On Possible Coexistence of Superconductivity and Charge Density Wave in Hole-doped C$_{60}$

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March 22, 2022

Abstract

Superconductivity in C$_{60}$ materials is modeled in terms of an intramolecular, nonretarded attraction. It was shown previously that, at intermediate coupling, the model possesses a state in which s-wave superconductivity coexists with a charge density wave, the latter stabilized by intersite repulsion. The CDW causes $T_c$ to decrease near half filling. We argue that hole-doped C$_{60}$, for which $T_c$ peaks away from half filling, is a possible candidate for this state. But the electron-doped C$_{60}$ and A$_3$C$_{60}$ are conventional superconductors, stabilized against a CDW by metallic screening, which is treated in a parameter-free fashion.

PACS: 74.10 +v, 74.20 -z, 74.70 Wz, 74.72 -h

About a decade ago, superconductivity with surprisingly high $T_c$'s (30−40 K) was observed in A$_3$C$_{60}$, where A is an alkali atom [1, 2]. Recently much higher $T_c$'s (52 K − 117 K) have been seen in hole-doped C$_{60}$ [3, 4]. Within the Bardeen-Cooper-Schrieffer (BCS) picture, origin of such high $T_c$'s has been attributed to special properties C$_{60}$, such as, high density of states (DOS) and large phonon frequency. However, variation of $T_c$ with the density $n$ does not follow the DOS. Also, in the electron-doped C$_{60}$ and A$_3$C$_{60}$ the maximum of $T_c$ occurs near half filling. But in the hole-doped material, $T_c$ peaks at a density of $n = 3 − 3.5$ holes/molecule, and decreases rapidly toward half filling (5 holes/molecule) [5]. Such a behavior has been predicted previously on theoretical grounds [5, 6]. The sharp decline in $T_c$ is caused by the appearance of a charge density wave (CDW) near half filling which, due to the frustration effects of the lattice, can coexist with superconductivity. Here we examine the conditions for the existence of such a state in C$_{60}$.

The possibility of a CDW instability in C$_{60}$ was recognized early by Zhang, Ogata and Rice [7]. As discussed below, it becomes more likely as $T_c$ increases. The key issue is the effect of Coulomb repulsion which opposes superconductivity, but favors the CDW. We will focus mostly on the normal state, and consider realistic potentials. We find that if there is no metallic screening, the
energy gained by the CDW increases monotonically with increasing interaction strength. However, in the presence of metallic screening, the gain has a maximum. It is too small to stabilize the CDW state in the lower $T_c$ materials such as $A_2C_{60}$. But for the hole-doped case, the CDW state can not be ruled out. We discuss some normal-state anomalies of this state.

Crystalline $C_{60}$ has a face-centered-cubic (FCC) structure, and is a semiconductor. The conduction band is formed from the 3-fold degenerate $t_{1u}$ molecular orbitals, and the valence band from the 5-fold degenerate $h_{1u}$ orbitals. In $A_2C_{60}$, each alkali atom donates one electron to the conduction band making it half-filled. Large molecular size leads to a large lattice spacing ($a \sim 10\text{Å}$), and consequently very narrow bands $\hbar$ of width $W \sim 0.5eV$, which can thus be adequately described by a tight-binding model with nearest-neighbor hopping. This implies that geometric effects such as frustration and nesting are important.

Our theory is based on two key assumptions. (1) Low energy physics of the doped system can be described by an effective Hamiltonian defined entirely within the relevant band, i.e., the $h_{1u}$ band for hole-doped $C_{60}$, and the $t_{1u}$ band for electron-doped $C_{60}$ and $A_2C_{60}$. The effect of integrating out other bands and phonon degrees of freedom is to renormalize the interactions. (2) The attractive interaction responsible for superconductivity is intramolecular in origin and effectively nonretarded, i.e, the characteristic frequency $\omega_0$ is comparable to the Fermi energy. Indeed, intramolecular phonons that are thought to be responsible have rather high frequencies: $\hbar\omega_0 \sim 0.15eV - 0.2eV$, easily comparable with the Fermi energy.

