Do the $A_4C_{60}$ fullerides have a broken-symmetry ground state?

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Abstract

Band theory predicts both $K_3C_{60}$ and $K_4C_{60}$ to be metals; various experimental probes show that while $K_3C_{60}$ is indeed metallic, $K_4C_{60}$ appears to be insulating. The standard view of this apparent failure of the single-particle picture is that electron correlation is predominant. We describe an alternative scenario, motivated on theoretical grounds, which invokes a spin- or charge-density-wave state to explain the observed insulating behavior.

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I. INTRODUCTION

Since the discovery of superconductivity in the potassium-intercalated fulleride $\text{K}_3\text{C}_{60}$, considerable theoretical attention has focused on the electronic properties of the $A_n\text{C}_{60}$ family ($A=$alkali), much of it assuming the validity of a single-particle band description. A growing body of evidence suggests that this assumption may rest on rather shaky ground, at least for some members of the family. A striking example is the contrast between $\text{K}_3\text{C}_{60}$ and $\text{K}_4\text{C}_{60}$. According to first-principles band calculations, both are metallic, with comparable Fermi-level densities of states. Photoemission gives a very different picture, however: for $\text{K}_3\text{C}_{60}$, strong Fermi-level emission is observed, while for $\text{K}_4\text{C}_{60}$ the spectrum is insulating [1]. Additional evidence is found in NMR, which also shows that $\text{K}_3\text{C}_{60}$ is metallic and $\text{K}_4\text{C}_{60}$ is insulating [2]. Several workers have argued that strong electron-electron correlation splits the conduction band (CB) into a filled lower Hubbard band and an empty upper Hubbard band [3].

In this paper, we propose a different scenario to explain the insulating nature of the $A_4\text{C}_{60}$ fullerides. We begin by discussing the results of first-principles band-structure calculations for $\text{K}_4\text{C}_{60}$, then explore possible broken-symmetry ground states such as a charge-density wave (CDW). We emphasize that our results do not in any sense prove that a CDW state is the thermodynamic ground state; rather, we make a plausibility argument and then describe model-Hamiltonian calculations which may give further insight.

II. BAND STRUCTURE OF $\text{K}_4\text{C}_{60}$

We use the local-density approximation (LDA) to density-functional theory. Bloch basis functions are linear combinations of occupied and unoccupied atomic orbitals for potassium and carbon; these are in turn expanded on a set of gaussian functions. This provides a compact basis, and allows us to perform accurate all-electron calculations—without the need for pseudopotentials—in which core, valence, and conduction states are treated on
equal footing. The potential and charge density are completely general and without shape approximation. We have previously used identical methods to study K$_6$C$_{60}$ [4], K$_3$C$_{60}$ [5], and Ba$_6$C$_{60}$ [6]; further details concerning numerical methods may be found in these references, and preliminary work on A$_4$C$_{60}$ may be found in Ref. [7].

The K$_4$C$_{60}$ geometry used in our calculation is taken from the x-ray refinement of Fleming et al. [8], who found a body-centered tetragonal (bct) lattice for the A$_4$C$_{60}$ family, with lattice constant $a=11.886\ \text{Å}$ and $c/a=0.906$ for $A=$potassium. The potassium positions were refined to (0.22,0.50,0)$a$ and symmetry-related sites. Fleming et al. observed that because C$_{60}$ lacks a four-fold symmetry axis, a tetragonal lattice ($a=b$) implies that the C$_{60}$ molecules are either orientationally disordered or are spinning rapidly; Zhou and Cox have shown that a merohedrally disordered model fits the data well [9]. Rabe has proposed an alternative structural model [10], consisting of an orientationally ordered crystal with a screw-axis symmetry that leads naturally to $a=b$. Here, we make the standard simplification of taking the K$_4$C$_{60}$ structure to be orientationally ordered, with one C$_{60}$ molecule per cell. Work currently in progress, which goes beyond this simplification, will be described in Sec. III.

In Fig. 1 we show the band structure for orientationally ordered K$_4$C$_{60}$. Since the bct conventional cell is a slightly distorted version of the body-centered-cubic (bcc) cell of K$_6$C$_{60}$, we show the bands along the bct route that corresponds most closely to the bcc route appearing in Fig. 2 of Ref. [4]. Indeed, the K$_4$C$_{60}$ bands bear a close resemblance to those of K$_6$C$_{60}$, with an important difference. The point group of orientationally ordered A$_4$C$_{60}$ (generated from three Cartesian mirror planes) has only one-dimensional irreducible representations, so that any band degeneracies must be accidental. This has the effect of smearing somewhat the spectral density throughout the CB, resulting in a DOS with few sharp features. The Fermi-level DOS $N(\epsilon_F)=18.3$ states/eV-cell (both spins) is $\sim 40\%$ larger than for K$_3$C$_{60}$, strongly at variance with the NMR and photoemission results discussed above.

