Important role of alkali atoms in $A_4C_{60}$

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We show that hopping via the alkali atoms plays an important role for the $t_{1u}$ band of $A_4C_{60}$ (A=K, Rb), in strong contrast to $A_3C_{60}$. Thus the $t_{1u}$ band is broadened by more than 40% by the presence of the alkali atoms. The difference between $A_4C_{60}$ and $A_3C_{60}$ is in particular due to the less symmetric location of the alkali atoms in $A_4C_{60}$.

I. INTRODUCTION

The alkali doped fullerene compounds $A_3C_{60}$ (A=K, Rb) and $A_4C_{60}$ show strikingly different properties. While $A_3C_{60}$ are metals and superconductors, $A_4C_{60}$ are insulators. The $t_{1u}$ band of $A_4C_{60}$ is only partly filled, and in contrast to $A_3C_{60}$, $A_4C_{60}$ is not a band insulator, since band structure calculations predict a metal with a large density of states at the Fermi energy. This raises interesting questions about what makes $A_4C_{60}$ an insulator. To understand the differences between $A_3C_{60}$ and $A_4C_{60}$, it is important to understand the electronic structure in more detail. It is, for instance, surprising that for K$_4C_{60}$ the $t_{1u}$ band width (0.56 eV) is not much smaller than for $A_3C_{60}$ (0.61 eV), although the separation of the closest carbon atoms on neighboring molecules is much larger in $A_4C_{60}$ (3.5 Å) than in $A_3C_{60}$ (3.1 Å).

In $A_3C_{60}$ it has been demonstrated that the alkali atoms (K, Rb) play a small role for the states in the partly filled $t_{1u}$ band. The reason is that the alkali atoms sit in very symmetric positions relative to the carbon atoms, and that there is a large cancellation between different contributions to the hopping matrix elements. Here, we find that in $A_4C_{60}$ the indirect hopping via the alkali atoms between $t_{1u}$ orbitals on different $C_{60}$ molecules is of great importance, due to the much less symmetric positions of the alkali atoms in $A_4C_{60}$. This indirect hopping increases the $t_{1u}$ band width by more than 40%.

In Sec. II we introduce a tight-binding (TB) formalism and apply it to $A_nC_{60}$ (n = 0, 3 and 4). We show that this leads to a good description of the $t_{1u}$ band for $C_{60}$ and $A_3C_{60}$ but not for $A_4C_{60}$. In Sec. III we include the hopping between the carbon and alkali atoms and show that this is important for $A_4C_{60}$ but not for $A_3C_{60}$. Finally, in Sec. IV we present a first-principles all-electron band structure calculation for the $A_4C_{60}$ structure with and without the alkali atoms, which demonstrates the importance of the alkali atoms.

II. TIGHT-BINDING DESCRIPTION OF THE $t_{1u}$ BAND

To address the differences between $A_3C_{60}$ and $A_4C_{60}$, we apply a TB formalism which was found to work well for $A_3C_{60}$.

We consider only the 60 $2p$ orbitals pointing radially out from a $C_{60}$ molecule, since these make the dominating contribution to the $t_{1u}$ band. A parametrization is then needed for the $2p-2p$ hopping integrals $V_{pp\sigma}$ and $V_{pp\pi}$. Following Harrison, we assume $V_{pp\sigma}/V_{pp\pi} = -1/4$. We make the parametrization

$$V_{pp\sigma} = v_\sigma R e^{-\lambda(R-1.43)},$$

where $R$ is the atomic separation in Å and $v_\sigma$ and $\lambda$ are parameters to be determined below. Like Harrison, we only use nearest neighbor hopping inside the $C_{60}$ molecule. For the intermolecular hopping this prescription is ill-defined, since many neighbors have similar separations. Since the intermolecular separations correspond to a range where the hopping integrals decay exponentially, we can include all hopping integrals and still have a small contribution from distant neighbors.

The TB Hamiltonian is solved for a free $C_{60}$ molecule with the bond lengths 1.40 Å and 1.46 Å. This gives the three $t_{1u}$ orbitals

$$|\nu\rangle = \sum_{i=1}^{60} c_{\nu i}^t |i\rangle,$$

where $|i\rangle$ is a radial 2p orbital on atom $i$ and $c_{\nu i}^t$ is the expansion coefficient of the $\nu$th $t_{1u}$ orbital. Using Eqs. (1), we can easily calculate the hopping matrix elements between the $t_{1u}$ orbitals on different $C_{60}$ molecules, and obtain an analytical Hamiltonian describing the $t_{1u}$ band.
structure. This was applied to $C_{60}$ in the fcc structure, adjusting the parameters $v_\sigma$ to reproduce the $t_{1u}$ band width and $\lambda$ to reproduce the lattice parameter dependence of a band structure calculation in the local density approximation (LDA) of the density functional formalism.

