Peierls instability and persistent current in mesoscopic conducting polymer rings

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Studying the relationship between the Peierls instability, the magnetic flux, and the persistent current in the mesoscopic conducting polymer ring threaded by a magnetic flux, we found that the magnetic flux enhances the Peierls distortion. The persistent current increases slightly with increase of temperature due to the competition between the effects of the Peierls distortion and thermal fluctuation. In addition, the phase parity of the persistent current for the odd-even electron number will vanish for the electronic number N_e in the range of $N<N_e\leqslant 2N$, where N is the one-third number of sites in the ring. This phase locking effect originates from the flat energy band of the conducting polymer ring.

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With the rapid advances in fabrication of nanoscale devices, one has realized that some interesting phenomena and properties occur in nanoscale systems, such as the ballistic transport and quantum interference in nanowires and quantum dots.[1] In particular, the physics of mesoscopic rings has gained increasing attention, which involves the persistent current, Aharonov-Bohm (AB) phase, and quantum interference.[2] One of the issues is the Peierls phase transition in these quasi-one-dimensional rings, in which the lattice may have instability with respect to a perodic static distortion of the lattice, and induces an energy gap in the electronic spectrum at the Fermi level.[3] This Peierls phase transition can be observed in the organic quasi-one-dimensional materials.[4] Theoretically, it was found that the Peierls instability depends on the magnetic flux in the mesoscopic ring,[5] and the spin-orbital coupling suppresses the Peierls distortion in the one-dimensional tight-binding mesoscopic ring.[6]

Another interesting issue is the persistent current in mesoscopic rings. Theoretical study predicts that the phase of the persistent current depends on the parity of the electron number, namely, there is a π shift of the persistent current for the odd and even spinless electrons.[7] Physically, the phase of the current may play an important role in mesoscopic systems, especially in the interference or resonance effects in the electron transport. Interestingly, It was found that the phase parity effect of the persistent current does not arise in a mesoscopic ring with a finite length lead.[8] When Anderson impurities are inherent in the ring or seeded artificially as quantum dots couplied to the ring, the phase parity of the persistent current also vanishes, which is the so-called phase locking effect.[9] Thus the phase of the persistent current can be tunned artificially by impurties or quantum dots. A similar odd-even parity effect on conductance in finite chains was predicted theoretically,[10] and recently this effect was observed experimentaly in the atomic wire.[11]

Although many novel properties may occur in some simplified models and some specific materials, it is still an interesting issue to seek for realistic nanoscale materials to implement these quantum effects. One of the possibilties could be to use organic chains like TTF-TCNQ or poly-BIOP to fabricate nanosized one-dimensional rings.[5,12] It was predicted theoretically that the Peierls distortion oscillates with the magnetic flux in the organic chain TTF-TCNQ.[5] The organic polymer chain poly-BIOP is another conducting quasi-one-dimensional material. The Peierls phase transition could also occur in this material. In this paper, we intend to study the Peierls distortion, how to influence the persistent current, and how to compete with the magnetic flux in this polymer ring.

Let us consider a typical conducting polymer ring, poly-BIOP, which consists of a primary zigzag chain containing π conjugated carbon atoms (see Fig. 1). The interchain coupling is much less than the intrachain overlap so that it can be usually described by a one-dimensional Su-Schrieffer-Heeger (SSH) Hamiltonian[13]

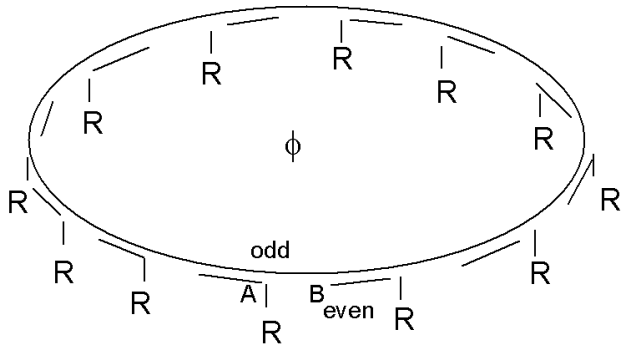

FIG. 1. The schematic structure of the conducting polymer poly-BIOP ring.

