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Length- and parity-dependent electronic states in one-dimensional carbon atomic chains on C(111)

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Using first-principles density-functional theory calculations, we find dramatically different electronic states in the C chains generated on the H-terminated C(111) surface, depending on their length and parity. The infinitely long chain has π electrons completely delocalized over the chain, yielding an equal C—C bond length. As the chain length becomes finite, such delocalized π electrons are transformed into localized ones. As a result, even-numbered chains exhibit a strong charge-lattice coupling, leading to a bond-alternated structure, while odd-numbered chains show a ferrimagnetic spin ordering with a solitonlike structure. These geometric and electronic features of infinitely and finitely long chains are analogous to those of the closed (benzene) and open (polyacetylene) chains of hydrocarbons, respectively.

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In organic chemistry, compounds composed of carbon and hydrogen (called hydrocarbons) mainly contain two fundamental ingredients, benzene rings and straight chains. Benzene and polyacetylene are simple hydrocarbons that contain such fundamental ingredients separately. Although the C atoms in the two hydrocarbons have one p_z electron per C atom, the coupling of such π electrons with the lattice is totally different from each other. The π electrons in benzene are completely delocalized over the benzene ring with the sixfold rotational symmetry, resulting in an equal C—C bond length [see Fig. 1(a)].[1] On the other hand, those in polyacetylene are coupled with the lattice, giving rise to a bond-alternated structure $(\text{–CH}{=}\text{CH})_n$ with single and double bonds [see Fig. 1(b)].[2] These different characters of π electrons in benzene and polyacetylene are caused by their topologically different structures, i.e., closed and open chain structures, respectively.

We here illustrate the presence of the above-mentioned structural and electronic features of benzene and polyacetylene in a linear C chain formed on the H-terminated C(111) surface [see Fig. 1(c)]. This C chain can be fabricated by the selective removal of H atoms along the chain direction from the H-terminated C(111) surface using the scanning-tunneling microscope nanolithography technique.[3,4] The fabricated C chain has one p_z electron per C atom, identical to the cases of benzene and polyacetylene. Especially, one-dimensional (1D) systems where electrons are confined within only one direction exhibit the existence of the complex interplay between electron-phonon and electron-electron interactions, thereby giving rise to many exotic physical phenomena such as Peierls instability,[5] Jahn-Teller distortion,[6] spin polarization,[7] or the formation of non-Fermi-liquid ground states.[8]

In this Rapid Communication, our first-principles density-functional theory (DFT) calculations for 1D infinitely and finitely long C chains find various results with respect to the length and parity of the chains. The chain of infinite length has π electrons completely delocalized along the chain, leading to the absence of dimerization as well as spin orderings. On the other hand, the chains of finite length exhibit dimerization and spin ordering, depending on their parity. Even-numbered chains have a bond-alternated structure driven by

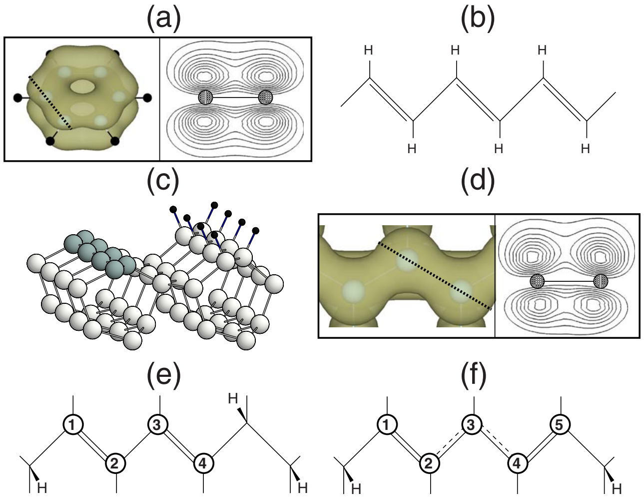

FIG. 1. (Color online) (a) Delocalized π electrons in benzene, (b) schematic diagram of the bond-alternated structure of polyacetylene, (c) linear C chain fabricated on the H-terminated C(111) surface, (d) delocalized π electrons in CC-∞, and schematic diagrams of (e) CC-4 and (f) CC-5. In (a) and (d), the contour plots of the charge density are also drawn in the vertical plane containing the C—C bond, where the first line is at 0.04 electrons/Å^3 with spacings of 0.03 electrons/Å^3. In (c), the large and small circles represent C and H atoms, respectively. For distinction, the C atoms composing the C chain are drawn in dark color.