The model always has a solution in which the normal state is conventional, and superconductivity is BCS like. In the BCS theory $T_c$ is given by

$$kT_c \approx 1.3\hbar\omega_0 e^{-1/\lambda},$$

where $\lambda \approx U \rho(\epsilon_F)$ is the dimensionless coupling constant, $\rho(\epsilon_F)$ is the density of states (DOS) at the Fermi level, $U$ is the attractive interaction. The observed high $T_c$’s are usually attributed to: (1) a relatively high DOS due to the narrow bandwidth ($\rho \propto W^{-1}$) and orbital degeneracy, and (2) a large prefactor due to high phonon frequency. Furthermore, in $A_2C_{60}$, $T_c$ increases with increasing size of the alkali atoms. This is because as the lattice expands, $W$ decreases. Similarly, the five-fold degeneracy of the $h_{1u}$ level should lead to higher DOS, which will account for the higher $T_c$ in the hole-doped material.

However, not everything fits. According to the simple BCS formula, the $n$-dependence of $T_c$ should track that of the DOS (through the $n$-dependence of the Fermi energy). This is actually not the case. For the FCC lattice the DOS has sharp features. The measured $T_c$ is smoother, its maximum is far removed from that of the DOS, both for the electron doped or hole doped materials.

We point out that the problem is partly due to the assumption that the attractive interaction is retarded, i.e., confined within $\hbar\omega_0 \ll \epsilon_F$ of the Fermi
surface. Then one can approximate the DOS by $\rho(\epsilon_F)$, and use $\hbar \omega_0$ as a cut-off in the energy integral which accounts for the prefactor. This procedure is not valid when $\hbar \omega_0$ is comparable to $\epsilon_F$. In fact, as shown previously [6], in the nonretarded case $T_c$ varies much more smoothly with $n$. The reason is that for general values of $\hbar \omega_0$, a more accurate approximation is given by

$$kT_c \approx 1.3 \hbar (w_1 w_2)^{1/2} e^{-1/\rho_0 U},$$

where $\hbar w_1 = \min(\epsilon_F, \hbar \omega_0)$, $\hbar w_2 = \min(W - \epsilon_F, \hbar \omega_0)$, and $\epsilon_F$ is measured from the bottom of the band. Here $\rho_0$ is the weighted average of the DOS $\rho(\epsilon)$ over the allowed region with a slowly varying weight factor $\epsilon^{-1} \tanh(\epsilon/2kT_c)$ (normalized to unity). For small $\hbar \omega_0$ we recover the usual BCS formula, whereas for large $\hbar \omega_0$, the variation of $T_c$ with $n$ is smoothed out considerably. In this case, a better estimate is $\rho_0 \approx 1/W$.

A more important issue is the possibility of a CDW instability which cannot be ignored when $\hbar \omega_0$ is comparable to $\epsilon_F$. We consider a one-band model, characterized by a single-particle energy $\epsilon_k$, an on-site attraction $U$, and an intersite repulsive interaction $V(r)$. The relevant dimensionless energy scales are $U \rho$ and $V \rho$. The effect of orbital degeneracy can be approximately taken into account by changing $\rho$, or, equivalently, by changing $U/W$ and $V/W$. The possibility of a CDW was studied in reference [8] using this model, but without the $V$ term. However, as shown previously, inclusion of even a nearest neighbor $V$ leads to nontrivial consequences [3, 5]. We now generalize to $V(r)$ of arbitrary range.

In the simplest mean-field approximation, and in the absence of superconductivity, a CDW with a wavevector $Q$ would appear for

$$(U + 2V_Q) \chi(Q) > 1,$$  \hspace{1cm} (2)

where $\chi(Q)$ is the charge susceptibility for the noninteracting system, and $V_Q = -\sum_{r \neq 0} e^{iQr} V(r)$. The minus sign is included in order to make $V_Q$ positive. For a bipartite (e.g., simple cubic, BCC etc) lattice, there is a $Q$ for which

$$\epsilon_{k+Q} = -\epsilon_k$$  \hspace{1cm} (3)

for all $k$. Then the Fermi surface is perfectly nested at half filling, leading to a logarithmically divergent $\chi$ at $T = 0$ and a CDW instability for any $(U + 2V_Q) > 0$. For the nonbipartite FCC lattice, $\chi(Q)$ is finite even at half filling as there is no nesting, i.e., no $Q$ for which Eq.(3) holds. A conventional metallic state is then stable for $(U + 2V_Q) < 1/\chi(Q) \approx 0.375W$. Above this, a CDW state appears with $Q = (0, 0, 2\pi/a)$, which corresponds to a CDW with a density $n(r) = n + n_1 e^{iQr}$, i.e., on successive planes perpendicular to the $z$ axis, the density alternates between $n + n_1$ and $n - n_1$.

