Flexible control of the Peierls transition in metallic C$_{60}$ polymers

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Abstract – The metal-semiconductor transition of peanut-shaped fullerene (C$_{60}$) polymers is clarified by considering the electron-phonon coupling in the uneven structure of the polymers. We established a theory that accounts for the transition temperature $T_c$ reported in a recent experiment. The theory also suggests that $T_c$ is considerably lowered by electron doping or prolonged irradiation during synthesis. The decrease in $T_c$ is an appealing phenomenon with regard to realizing high-conductivity C$_{60}$-based nanowires even at low temperatures.

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Introduction. – With the developments in nanotechnology in the last decades, nano-carbon materials are regarded as highly significant for potential electronic device applications. In particular, peanut-shaped fullerene (C$_{60}$) polymers are promising materials for application in nanometric conducting devices $[1,2]$. C$_{60}$ polymers, produced through electron-beam irradiation (EBI) of pristine C$_{60}$ films, possess a quasi-one-dimensional (1D) hollow tube geometry with a periodically modulated radius. It is a sort of $\pi$-electron conjugated systems, having metallic nature with the resistivity of 1–10 $\Omega$cm at room temperature $[1]$. A practical advantage of the synthesis is that it requires only EBI-induced polymerization of C$_{60}$ films deposited by dry (evaporation) or wet (spin coat) processes; hence, metallic C$_{60}$-based nanowires can be easily fabricated within a specified area on any substrate. This feature indicates the superiority of C$_{60}$ polymer applications to electronic devices through conventional integration techniques.

The uneven structure and reduced dimensionality of the C$_{60}$ polymers strongly affect their electronic and phononic properties at low temperature. For instance, their peanut-like curved shape results in a significant increase in the Tomonaga-Luttinger exponent, which describes the collective excitations of electrons in quasi-1D systems $[3,4]$. In the case of phononic excitations, infrared spectral measurements evidenced a rapid growth of specific eigenmode peaks with the increase in the EBI time $[5]$; this peak growth is attributed to the anomaly in the phonon density of states peculiar to quasi-1D systems $[6]$.

In contrast to the well-understood effects mentioned above, the effect of electron-phonon (e-ph) couplings on the low-temperature physics of the C$_{60}$ polymers remains to be explored. An important problem to be considered is the possibility of a coupling-induced metal-semiconductor transition (i.e., the Peierls transition) in the system. Recently, through pump-probe spectroscopy, an energy gap formation was found in the conduction band of C$_{60}$ polymers below 60 K; this energy gap formation suggested the Peierls transition, driven by e-ph couplings $[7]$. However, theoretical understanding of the transition is still inadequate. From the perspective of device applications, it is fundamental to know why the conducting nature of the C$_{60}$ polymers vanishes across the transition temperature, $T_{c,\text{exp}} \sim 60$ K, and how the e-ph coupling in the uneven structure contributes to the transition.

In this letter, we provide a theoretical interpretation of the observed Peierls transition in the C$_{60}$ polymers by considering the structure-property relationship of the polymers. The theory leads us to an artificial manipulation of the transition temperature by alkali doping or a prolonged EBI procedure, whose realizations are directly linked to developing the potential of the C$_{60}$ polymers as conducting nanowires.

Formulation. – For making an analytic argument, we map the C$_{60}$ polymer to a continuum thin hollow cylinder whose radius $R(z)$ is modulated along the axial (z) direction as $R(z) = R_0 - a \sin^2(\pi z/s)$; we set $R_0 = 3.5$ Å, $a = 1.5$ Å, and $s = 7$ Å (see fig. 1). The radius modulation yields two effective potential fields, each of which affects the motion of the electrons $[3,4,8,9]$ or phonons $[10]$...
Fig. 1: (Color online) Continuum model of a 1D peanut-shaped C_{60} polymer. The geometric values R_0, a, and s are drawn. The square depicted by the dashed line (blue) indicates the unit cell.

Fig. 2: (Color online) Electronic band structure of thin hollow cylinders with periodically varying radius. Each band is labeled by two quantum numbers (|γ|, H), as a few examples are shown in the panel, where γ is the angular momentum of electrons and H is the band index for a fixed γ. The Fermi energy μ_0 prior to doping lies nearly at the center of the (4,2) band.

confining in the system. Due to the structural symmetry, a set of three quantum numbers P = (k, γ, H) is required to specify the electronic states; here, k is the electron’s wave number, γ indicates the angular momentum, and H labels the electronic band [3,4]. Figure 2 illustrates the electronic band structure obtained via the continuum approximation [3], by which we can grasp visually how the set of three labels (i.e., k, γ and H) indicates single-particle states. In the same manner, the phononic states are classified by a three-number set J = (q, m, M), where q and m are the phonon wave number and angular momentum, respectively, and M is the phononic band index [10].

