band structures. However, the density of states apparently does not reflect this orientation dependence of the band structures: the density of states is largely similar in the three studied orientations, as it can be seen in Fig. 3. The mean position and width of both the valence and the conduction band is very similar in the different orientations. This is most likely due to that the density of states is obtained by taking the bands in the entire Brillouin zone into account and this averages out the orientational effects. As it can be seen in Fig. 3, there are many narrow peaks in the density of states. In the real system, where the fullerenes can freely rotate, these peaks are at a different position for pretty much every unit cell, and therefore they are totally averaged out. The density of states is expected to correspond to the envelope curve of these peaks, which can be approximated by calculating the density of states with increased broadening. In Fig. 4, we make a comparison between the calculations on fcc C_{60} and the $C_{60}C_8H_8$ cocrystal for the different orientations when using different values for the electronic linewidths. At large linewidths, the narrow peaks are averaged out and the density of states for the three orientations become very similar. Note that the conduction-band and valence-band contributions in the density of states of $C_{60}C_8H_8$ are visibly narrower than those of C_{60} even at these large electronic

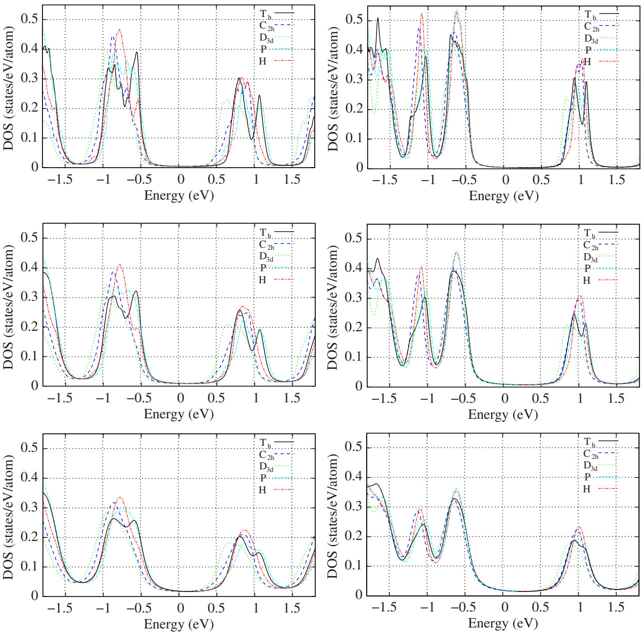

FIG. 4. (Color online) Electronic density of states for fcc C_{60} (left side) and the $C_{60}C_8H_8$ cocrystal (right side) in five different orientations (see text) with the Fermi levels shifted to 0 eV. The upper panel corresponds to a width of 0.02 eV for the γ linewidth of the electronic states, while the middle and lower panels correspond to 0.04 and 0.08 eV, respectively. The large electronic linewidth in the lower panel models the case of freely rotating C_{60}, resulting in a nearly identical density of states for the five orientations, thus evidencing that while orientation has an important effect on the band structures, orientational effects are averaged out in the density of states and can be safely neglected.

linewidths. In order to make one final test on the orientational effects, we calculated the electronic density of states for C_{60} and $C_{60}C_8H_8$ in two more orientations. We used the intermolecular Hückel model[36–38] to calculate the total energy of fcc C_{60} as a function of the orientation of the fullerene. Starting from the standard orientation and scanning the total energy according to polar angles ϑ and φ, we have found very small dependence on φ, while we found two distinct minima in ϑ. (One at 32° and another at 82°, in the former case the short bonds of the fullerenes roughly face pentagons of the neighboring fullerenes, while in the latter the short bonds roughly face hexagons; in Fig. 4 we refer to these two orientations as P and H, respectively. These two energy minima are actually in reasonable agreement with the minima of the total energy in the low-temperature simple cubic phase of the C_{60} fullerene.[39]) We have calculated the LDA density of states for C_{60} and $C_{60}C_8H_8$ in these two orientations. These are also plotted in Fig. 4. As it can be seen, both of these orientations give an extremely similar density of states as the three orientations, which we studied in detail above. Thus it is apparent that the density of states is largely independent of the orientation of the fullerene molecules as long as the broadening of the electronic states is set to be large enough to model the averaging of orientations, and therefore the density of states should look largely similar if the free rotation of the C_{60} molecules was taken into account. We conclude therefore that the electronic density of states can be studied well even with the approximation of neglecting orientational effects.