From (2), it appears that a CDW can exist even $V = 0$. However, such a state is unstable against s-wave superconductivity, since the pair susceptibility is logarithmically divergent. The inclusion of $V(r)$ changes this picture,
due to two reasons. First, the $V$ term favors the CDW energetically. At the mean-field level, the excess potential energy per site in the CDW state equals $-(U+2V Q)n^2_1/4$. Physically, the CDW forms an “ionic crystal” with $V Q$ proportional to the appropriately generalized Madelung energy $[9]$. However, compared with a bipartite (e.g., BCC) lattice, charge ordering on an FCC lattice is frustrated, leading to a somewhat lower energy gain. Nonetheless, we have verified numerically that $V Q > 0$, for the screened Coulomb potentials (Fig 1) which are the potentials of interest. Second, $V(r)$ always opposes superconductivity by keeping particles apart, stabilizing the CDW state at larger $V Q$.

The CDW splits the noninteracting band into two bands of energy

$$E_{\pm}(k) = \epsilon_1(k) \pm \left[\epsilon_2^2(k) + \Delta_C^2\right]^{1/2},$$

where $\epsilon_1(k) = \frac{1}{2}(\epsilon_k + \epsilon_{k+Q})$ and $\epsilon_2(k) = \frac{1}{2}(\epsilon_k - \epsilon_{k+Q})$. At the same $k$, the bands are separated by a gap $\Delta_C = n_1(U + 2V Q)/2$. For a bipartite lattice, the geometrical property, Eq. (3), ensures that $\epsilon_1(k) = 0$, leading to insulating behavior. However, Eq.(3) does not hold for the FCC lattice. Then for small enough $\Delta_C$, the maximum of the lower band lies above the minimum of the upper band which, in general, is at a different $k$ point. This leads to a semimetal with a partially gapped Fermi surface. This is a direct consequence of geometric properties frustration and (lack of) nesting. Eventually, there is a transition to a an insulating state for $(U + 2V Q) > 0.562W$.

Furthermore, residual attractive interaction within the semimetal leads to superconductivity. For a nearest-neighbor $V$, the CDW has been shown to coexist with superconductivity over a substantial region in the parameter space $[5]$. The presence of the CDW lowers $T_c$, and yields $[6]$ a $T_c(n)$ which is very different from that in the conventional state (no CDW). In either case, $T_c$ does not track the DOS. In the conventional state, it peaks near half filling and gradually decreases to zero at the band edges. This is similar to the behavior observed in electron doped $C_{60}$ and $A_3C_{60}$.

By contrast, in the CDW-superconductor $T_c$ has a minimum near half filling where the CDW instability is strongest. Away from half filling, $T_c$ increases as the CDW weakens. Eventually, there is a transition to the conventional state. Consequently $T_c$ reaches a maximum near the transition point and then decreases following the behavior in the conventional state. This is very similar to the behavior observed in the hole doped $C_{60}$. So far only one maximum has been seen because experiments have been limited to only one side of half filling. The theory predicts two, one on each side. These results should be qualitatively correct for the more realistic screened Coulomb potential, although one expects a more rapid decline of $T_c$ toward the band edges since screening length increases with distance between particles.

Are the observed $T_c$'s consistent with the theory? Consider the conventional state at half filling which exists for $(U + 2V Q)/W < 0.375$. To estimate $U/W$ from the measured $T_c$, we use formula (1), conveniently rewritten as
\[ 1/\lambda = -\ln(kT_c/1.3\hbar\omega_0), \]
to compute \( \lambda \), which is treated as a phenomenological coupling constant. At half filling, we can take \( \omega_0 \) to be the (intramolecular) phonon frequency, which is same for all materials. Noting that \( \lambda \) varies slowly with \( \omega_0 \), we set \( \hbar\omega_0 = 1500K \), which is reasonable. For the electron doped C\(_{60}\) \((T_c = 11K)\) this gives \( \lambda = 0.146 \). However, for Rb\(_3\)C\(_{60}\) \((T_c = 33K)\), \( \lambda = 0.245 \).