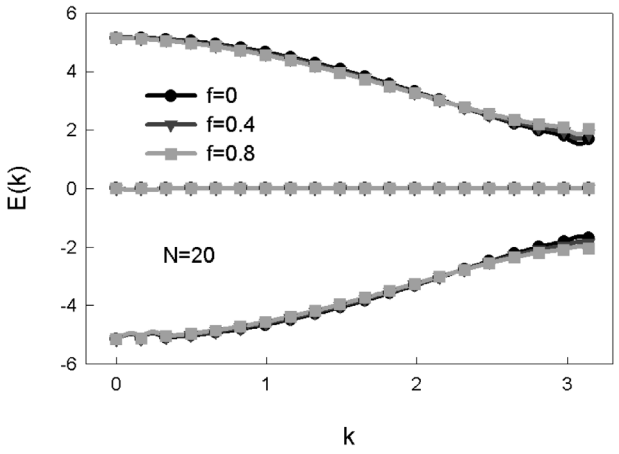

FIG. 2. The energy band of the conducting polymer poly-BIOP ring.

$$H = -\sum_i t_i (e^{i\theta} c_i^\dagger c_{i+1} + \text{H.c.}) - t_R \sum_{i=odd} (c_{i,A}^\dagger c_{i,R} + \text{H.c.}) + \frac{1}{2} K \sum_i (x_{i+1} - x_i)^2, \tag{1}$$

where $c_i^\dagger(c_i)$ is the creation (annihilation) operator for spinless electrons at the site i, and the subscript R in the second term represents the electron operator at the radical. The t_i is the phonon-dressed hopping amplitude, $t_i = t - \alpha(x_i - x_{i+1})$; the t_R is the hybrization constant between the odd-site atoms and the radicals. The α is the electron-phonon coupling constant, and x_i is the lattice displacement. As a typical case, we consider a uniform dimerization $[x_i = (-1)^i u]$ and set the lattice constant to be unity $a=1$. We suppose that there are $3N$ lattice sites in this polymer system, namely $2N$ along the ring and N in the radical (see Fig. 1). In the tight-binding approximation, $\theta = \frac{\pi}{N}\frac{\phi_{AB}}{\phi_0}$, where $\phi_{AB} = \oint \mathbf{A} \cdot d\ell$ as the AB flux, and $\phi_0 = h/e$ as the flux quantum. Using Fourier transformation the Hamiltonian can be rewritten as

$$H = \sum_k [(\gamma_k c_{k,A}^\dagger c_{k,B} + \text{H.c.}) + t_R (c_{k,B}^\dagger c_{k,R} + \text{H.c.})] + 4KNu^2, \tag{2}$$

where $\gamma_k = -t(1 + e^{i(k+\theta)}) + 2\alpha u(1 - e^{i(k+\theta)})$. To diagonalize the Hamiltonian in Eq. (2) we obtain the three-band energy dispersion

$$\epsilon(k,\theta) = \begin{cases} \pm \sqrt{4t^2 \cos^2\left(\frac{k+\theta}{2}\right) + 4\Delta^2 \sin^2\left(\frac{k+\theta}{2}\right) + t_d^2} \equiv \pm \lambda(k,\theta) \\ 0 \end{cases}, \tag{3}$$

where $\Delta = \alpha u$ is the order paramenter of the Peierls distortion, and $k = \frac{\pi}{N} m$ is the wave vector, where $m = 0, 1, 2, \ldots N-1$. It is interesting that one of three bands is flat, $\epsilon(k,\theta) = 0$, which corresponds to a highly degenerate state shown in Fig. 2, where we use the parameters $t = 2.5$ eV, $t_R = 0.5t$, $K = 25$ eV/Å, and $\alpha = 3.9$ eV/Å.[14] The Hamiltonian in Eq. (1) is invariant under the even-odd size transformation of the radicals. Nevertheless, this symmetry does not give any new phenomena.