Finally, let us briefly discuss the charge-transfer results. Charge transfer is based on Bader charge analysis, which is a well-known and reliable method for obtaining atomic charges.[13] The charge-transfer analysis in the case of the potassium doped materials gives exactly what one would expect, electrons are transferred from the potassium ions to the fullerenes. However, in the case of the undoped $C_{60}C_8H_8$, we found a small electron transfer from the fullerene to the cubane. As mentioned above, similar charge-transfer magnitudes were obtained with the same method in the case of double walled carbon nanotubes,[31,32] and those results have since been experimentally confirmed.[33,34] The direction of the charge transfer is also consistent with the Fermi-level calculations. However, this result is still surprising in light of the well-known high electronegativity of C_{60}.

Therefore we performed test calculations on small molecules to examine the reliability of the LDA Bader charge analysis. Using GAUSSIAN 03, we performed calculations on the mesylate (CH_3-SO_2-OH) molecule, as well as a small fullerene-cubane cluster composed of a single C_{60} molecule surrounded by six C_8H_8 molecules in an octahedral arrangement with van der Waals distance between the fullerene and the cubanes. We performed the calculations in a minimal basis set and in the 6-31G* basis set as well. For the mesylate, Hartree-Fock and MP2 calculations were both performed, as well as LDA. For the fullerene-cubane cluster, only Hartree-Fock and LDA calculations were performed.

We have found in all cases, that the Hartree-Fock and MP2 methods give almost the same Bader charges for the atoms of mesylate. The LDA calculations agree well with these results within a few percent. In the case of the fullerene-cubane cluster, the Hartree-Fock calculations and the LDA calculations also agree within a few percent. We mention that in the case of this small cluster the direction of the charge transfer was the opposite of what was obtained for the periodic $C_{60}C_8H_8$.

In relation to the problem of reliability of CT values in LDA, we must also mention the reason we used the local-density approximation instead of gradient corrected functionals in this work. The generalized gradient approximation (GGA) includes nonlocal terms in the functional, a feature which is essential for the accurate study of heavy elements, such as, e.g., transition metals. In the case of carbon-based materials however, local-density approximation is generally more reliable, giving very accurate geometries and vibrational frequencies (see, e.g., some calculations on carbon nanotubes, Refs. 40–42). In our case, the main reason for using LDA is that the cubane and fullerene molecules interact weakly via van der Waals type interactions.

It is well known that in density-functional theory, van der Waals type interactions are generally not well described. One of the fortunate exceptions is carbon within LDA. It is well established in the literature that LDA gives very accurate interlayer spacing values for three-dimensional graphite.[43] GGA on the other hand, while yielding much more accurate cohesive energies, considerably overestimates this interlayer distance.[44] Since one of the most important questions about the geometry of fullerene-cubane cocrystals is precisely the lattice constant (and its effect on the electronic band structures), it is crucial to employ a method, which gives reliable values for the distance of weakly interacting structures. This makes LDA preferable over GGA for the calculations in this work.

V. CONCLUSION

In conclusion, we have performed first-principles calculations on the electronic structure of fullerene-cubane cocrystals using density-functional theory at the local-density approximation level. The electronic structure of $C_{60}C_8H_8$ shows a narrowing of the bands compared to the bands of C_{60}, exactly as expected due to the expansion of the fcc lattice caused by the presence of cubane. Potassium doping of $C_{60}C_8H_8$ results in charge transfer from the potassium ions to the fullerenes, suggesting that the $C_{60}C_8H_8$ cocrystal may become metallic upon certain kinds of intercalation, partially similar to A_3C_{60}. Bader charge analysis shows that a very small charge transfer may be possible between the cubane and the fullerene in the undoped semiconducting $C_{60}C_8H_8$ with the cubane slightly negatively charged.

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