Next step is to relate \( \lambda \) with the theoretical parameter \( U/W \). As discussed before, in the absence of \( V(r) \), and for large \( \hbar\omega_0 \), \( \lambda \approx U/W \). However, when \( V(r) \) is included, \( \lambda \) will be reduced so that \( U/W > \lambda \). This means that electron-doped C\(_{60}\) and A\(_3\)C\(_{60}\) can be conventional metals, but for the larger alkali (Rb etc) materials \( V_Q/W \) has to be rather small.

For the hole-doped C\(_{60}\), the maximum \( T_c \) of 52\( K \) yields a larger value of \( \lambda \) \((\approx 0.28)\) which could be sufficient for the CDW state. However, the maximum is away from half filling which in our theory is due to the transition to the CDW-superconducting state. In order to be consistent, we have to use the \( T_c \) of the corresponding conventional state at half filling. This is about 30 to 50 percent higher, which gives \( U/W > \lambda \approx 0.32 - 0.34 \). For any reasonable values of \( V_Q \) these materials should be CDW metals near half filling. Any expansion of lattice will increase \( U/W \), making the CDW even more likely.

The intriguing question is, why is A\(_3\)C\(_{60}\) not a CDW metal, as suggested previously? For example, for Rb\(_3\)C\(_{60}\) to be conventional, \( V_Q/W \) has to be \( \sim 0.05 \) or less, almost two orders of magnitude smaller than the bare Coulomb energy scale \( e^2/a \approx 2.6W \). Now, there are two sources of screening. (1) Screening by other molecular bands which can be approximated by a static dielectric constant \( \epsilon \). One expects \( \epsilon \) to be somewhat larger than that in ordinary semiconductors because of small (molecular) band gaps. (2) Since the transition is from one metallic state to another, we must include metallic screening which leads to exponentially short-range potential and much smaller \( V_Q \). To see this, we consider the screened Coulomb potential

\[ V(r) = \frac{e^2}{\epsilon r} e^{-r/\xi}, \tag{5} \]

where \( \xi \) is the Thomas-Fermi screening length.

Let us define the dimensionless quantity \( \alpha \) by writing \( V_Q = v_0 \alpha(\xi/a) \), where \( v_0 = e^2/\epsilon a \) sets the energy scale for the long-range part. Then \( \alpha(x) \) is generalized Madelung constant, defined for screened-Coulomb potential. As shown in Fig. (1) \( \alpha \), which measures the energy gained by the CDW, increases with the range of interaction \( \xi/a \). In the absence of metallic screening, \( \xi = \infty \), and \( \alpha \approx 1.6 \). With decreasing \( \xi \), \( \alpha \) decreases rapidly below \( \xi \approx a \), which is essentially the metallic region. Fig. 1 also shows that \( \alpha \) is always smaller for the FCC lattice than the bipartite BCC lattice. This is due to frustration which is another — albeit smaller — source of reduction of \( V_Q \).

It is possible to have a CDW state in every case by choosing the parameters \( v_0 \) (i.e., \( \epsilon \)) and \( \xi \) appropriately. However, a much better parameter-free understanding of screening can be obtained as follows. First, note that \( \xi \) itself
depends on $v_0$. The Thomas-Fermi expression for $\xi$ [10], written in the lattice language, reads:

$$\xi/a = \left[4\pi\gamma v_0 \frac{dn}{d\mu}\right]^{-1/2},$$  \hspace{1cm} (6)

where $\mu$ is the chemical potential, and the geometrical parameter $\gamma = \sqrt{2}$ for the FCC lattice. At low $T$, $dn/d\mu \approx \rho(\epsilon_F) \sim 2/W$. Let us define an effective bandwidth by $2/W_{eff} = dn/d\mu$. Since $\alpha$ depends only on $\xi/a$, we see that the dimensionless quantity $V_Q/W_{eff}$ is a universal function of the dimensionless coupling constant $v_0/W_{eff}$ only. This is plotted in Fig. 2. Notice that $V_Q/W_{eff} \sim V_Q/W$, the quantity of interest. Naively one would expect $V_Q$ to keep increasing as $v_0$ increases. On the contrary, $V_Q/W_{eff}$ has a broad maximum. This is because an increased $v_0$ (i.e., a larger charge) makes the screening length $\xi$ shorter (Eq. 6) which decreases $\alpha$. The maximum occurs at $\rho v_0 \approx 0.15$ and has a value of about 0.042. This is a pure number, which depends only on the lattice type, but not any parameters. Hence, we have the remarkable result that irrespective of how large or small $v_0$ (i.e., $\epsilon$) is, $2V_Q/W_{eff} < 0.084$. The smallness of this number, combined with the above estimates of $U/W$, explains why $A_2C_{60}$ is conventional. We stress that this drastic reduction of $V_Q$ would not occur if the CDW state were an insulator since there is no metallic screening at the transition.