The Fermi surface (FS) has 3 sheets, shown in Fig. 2. Two form closed hole pockets centered at $\Gamma$. The third forms quasi-two-dimensional sheets, large parts of which are nearly
flat over much of the zone and roughly normal to the \( c \)-axis. To the extent that these sheets are truly flat, they represent an unusual form of FS nesting, with a nesting vector \( \mathbf{Q} = Q \hat{z} \). It is well known that FS nesting can lead to electronic instabilities, by enhancing the susceptibility \( \chi(\mathbf{Q}) \) for the formation of a charge- or spin-density-wave (SDW) ground state. The simplest illustration of this occurs in a linear chain of atoms equally spaced by \( a \), for which a half-filled cosine band has a nesting vector equal to half the zone, \( Q = \pi/a \). The Peierls mechanism provides a route to lowering the total energy, by chain dimerization (that is, by forming a commensurate CDW with period \( 2a \)) and the opening of a gap.

To quantify the degree of nesting and identify possible nesting vectors in \( \text{K}_4\text{C}_{60} \), we calculate

\[
\xi_{nm}(\mathbf{Q}) = N^{-1} \sum_{\mathbf{k}} \delta(\epsilon_{n,k} - \epsilon_F) \delta(\epsilon_{m,k+\mathbf{Q}} - \epsilon_F),
\]

which measures the phase space available for any process that scatters electrons from point \( \mathbf{k} \) on the \( n \)th FS sheet to \( \mathbf{k} + \mathbf{Q} \) on the \( m \)th sheet. This factor also enters into the second-order susceptibility, \( \partial^2 E_t / \partial h_{\mathbf{Q}} \partial h_{-\mathbf{Q}} \), of the total energy \( E_t \) with respect to density variations \( h_{\mathbf{Q}} \), making explicit the connection between nesting vectors and CDW wave vectors. In Fig. 3 we plot the function \( \xi_{33}(\mathbf{Q}) \) in the \( Q_x, Q_z \) plane, revealing a single moderately strong nesting vector centered near \( \mathbf{Q} = \pm(0, 0, \pi/c) \). This is precisely the nesting vector required for the smallest possible commensurate density wave, namely, period doubling along the \( c \)-axis. In the following section we describe preliminary work, using a model Hamiltonian, that may lend further insight into this scenario.

**III. MEAN-FIELD HUBBARD MODEL**

Shortly after the discovery of superconducting \( \text{K}_3\text{C}_{60} \), Zhang, Ogata, and Rice proposed a negative-\( U \) model for fulleride superconductivity mediated by alkali-ion optical phonons [11]. They argued that if the interaction is attractive, then superconductivity would result from the competition between a CDW ground state and a superconducting ground state, for which
the fcc lattice of K$_3$C$_{60}$ frustrates the former in favor of the latter. Since this proposal, isotope experiments have demonstrated that alkali optical phonons are not involved in pairing. Moreover, considerable experimental and theoretical evidence has shown that the electron-electron interaction is intrinsically repulsive. Nevertheless, we discuss the negative-$U$ model here for two reasons: (1) we will later use the same formalism to study the consequences of a repulsive interaction, and (2) it provides a pedagogically instructive context for a theorem which states that for the $U < 0$ Hubbard model with a single band and nearest-neighbor hopping, the CDW and superconducting ground states are exactly degenerate when the band is half filled and the lattice is bipartite \[12\]. For K$_3$C$_{60}$, the band is half filled but the lattice is not bipartite; the authors of Ref. \[11\] showed numerically that the degeneracy is broken in favor of a superconducting ground state. For K$_4$C$_{60}$, the situation is reversed: the lattice is bipartite but the filling is two-thirds, again breaking the degeneracy. It is tempting to hypothesize that since (1) the bct lattice is bipartite, and hence no longer obviously frustrates the CDW state, and (2) the ratio $c/a < 1$ provides a preferred direction for the CDW wave vector, then perhaps the degeneracy might be broken in favor of the CDW state.