In the following we compare with LDA calculations based on a Gaussian basis set which gives slightly different band width than the atomic sphere LMTO calculation in Ref. 12. The prefactor $v_\sigma = 8.07$ eV/Å has therefore been readjusted to reproduce the band width of Ref. 12. The value of $\lambda = 1.98$ Å$^{-1}$ in Ref. 12 was kept unchanged. In Fig. 1 we compare the TB and LDA band structure calculations for $C_{60}$. The agreement is very good, given that only the overall band width has been adjusted to the LDA calculation. Within the present TB formalism, the band structure for $A_3C_{60}$ is the same as for $C_{60}$, apart from a small change in the band width due to the difference in lattice parameter. Since the band structures of $C_{60}$ and $A_3C_{60}$ are very similar, it follows that our TB formalism also describes $A_3C_{60}$ well. $A_3C_{60}$ is further discussed below.

![FIG. 1. Band structure for $C_{60}$ (a) according to LDA and (b) according to the tight-binding (TB) formalism.](image1)

We have next applied the same TB formalism to $K_4C_{60}$. Fig. 2 compares the result of the TB approach (d) with the LDA result (a). There are striking differences between the results. In particular, the TB band width (0.37 eV) is substantially (34%) smaller than the LDA band widths (0.56 eV). Given the difference in the separation between the closest carbon atoms on neighboring $C_{60}$ molecules for $C_{60}$ (3.1 Å) and $K_4C_{60}$ (3.5 Å), it is, however, not surprising that the band width is strongly reduced compared with $C_{60}$ (0.55 eV). Actually, from the difference in separation alone, one would have expected an even larger reduction (44%) in the $t_{1u}$ band width relative to $C_{60}$. In the following we analyze the reason for the large deviation between the TB and LDA results for $K_4C_{60}$ in spite of the good agreement for $C_{60}$ and $A_3C_{60}$.

![FIG. 2. The $t_{1u}$ band for $K_4C_{60}$ according to (a) LDA with alkalis, (b) TB with alkalis, (c) LDA without alkalis and (d) TB without alkalis.](image2)

### III. INDIRECT HOPPING VIA THE ALKALI ATOMS

So far the alkali atoms have been completely neglected in the discussion. It is well-known that they indeed play a very small role for the $t_{1u}$ band in $A_3C_{60}$. It was, however, observed by Satpathy et al. that the unimportance of the alkalis is rather accidental. For instance, an alkali atom at the tetrahedral position sits above a hexagon and has six nearest neighbor C atoms on a given $C_{60}$ molecule. The coefficients $c''_i$ (Eq. (2)) for a given $t_{1u}$ orbital, however, tend to change sign between each atom along a hexagon since the $t_{1u}$ orbital is antibonding. The result is therefore that the hopping integral between a $t_{1u}$ orbital and an alkali orbital is strongly reduced. One can therefore estimate that the mixing of s-character into the $t_{1u}$ orbital from the tetrahedral alkali atoms is reduced by about a factor of 22 due to cancellations between the contributions from the different $c''_i$. The mixing of the octahedral alkali atoms into the $t_{1u}$ orbital is even more strongly reduced. It is then an interesting question to ask if such a cancellation
does not take place for $A_4C_{60}$.

In $A_4C_{60}$ the alkali atoms are in general in less symmetric positions relative to the neighboring $C_{60}$ molecules than in $A_3C_{60}$. Relative to a given $C_{60}$ molecule, the 16 nearest neighbor alkali atoms can be grouped in four groups with four atoms in each. In the first group the alkali atoms sit symmetrically above a pentagon, in the second they sit strongly asymmetrically above a hexagon, being much closer to two of the hexagon atoms, in the third they sit weakly asymmetrically above a hexagon and in the fourth they sit strongly asymmetrically above a pentagon, being much closer to one of the pentagon atoms.