In principle, the physical properties of this system depend on the Peierls distortion, the magnetic flux, and the temperature. The Peierls distortion is determined by minimizing the ground-state energy or the free energy for zero temperature or finite temperature, respectively. For the electron filling, $N_e = N$, the ground-state energy of the ring can be expressed as

$$E_g(\theta,\Delta) = -\sum_k \lambda(k,\theta) + \frac{KN_e}{\alpha^2}\Delta^2. \tag{4}$$

In finite temperature, the free energy of the ring can be obtained,

$$F(\theta,\Delta) = \frac{KN_e}{\alpha^2}\Delta^2 - 2k_B T \sum_k \ln\cosh\left(\frac{\lambda(k,\theta)}{2k_B T}\right). \tag{5}$$

By minimizing the ground-state energy $E_g(\theta,\Delta)$ and the free energy $F(\theta,\Delta)$ we can obtain the Peierls order parameter Δ satisfying the equation

$$1 = \begin{cases} \frac{8\alpha^2}{KN_e} \sum_k \frac{1}{\lambda(k,\theta)} \sin^2\left(\frac{k+\theta}{2}\right), & \text{for } T = 0, \\ \frac{8\alpha^2}{KN_e} \sum_k \tanh\left(\frac{\lambda(k,\theta)}{2k_B T}\right) \frac{1}{\lambda(k,\theta)} \sin^2\left(\frac{k+\theta}{2}\right), & \text{for } T \neq 0. \end{cases} \tag{6}$$

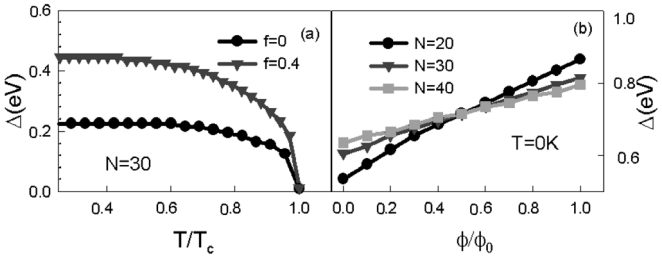

FIG. 3. (a) The Peierls order parameter vs temperature, where T_c is the critical temperature of the Peierls phase transition. (b) The Peierls order parameter vs the magnetic flux.

The Peierls distortion opens an energy gap at the Fermi level. The energy gap can be obtained by $E_{gap}=2\min\lambda(k,\theta)=2\sqrt{4\Delta^2+t_R^2}$ at $k+\theta=\pi$. The magentic flux plays an *AB* phase role to modify the energy-band structure. Solving Eq. (6) numerically, we give the Peierls order parameter vs temperature in Fig. 3(a). It can be seen that the thermal fluctuation disturbs the Peierls distortion. Interestingly, the magnetic flux enhances the Peierls distortion. In order to examine the behavior of the Peierls distortion with the magnetic flux, we plot the Peierls order parameter as a function of the magnetic flux at zero temperature in Fig. 3(b). It can be found that the Peierls distortion increases linearly with the magnetic flux and the slope depends on the ring size. Physically, the magnetic flux as an *AB* phase modifies the energy-band structure and the Peierls distortion opens an energy gap at the Fermi level. These two effects compete energetically, which leads to the Peierls distortion increasing with the magnetic flux increasing. Interestingly, the Peierls distortions of different ring sizes are the same at half of the magnetic flux quanta. On the other hand, we investigate the size dependence of the Peierls distortion in different magneic fluxes shown in Fig. 4. It can be seen that the Peierls order parameter depends on the ring size and its behavior depends on the magnetic fluxes whether larger or smaller than the half magnetic flux quanta. In the thermodynamical limit $N>80$, the Peierls order parameter trends to about 0.7 and 0.5 eV at zero and room temperatures, respectively. This is because as the ring size increases both the *AB* effect and the size dependence of the Peierls distortion become so weak that the Peierls distortion trends to a constant in the thermodynamical limit.