Since $V_Q/W_{eff}$ varies slowly (fig. 2), its maximum value also provides an estimate for its magnitude. For example, $2V_Q/W_{eff} > 0.06$ in the entire range of $0.05 < v_0/W_{eff} < 0.4$ ($52 > \epsilon > 6.5$). This is sufficient for the hole-doped $C_{60}$ to be a CDW semimetal. This analysis is of course approximate. One way to see if the state is experimentally realized is to look for normal state anomalies.

The semimetal is described in terms of two bands separated by a direct gap $\Delta_C(T)$, as well as a Fermi surface. The gap vanishes at $T_{CDW}$, above which the normal state is conventional. Below $T_{CDW}$, the band parameters become temperature dependent through $\Delta_C(T)$, leading to distinct features. Thus, the carrier density increases with increasing $\Delta_C$, leading to peak or a shoulder in the resistivity as a function of $T$. Other quantities, such as the specific heat, also show similar behavior. To see this, consider the approximate low $T$ expression for energy

$$E(T) = E_0(\Delta_C) + \frac{\pi^2}{6} (kT)^2 \rho(\epsilon_F),$$  \hspace{1cm} (7)

where $E_0(\Delta_C)$ is the ground-state energy and $\epsilon_F$ is the corresponding Fermi energy for a given $\Delta_C(T)$. For $T > T_{CDW}$, $\Delta_C = 0$, and $E_0$ and $\rho$ are independent of $T$, leading to linear heat capacity and $T$-independent magnetic susceptibility. Below $T_{CDW}$, $E_0$ and $\rho(\epsilon_F)$ become temperature dependent through $\Delta_C(T)$. We have solved the mean-field equations numerically at finite $T$. Fig. 3 shows typical behavior of specific heat as a function of $T/T_{CDW}$, which is linear in $T$ above $T > T_{CDW}$, and again becomes linear at low $T$, as $\Delta_C(T)$ saturates, but with a smaller slope, corresponding to reduced value of $\rho(\epsilon_F)$. The sharp feature
below $T_{CDW}$ is due to the rapid decline in $\rho(\epsilon_F)$ as function of temperature, also shown in Fig. 3. These features should be experimentally observable in the region where $T_{CDW} > T_c$, i.e., close to half filling.

In conclusion, we have shown that despite relatively high $T_c$'s, frustration and metallic screening suppresses a CDW instability in $A_3C_{60}$. But for hole-doped $C_{60}$, a mixed state can not be ruled out. If the anomalies discussed above are not observed, then the CDW is absent. This is possible, given the simplicity of the model and approximate nature of the analysis. Even then the instability can not be be very far away, and can occur as $T_c$ is increased further by lattice expansion. The author thanks C. Jayaprakash and T. L. Ho for discussions.

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FIGURE CAPTIONS

Fig.1: The generalized Madelung constant $\alpha = V_Q/v_0 = \sum_{r \neq 0} \frac{e^{iQ \cdot r/a}}{(r/a)^{1+\xi}}$ plotted against dimensionless screening length $\xi/a$, where $a$ is the nearest neighbor distance. Note that $\alpha$ depends only on $\xi/a$ and the lattice type. The solid line is for the FCC lattice and the dashed line for the bipartite BCC lattice, showing that energy gain from the CDW is less for the FCC lattice due to frustration. In usual metals, $\xi/a < 1$.

Fig.2: The dimensionless quantity $V_Q/W_{eff}$ is plotted (solid line) against $v_0/W_{eff}$ where $W_{eff} = 2/dn = 2/\alpha a$ ~ $W$. Also shown (dashed line) is $10\xi/a$ which, like $\alpha$, is slowly varying except for very small $v_0$. 

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Fig. 3: Scaled specific heat (solid line) and density of states at the Fermi level (dashed line) are plotted vs $T/T_{CDW}$ for the CDW-metal at half filling. The parameter values are $U + 2V_q = 6.71t$, $T_c = 0.768t$. The prominent feature below $T_{CDW}$ is due to the CDW and reflects the rapid rise in the DOS.