We define T_c as the temperature at which a renormalized phonon frequency becomes zero. Let us suppose that the eigenfrequency ω_J of bare phonons are renormalized into ω by the e-ph interaction. Then, the phonon Green’s function can be expressed as

\begin{equation}
D(J, iν) = \frac{2ℏω_J}{(iν)^2 - (ℏω_J)^2 - 2ℏω_JΠ(J, iν)},
\end{equation}

where Π(J, iν) is the self-energy due to the interaction within the random phase approximation (RPA), and νt ≡ 2πk_B T (k_B being the Boltzmann constant) with integer l is the Matsubara frequency for bosons [11]. By carrying out the analytic continuation iν → ℏω + i0, we obtain the retarded Green’s function D(J, ω), whose pole gives the renormalized phonon frequency ω:

\begin{equation}
(ℏω)^2 - (ℏω_J)^2 - 2ℏω_JRe[Π(J, ℏω + i0)] = 0.
\end{equation}

Taking the limit ω → 0 in eq. (2), we obtain the following equation, which determines T_c:

\begin{equation}
hω_J = Q_J(T_c) \equiv 4 \sum_{P_i} \sum_{P_f} |g_{P_i, P_f}^{P_i, P_f}|^2 S_{P_i, P_f}(T_c),
\end{equation}

\begin{equation}
S_{P_i, P_f}(T) = -\frac{f(ε_{P_f} - μ, T) - f(ε_{P_i} - μ, T)}{ε_{P_f} - ε_{P_i}}.
\end{equation}

Here, g_{P_i, P_f}^{P_i, P_f} ∝ ∫ ψ_{P_i}^* ψ_{P_f} dS is the coupling strength of two electrons, designated by ψ_{P_i} and ψ_{P_f}, in the case where the coupling is mediated by a phonon whose displacement vector is given by u_J; the integral ∫ dS is carried out over the entire surface of the modulated cylinder depicted in fig. 1 [10]. In eq. (4), f is the Fermi distribution function, ϵ_{P_i} is the electron energy, and μ ≡ μ_0 + Δμ is the Fermi energy, with Δμ representing the deviation from the initial value μ_0 by carrier doping.

From the definition, T_c is dependent on the choices of μ and J. In the following discussion, we restrict our attention to the specific phonon mode with J that yields the highest T_c for a given μ. This is because such the highest T_c is what should be observed in practical measurements. To solve eq. (3) with respect to T_c, we define μ_0 such that 60 electrons per a unit cell occupy single-particle states from the bottom of the electronic band. It is natural to assume that each carbon atom within a C_{60} molecule gives a π-electron, and each band accommodates two electrons per a unit cell due to spin degeneracy. As a result, μ_0 is located in the band labeled by (|γ|, H) = (4,2) and it slightly deviates from the half-filling energy of the band (see fig. 2). The width of the conduction band is set to be 1 eV by referring to the ab initio calculations [13].

Results. – Figure 3(a) shows the μ-dependence of T_c; see fig. 4(a) for the relevant phonon mode at μ = μ_0. We observe that T_c decreases monotonically as μ increases; this decrease results from a reduction in the commensurate effect [12,14] that maximizes T_c at the half-filling state (i.e., Δμ ∼ 50 meV in the present condition; see inset of fig. 3(a)). In the half-filled situation, electrons near the

\begin{footnote}{Among many bands that across μ_0, the (4,2) band gives the strongest e-ph coupling [10] and pronounced commensurate effect [12], i.e., the largest values of g^{P_i, P_f}_{P_i, P_f} and S_{P_i, P_f} in eq. (3), respectively. This fact allows us to examine only the contribution from the (4,2) band to the right side of eq. (3).} \end{footnote}
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Fermi level can be coupled with electrons not only inside but also outside the first Brillouin zone (BZ) via a phonon with $q$. This coupling enhancement is depicted in the inset of fig. 3(a), resulting in a high $T_c$. In contrast, when the Fermi level is shifted away from the half-filling state, the downward shift of the $Q_J$ curve with decreasing $a$. The intersection of the $Q_J$ curve and the horizontal line with $\hbar \omega_J$ gives the $T_c$.

(c) Dependence of $T_c$ on the radius modulation amplitude $a$.