Another interesting issue for mesoscopic rings is the persistent current, which can be expressed as

$$I(\theta)=\begin{cases} I_0\left(-t+\dfrac{\Delta^2}{t}\right)\displaystyle\sum_k \frac{1}{\epsilon(k,\theta)}\sin(k+\theta), & \text{for } T=0, \\ I_0\left(-t+\dfrac{\Delta^2}{t}\right)\displaystyle\sum_k \frac{1}{\epsilon(k,\theta)}\tanh\left(\frac{\epsilon(k,\theta)}{2k_BT}\right)\sin(k+\theta), & \text{for } T\neq 0, \end{cases} \tag{7}$$

where $I_0=\frac{2et}{\hbar N}$. The sum in Eq. (7) runs from the bottom to the top of the energy bands, which depends on the electronic filling number of the ring. It should be noticed that electrons lying in the flat band will not contribute to the persistent current because the states in the flat band are localized states. Because there are N degenerated states in the flat band, the persistent currents for the ring with the electron number from $N+1$ to $2N$ are the same, namely, the phase parity of the persistent current for the odd-even electron number vanishes for the electron number N_e in the range of $N<N_e\leqslant 2N$. In Fig. 5(a) we show the persistent current of the ring with the electronic filling $N_e=N$ at room temperature. This phase locking effect results from the radicals in the ring, which is independent of the Peierls distortion. This effect arises also in the Anderson lattice model,[12] and a mesoscopic ring with a finite length lead.[8]

Physically, the persistent current depends on the magnetic flux, the Peierls distortion, and the temperature. As we know, the Peierls distortion opens an energy gap at Fermi level, which reduces the group velocity of the energy-band electrons, leading to the persistent current decreasing. The temperature suppresses the persistent current and the Peierls distortion due to the thermal fluctuation. However, the Peierls distortion decreasing will increase the persistent current. In

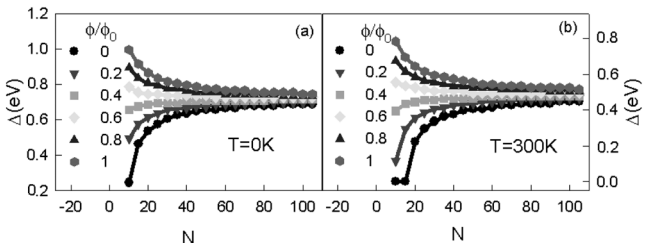

FIG. 4. The Peierls order parameter verus the ring size at zero temperature in (a) and at room temperature in (b).

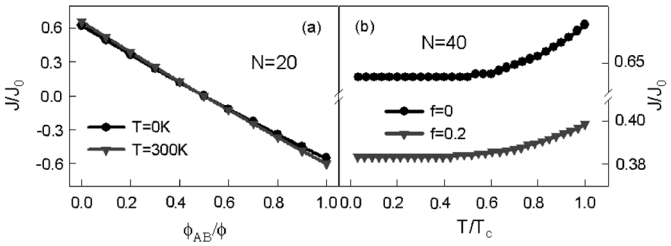

FIG. 5. The persistent currrent vs the magnetic flux in (a) and temperatures in (b).

other words, the temperature behavior of the persistent current depends on the competition between the thermal fluctuation and the effect of the Peierls distortion on the persistent current. We plot the persistent currents vs temperature for two different magnetic fluxes in Fig. 5(b). It is interesting that the persistent current slightly increases with an increase of temperature. This is because the effect of the Peierls distortion dominates the persistent current.

In summary, the theoretical study of the conducting polymeric mesoscopic ring reveals some interesting properties. The magnetic flux enhances the Peierls distortion for the small rings $N<50$. In the thermodynamical limit $N>80$, the Peierls order parameter will trend to about 0.7 and 0.5 eV in zero and room temperature, respectively. The persistent current indicates a phase locking effect for the electronic filling in the range of $N<N_e\leqslant 2N$ due to the flat energy band of this polymer ring. Because of the competition between the effects of the Peierls distortion and thermal fluctuation on the persistent current, the persistent current slightly increases with temperature increasing.

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