We now use

$$C = \sum_{\nu \in t_{1u}} \left| \sum_{\gamma \in \text{nn}} \epsilon_{\gamma}^{\nu} \right|^2$$

as a measure of the coupling to a given alkali atom. The sum is over the $t_{1u}$ states $\nu$ and over the carbon atoms on a given $C_{60}$ molecule which are near neighbors (atoms which are less than five per cent further away than the nearest neighbors) of the alkali atom considered. If we assume that the corresponding C-A hopping integrals are equal, $C$ is proportional to the square of the $t_{1u}$-A hopping integrals and a measure of how much $s$-character is mixed into the $t_{1u}$ orbitals from this alkali atom. We find that $C$ is 0.14, 0.14, 0.03 and 0.05 for an alkali atom in the first, second third or fourth groups, respectively. The corresponding number for each of the eight alkali atoms above a hexagon (tetrahedral position for $A_3C_{60}$) is 0.07.

As a result, the mixing of alkali character into the $t_{1u}$ orbitals is about a factor of $2 \frac{1}{3}$ larger for $A_4C_{60}$ than for $A_3C_{60}$. The large coupling of an alkali atom to a pentagon is due to the less drastic cancellation between the contributions from the different atoms than in the case of a hexagon, as has also been observed in other contexts. This cancellation still reduces the coupling by about a factor of seven for the pentagon, but much less than for a hexagon (factor 22). In the same way, the cancellation is much less severe in the strongly asymmetric position above a hexagon, since there are only two nearest neighbors. For the weakly symmetric hexagon the cancellation is large. For the asymmetric pentagon, finally, the coupling to mainly just one atom, considering only nearest neighbor interaction, is not quite enough to give a strong coupling, although the cancellations are now less important.

To be able to treat the C-A hopping more quantitatively, we introduce matrix elements which decay as the separation of the atoms squared. To follow the spirit of Harrison, with only nearest neighbor interaction in a system where the nearest neighbors are ill-defined, we further introduce an exponential cut off in the matrix elements

$$V_{\text{spec}} = 1.84D \frac{\hbar^2}{m d^2} e^{-3(d-R_{\text{min}})}$$

where $d$ is the A-C separation and $m$ is the electron mass. $R_{\text{min}}$ is the shortest A-C separation for a given alkali atom and $C_{60}$ molecule. The exponential cut off means that we essentially have only nearest neighbor interaction for each A-C$_{60}$ pair. The precise value of the factor three in the exponent is unimportant for the following discussion, which is determined by the signs of the coefficients $e_{\nu}^\gamma$. We have introduced an adjustable parameter $D$ to be discussed below. The indirect hopping via the alkali atoms introduces new effective matrix elements for the $C_{60}$-$C_{60}$ hopping

$$t_{\alpha\mu,\beta\nu} = \sum_{\gamma} \frac{t_{\alpha\mu,\gamma} t_{\beta\nu,\gamma}}{\epsilon_{t_{1u}} - \epsilon_s},$$

where $t_{\alpha\mu,\gamma}$ is a hopping matrix element between the $\mu$th $t_{1u}$ orbital on the $\alpha$th $C_{60}$ molecule to the $\gamma$th alkali atom and $\epsilon_{t_{1u}}$ and $\epsilon_s$ are the $t_{1u}$ and alkali $s$ eigenvalues, respectively. We have put $\epsilon_s - \epsilon_{t_{1u}} = 4$ eV. Adding these matrix elements to the direct $C_{60}$-$C_{60}$ hopping matrix elements gives the band structure in Fig. 2b. The parameter $D$ in Eq. (5) has been set to 0.47, which reproduces the LDA band width for $K_4C_{60}$. We can see that the indirect alkali hopping increases the band width by about 50%, although the C-A matrix elements have been reduced by a factor of two (1/$D = 2.1$) compared with Harrison’s prescription.

We next apply the same formalism to $K_3C_{60}$. $K_3C_{60}$ differs from $C_{60}$ due to a slightly different lattice parameter and the presence of the alkali atoms. The presence of the alkali atoms increases the band width by only about 6% and the largest indirect contribution to the hopping matrix elements is down by about a factor of five compared with $A_4C_{60}$. This illustrates how much less important the alkali hopping is for $A_3C_{60}$ than $A_4C_{60}$. We consider the lattice parameter $a = 14.24$ Å, which is somewhat larger than $a = 14.2$ Å used for $C_{60}$. The increase in $a$ reduces the band width to about 0.53 eV (from 0.55 eV for $C_{60}$), but the inclusion of the alkali atoms in $A_3C_{60}$ increases the band width again to 0.56 eV. This is still somewhat smaller than the width 0.61 eV found in LDA.