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charge-lattice coupling while odd-numbered chains show a ferrimagnetic spin ordering where the spin density is distributed over the chain with a total spin moment of 1 μ_B. These localized π-electron characters in finitely long chains can be traced back to symmetry breaking due to the presence of their open boundaries. Therefore, the infinitely long chain that has an equal C—C bond length is in analogy with benzene, whereas the finitely long chains reproduce the geometric and electronic features of polyacetylene.[9,10]

The total-energy and force calculations were performed using nonspin-polarized or spin-polarized DFT within the generalized-gradient approximation.[11] The C and H atoms are described by ultrasoft[12] and norm-conserving[13] pseudopotentials, respectively. The surface was modeled by periodic slab geometry. Each slab contains eight C atomic layers plus one H atomic layer and the bottom C layer is passivated by one H atom per C atom. For simulations of the chains, we used a 4×6 unit cell that includes 12 C surface atoms along the chain direction and one additional H-passivated C chains parallel to the chain direction. The electronic wave functions were expanded in a plane-wave basis set with a cutoff of 25 Ry. The k-space integration was done with 32 $\mathbf{k}$ points in the 4×6 surface Brillouin zone. The present calculational scheme has been successfully applied for other diamond surfaces.[14]

We first optimize the atomic structure for an infinitely long C chain (hereafter designated as CC-∞). We find that CC-∞ exhibits the absence of Peierls dimerization or spin orderings. The C—C bonds in CC-∞ have an equal bond length of 1.45 Å, which is intermediate between single and double bond lengths. This symmetric structural feature of CC-∞ is analogous to benzene where the six C—C bonds are equal in length. Figure 1(d) shows that the π electrons in CC-∞ are delocalized along the chain, thereby being highly stabilized against bond alternation. This aspect of π electrons in CC-∞ is also present in benzene where the equivalent nature of the six C—C bonds is attributed to the delocalization of π electrons over the benzene ring [see Fig. 1(a)].

We continue to optimize the atomic structures for the C chains of finite length containing up to seven C atoms (designated as CC-2, CC-3, CC-4, CC-5, CC-6, and CC-7, respectively) using nonspin-polarized DFT calculations. These optimized structures will be termed the nonmagnetic (NM) configuration. Unlike the case of CC-∞, each chain of finite length shows bond alternation driven by electron-phonon coupling. To obtain the energy gain caused by such a Jahn-Teller distortion, we calculate the energy of the NM configuration relative to the *undistorted* NM configuration (designated as NM_0), in which the C atoms composing the chain are constrained to have no dimerization along the chain direction. The results with respect to the chain length are plotted in Fig. 2. The energy difference per C atom between the NM_0 and NM configurations is found to be 56, 54, and 42 (19, 24, 23) meV for CC-2, CC-4, and CC-6 (CC-3, CC-5, CC-7), respectively, indicating that even-numbered chains in which C atoms are paired have relatively larger Jahn-Teller energy gains compared to odd-numbered chains. Here, the presence of electron-phonon coupling reflects π-electron localization. Thus, it is interesting to examine the influence of magnetism on the chains of finite length where the electron-electron interactions among localized π electrons may be competing with the electron-phonon coupling.

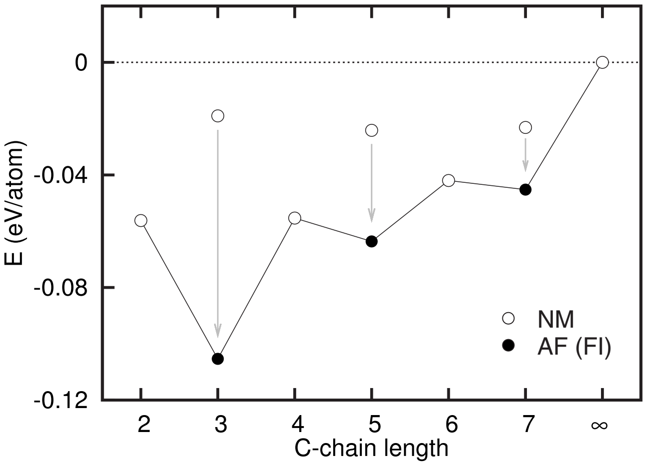

FIG. 2. Calculated energies of the NM and AF (FI) configurations relative to the NM_0 configuration as a function of the chain length.

For the C chains of finite length, we consider spin orderings within the ferromagnetic (FM) and antiferromagnetic (AF) configurations using spin-polarized DFT calculations. For even-numbered chains, we are not able to find any spin ordering. However, for odd-numbered chains, we find that the spins of adjacent π electrons are aligned antiferromagnetically. Here, our calculations starting with an initial FM configuration converged to the AF configuration. As shown in Fig. 2, the AF configuration for CC-3, CC-5, and CC-7 is energetically more favored over the NM configuration by 86 meV, 39 meV, and 22 meV, respectively. Therefore, the energy difference between the NM_0 and AF configurations for CC-3, CC-5, and CC-7 becomes 105 meV, 64 meV, and 45 meV, respectively, indicating that the stability of the AF configuration is relatively weakened with increasing the chain length.[15]

The calculated spin moment within the muffin-tin sphere centered at each C atom is given in Table I. We find that the opposing spin moments of neighboring C atoms are unequal, showing a ferrimagnetic (FI) spin ordering. Here, we note

TABLE I. Calculated spin moment (in μ_B) within the muffin-tin sphere centered at each C atom in odd-numbered chains. The muffin-tin sphere radius was chosen as 0.7 Å. The spin moments calculated from the Heisenberg Hamiltonian are also given.