Discussions. – It follows from eq. (3) that $T_c$ strongly depends on the e-ph coupling strength $g_{J}^{P_i P_f}$ as well as $S_{P_i P_f}$. For a better understanding of the e-ph coupling contribution to $T_c$, fig. 4(a) illustrates the phonon mode that plays a dominant role in the occurrence of the Peierls transition at $\Delta \mu = 0$ and $a = 1.5 \, \text{Å}$. Since the radius modulation yields an effective potential field with the same period of $a = 7 \, \text{Å}$, the resulting div$\mathbf{u}_J$ becomes significant around the swelling region, as shown in fig. 4(b). Similarly, the spatial profile of $\psi_{P_i}^{f} \psi_{P_f}$ at the Fermi level has a large amplitude in the vicinity of the swelling region (see fig. 4(c)), owing to the curvature-induced potential effect [3,4]. The synchronized oscillation of div$\mathbf{u}_J$ and $\psi_{P_i}^{f} \psi_{P_f}$ results in an enhancement of $g_{J}^{P_i P_f}$ (or equivalently, $Q_J$) in eq. (3), which is sufficient to achieve the Peierls transition at an experimentally feasible temperature range. Artificial variances in $\Delta \mu$ and $a$ cause changes in the profiles of div$\mathbf{u}_J$ and $\psi_{P_i}^{f} \psi_{P_f}$ of the relevant modes, thus yielding a change in the associated $T_c$, as demonstrated in the present work.

We point out that our first result, the well-defined energy gap formation at $60 \, \text{K}$, is consistent with the

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2Thus far, several synthetic procedures have been developed to produce alkali metal-intercalated fullerite compounds [16,17]. In particular, a potassium dispenser is useful to incorporate potassium into the pristine C$_{60}$ film [17]. Thus, it may lead to an experimental realization of the alkali-doped C$_{60}$ polymers.

A similar reduction in the Peierls transition temperature by alkali doping has been reported in In atomic wires [18].

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Fig. 3: (Color online) (a) Transition temperature $T_c$ as a function of the Fermi level shift $\Delta \mu$ due to carrier doping. Without doping, we have $T_c \sim 130 \, \text{K}$ as indicated by a vertical line. Inset: Schematic of the commensurate effect. It illustrates the electron band structure and relevant electron-phonon couplings via the phonon wave number $q$ that enhance $S_{P_i P_f}$ (see eq. (4)) near the half-filling state. (b) Downward shift of the $Q_J$ curve with decreasing $a$. The intersection of the $Q_J$ curve and the horizontal line with $\hbar \omega_J$ gives the $T_c$. (c) Dependence of $T_c$ on the radius modulation amplitude $a$. The rapid decrease in $T_c$ with the increase in $\mu$ is significant in light of controlling the low-temperature electronic conductivity of the C$_{60}$ polymers. For example, we have found that an increment $\Delta \mu = 0.3 \, \text{eV}$ causes a drastic reduction in $T_c$ from 130 K to 1 K; this value of $\Delta \mu$ coincides with the upward shift in the Fermi level that is observed when one additional alkali atom per C$_{60}$ molecule is inserted into the hollow cavity of the C$_{60}$ polymer."
Fig. 4: (Color online) (a) Displacement distribution of the phonon mode that mainly contributes to the Peierls transition under $\Delta \mu = 0 \text{ and } a = 1.5 \text{ Å}$, (b) Profile of $\text{div} u$ of the phonon mode, shown in the plot of (a), (c) Profile of the wave function product, $\psi_p \psi_{p'}$, of two electrons coupled via the phonon shown in (a).

transient optical data for the C$_{60}$ polymer. Recently, Toda et al. have observed a moderate increase in the carrier relaxation time $\tau$ as the temperature decreases from 60 K down to absolute zero [7]. They attributed the moderate increase in $\tau$ to critical fluctuation of the energy gap. However, we can prove that critical fluctuation is not a necessary condition for the $\tau$ enhancement. In fact, by applying Kabanov’s theory [19] to quasi-1D systems, we have revealed that the system having a well-defined gap exhibits a moderate increase in $\tau$ as far as anharmonic interactions occur between longitudinal and twisting vibration modes [20]. We thus conclude that the $\tau$ increase observed by Toda et al. is in the realm of the e-ph coupling theory we have developed.

Our numerical condition that $\mu_0$ slightly deviates from the half-filling energy can be examined by spectroscopy techniques. For instance, the angular-resolved photoemission spectroscopy measurement is in general useful to determine the electronic band structure. In addition, the ultraviolet photoelectron spectroscopy provides us information as to the Fermi energy and density of states of the system [21]. Summary of the spectroscopic data, therefore, enables to estimate the filling factor of the electrons in the conduction band. Systematic investigation along these techniques would give an evidence of the nearly half-filled band of the C$_{60}$ polymers, which supports the controllability of their Peierls transition temperatures.

Conclusion. – In conclusion, we have made clear the microscopic mechanism of the Peierls transition in C$_{60}$ polymers. The estimated transition temperature is quantitatively consistent with the existing experimental result. Furthermore, we suggest that carrier doping and/or EBI time manipulation enable a significant reduction of the low-temperature resistivity of the C$_{60}$ polymers, which is an appealing feature with regard to C$_{60}$-based nanodevice fabrication.

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