To explore this possibility, we proceed along similar lines to Ref. \[11\], solving the negative-$U$ Hubbard model within the mean-field approximation. We begin with the Hamiltonian

$$H = -t \sum_{\langle i,j \rangle} (c_i^+ c_j + \text{h.c.}) + U \sum_i n_{i\uparrow} n_{i\downarrow}. \quad (2)$$

We assume a single band with nearest-neighbor hopping on the bct lattice; the dispersion is then

$$\beta_k = -8 \cos(k_x a/2) \cos(k_y a/2) \cos(k_z c/2). \quad (3)$$

For the CDW state, the energy per electron is

$$E^{CDW} = \frac{1}{\zeta N} \sum_{k,s=\pm 1} \epsilon_{k,s}^{CDW} + \frac{\zeta U}{4} \left[1 - (\delta/\zeta)^2\right], \quad (4)$$

where $\delta$ is the order parameter given by $\langle n_i \rangle = 1 \pm \delta$, and $\zeta = 4/3$ is (twice) the band filling. The sum is over filled states and the band energy is given by
For the superconducting state (SS), the energy per electron is

\[
E^{SS} = -\frac{1}{\zeta N} \sum_k \epsilon_k^{SS} + \epsilon_F + \frac{\zeta U}{4} \left[ 1 - (2\Delta/\zeta)^2 \right],
\]

where \( \Delta = \langle c_{i\uparrow}^\dagger c_{i\downarrow}^\dagger \rangle \) is the superconducting order parameter, and the band energy is now

\[
\epsilon_k^{SS} = \left[ (\beta_k - \epsilon_F)^2 + (U\Delta)^2 \right]^{1/2}.
\]

In both Eqs. (4) and (6), the total energy is evaluated by minimization with respect to the order parameter.

We have calculated the CDW and SS energies for \( 0 \leq |U|/t \leq 10 \); the model predicts the SS state to be favored throughout this range. This is strongly at odds with experiment (which finds no evidence for superconductivity) and with our hypothesis of a favored CDW state. We discuss this below.

Although instructive, the Hamiltonian of Eq. (2) is too crude in several important ways:

1. A single tight-binding band does not reproduce the nesting features of Fig. 2.
2. Recent work on tight-binding parameterizations of the LDA energies shows that nearest-neighbor interactions alone are inadequate for reproducing the LDA spectrum, and that two coordination shells are necessary \[13\].
3. A variety of experimental and theoretical evidence has led to a consensus that \( U \) is positive, with a value of order 1 eV. To address these deficiencies, we have begun to study the Hamiltonian

\[
H = \sum_{i\mu,j\nu} \left( c_{i\mu}^\dagger T_{i\mu,j\nu} c_{j\nu} + h.c. \right) + U \sum_i n_{i\uparrow} n_{i\downarrow},
\]

where \( c_{i\mu}^\dagger \) creates an electron on site \( i \) in orbital \( \mu = x, y, z \). The parameter \( t \) has been generalized here to a set of \( 3 \times 3 \) matrices giving the amplitude for hopping between different orbitals on different sites (possibly between molecules in different orientations). We retain hopping terms between first and second neighbors. The matrix elements \( T_{i\mu,j\nu} \) are obtained from the LDA eigenvalue spectrum by Fourier inversion, giving the optimal tight-binding
representation of the LDA dispersion. Finally, we study both positive- and negative-$U$ solutions, i.e., both SDW and CDW states. Preliminary indications are of an enhanced susceptibility for forming a density-wave state with $Q$ oriented along the $c$-axis, corresponding to a value of $|U| \sim 1$ eV [13].

IV. PERIOD DOUBLING AND BAND STRUCTURE

A complementary line of inquiry can be followed within the single-particle picture. LDA has previously been used to study commensurate CDW’s by first assuming, say, a doubled unit cell and then minimizing the total energy with respect to a dimerization coordinate. Whether or not this procedure works in principle is the subject of debate: Overhauser has argued that correlation effects are important for density-wave ground states and are too crudely represented by LDA [14], while Ashkenazi et al. have shown numerically that LDA fails to predict any dimerization even for the textbook Peierls system, polyacetylene [15].

For these reasons, we focus on band-structure effects. We assume that a density wave in $K_4C_{60}$ leads to period-doubling along the $c$-axis (as suggested by the FS nesting), with an amplitude of 5%. The orientations of the $C_{60}$ molecules are assumed not to change. The resulting LDA band structure for this doubled cell is suggestive, but not definitive: no gap appears, but the extended flat FS sheet disappears, leaving only small electron and hole pockets. We estimate, from simple FS-area scaling arguments, that the dc conductivity is smaller by a factor of 5–10. While not insulating per se, the reduced conductivity may be manifested in NMR as a small Korringa component plus an activated component. Additional effects from disorder (orientational or defects) are expected to reduce further the measured conductivity.

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FIGURES

FIG. 1. Theoretical LDA band structure for (orientationally ordered) K$_4$C$_{60}$. The Fermi level is the energy zero.

FIG. 2. Fermi surface corresponding to the LDA bands of Fig. 1, in a repeated-zone representation.

FIG. 3. Surface plot of $\xi_{33}(Q)$ in the $Q_x, Q_z$ plane. The plotting rectangle is centered on $Q = 0$, and has sides of length $3(\pi/a)$ and $3(\pi/c)$ in the $Q_x$ and $Q_z$ directions, respectively. The singularity at $Q = 0$ is physically meaningless.