The large increase in the band width for $A_4C_{60}$ is primarily due to a large increase in the nearest neighbor $y-y$ hopping, where $y$ is one of the $t_{1u}$ orbitals. The nearest neighbor indirect hopping goes via four alkali atoms in $A_4C_{60}$ but just via two atoms in $A_3C_{60}$. The large $y-y$ indirect hopping in $A_4C_{60}$ goes via the two alkalis which are strongly asymmetric with respect to a hexagon on one $C_{60}$ molecule and a pentagon on the other $C_{60}$ molecule. Due to the lob-structure of the $t_{1u}$ orbitals, $y-y$ hopping via these alkalis is very favorable, while there is no $x-x$ or $z-z$ hopping for symmetry reasons via these alkalis. The indirect $x-x$ hopping instead takes place via alkalis located over a pentagon on one molecule and weakly asymmetrically over a hexagon on another molecule. The lob structure is, however, less favorable for this hopping. The indirect nearest neighbor $z-z$ hopping is for
symmetry reasons suppressed for hopping over all four alkalis which are the common nearest neighbors of two neighboring C_{60} molecules. Finally, there is efficient indirect \( z - z \) hopping to the second nearest neighbor in the \( z \)-direction and \( y - y \) hopping to the second nearest neighbor in the \( z \)-direction. We observe that it is not surprising to find a large indirect second nearest neighbor hopping via the alkalis, since the larger molecular separation does not inhibit this hopping. In addition to this large indirect hopping, there is also a large direct second nearest neighbor hopping for \( A_4C_{60} \). The second nearest neighbor molecules in the \( z \)-direction are unusually close together due to the compression of the bct lattice in the \( z \)-direction. In addition, the coefficients \( c_1' \) in Eq. (2) are unusually favorable for the second nearest neighbor hopping. In the present TB formalism, the largest total (direct plus indirect) second nearest neighbor hopping is therefore more than 70% of the largest nearest neighbor hopping, i.e., unusually large.

The diagonal indirect \( t_{\text{eff}}^{\alpha \beta} \) and direct hopping terms have the same sign as for both \( A_3C_{60} \) and \( A_4C_{60} \), while the nondiagonal terms have the same sign for \( A_4C_{60} \) but different signs for \( A_3C_{60} \). In the present parameter range, the band width is determined by the diagonal elements. The differences in signs for the nondiagonal terms therefore do not influence the band width, but they do increase the second moment for \( A_4C_{60} \). Thus the increased dispersion can be traced to three effects: (i) a general increase of the alkali hopping due to the less symmetric positions of the alkali atoms relative to the C_{60} molecules, (ii) the particularly large increase of a certain matrix element crucial for the band width and (iii) constructive interference of the direct and indirect contributions to the off-diagonal matrix elements, leading to an additional increase of the second moment.

IV. COMPARISON BETWEEN \( A_4C_{60} \) AND \( V_4C_{60} \)

To test these considerations, we have performed a LDA calculation for “\( V_4C_{60} \),” where the C_{60} molecules are in exactly the same positions as for K_{4}C_{60} but where the the potassium atoms are missing (“vacancies”). The calculation method was the same as described in Ref. 18. The results are shown in Fig. 2b. Comparison with the K_{4}C_{60} calculation in Fig. 2a illustrates that the \( t_{1u} \) band is indeed substantially narrower in the absence of the alkali atoms, and that the inclusion of these atoms increases the band width by more than 40%. This emphasises the importance of the alkali atoms for \( A_4C_{60} \).

The TB \( V_4C_{60} \) width (0.37 eV) is close to the LDA result (0.39 eV). The shapes of the TB and LDA \( V_4C_{60} \) bands also agree rather well, the main difference being a too small TB splitting at the \( \Gamma \)-point. This suggests that the TB formalism describes the C-C hopping rather well in all three structures studied.

V. SUMMARY

To summarize, we have illustrated that the alkali atoms have a large influence on the \( t_{1u} \) band in \( A_4C_{60} \), contrary to their small influence on \( A_3C_{60} \). The reason is, in particular, the nonsymmetric positions of the alkali atoms relative to the carbon atoms in \( A_4C_{60} \), which leads to a less efficient cancellation of the contributions to the \( t_{1u} \)-alkali hopping integrals than in \( A_3C_{60} \).

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The $C_{60}$ molecule has been oriented so that the double bond with the largest $z$ coordinate is along the $x$-axis. The band structure therefore differs from Ref. 12 where the orientation is along the $y$-axis.

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