	C_1	C_2	C_3	C_4	C_5	C_6	C_7
CC-3 (DFT)	0.22	−0.06	0.22				
CC-3 (model)	0.67	−0.33	0.67				
CC-5 (DFT)	0.17	−0.05	0.15	−0.05	0.17		
CC-5 (model)	0.51	−0.29	0.57	−0.29	0.51		
CC-7 (DFT)	0.13	−0.04	0.12	−0.05	0.12	−0.04	0.13
CC-7 (model)	0.42	−0.25	0.48	−0.30	0.48	−0.25	0.42

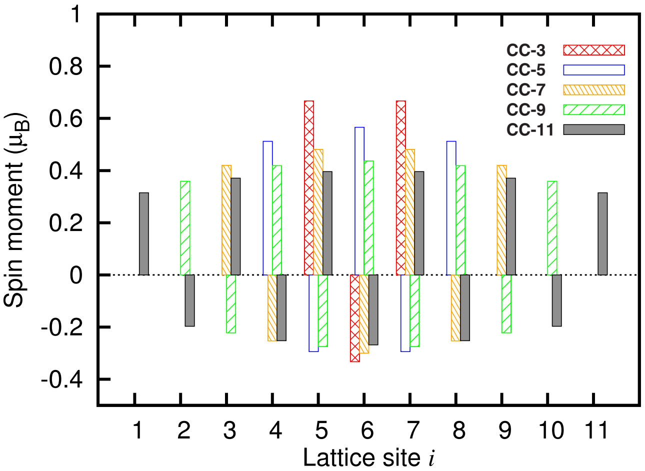

FIG. 3. (Color online) Local spin moments in odd-numbered chains containing up to $N=11$, calculated from the spin-1/2 Heisenberg Hamiltonian. On the x axis, $i=6$ represents the center site of each chain.

that the total spin moment in the unit cell is 1 μ_B. To understand the feature of the FI ordering in odd-numbered chains, we consider the spin-1/2 Heisenberg Hamiltonian (HH) $\hat{H} = J\Sigma_{i=1}^{N-1}\mathbf{S}_i\cdot\mathbf{S}_{i+1}$, where N is the number of C atoms in the chain. Since the z component of the total spin operator $\hat{S}_z \equiv \Sigma_{i=1}^{N}\hat{S}_{iz}$ commutes with $\hat{H}$, its eigenvalue S_z is a good quantum number. Here, $\hat{S}_{iz}$ is the z component of the local spin operator $\mathbf{S}_i$. The ground state of odd-numbered chains is twofold degenerate with $S_z=\hbar/2$.[16] We obtain the local spin magnetic moment $m_i = g\mu_B\langle\hat{S}_{iz}\rangle/\hbar$ at the site i by calculating the expectation value of $\hat{S}_{iz}$ for its broken-symmetry ground state. The results for odd-numbered chains containing up to $N=11$ are displayed in Fig. 3. We find that the local spin moments are aligned ferrimagnetically and that the sum of the local spin moments is 1 μ_B because of $S_z=\hbar/2$. Although the magnitude of the local spin moments calculated from the HH is larger than that of the DFT results within the muffin-tin sphere (see Table I), the ratios of up- and down-spin moments are qualitatively comparable with each other. Some deviations in these ratios between the HH and DFT results may be reduced by the inclusion of spin-Peierls (SP) effects in the HH model, as discussed below.

Table II shows the calculated C—C bond lengths ($d_{\text{C—C}}$) from the finitely and infinitely long chains. For CC-2, we obtain $d_{\text{C—C}}=1.37$ Å, assigning to a double bond. For CC-4 (CC-6), the values of $d_{\text{C—C}}$ are 1.39, 1.46, 1.39 (1.39, 1.47, 1.40, 1.47, 1.39) Å, indicating a bond-alternated structure with double and single bonds [see Fig. 1(e)]. However, this feature of bond alternation is frustrated in odd-numbered chains. The CC-3 chain has $d_{\text{C—C}}=1.42$ and 1.42 Å, intermediate in length between single and double bonds, and the CC-5 (CC-7) chain has $d_{\text{C—C}} = 1.41, 144, 1.44, 1.41 (1.41, 145, 1.43, 1.43, 1.45, 1.41)$ Å, resembling a solitonlike structure [see Fig. 1(f)] (Ref. 9)

TABLE II. Calculated C—C bond lengths (in Å) in finitely and infinitely long C chains.

	$d_{\text{C}_1\text{—C}_2}$	$d_{\text{C}_2\text{—C}_3}$	$d_{\text{C}_3\text{—C}_4}$	$d_{\text{C}_4\text{—C}_5}$	$d_{\text{C}_5\text{—C}_6}$	$d_{\text{C}_6\text{—C}_7}$
CC-2	1.37					
CC-3	1.42	1.42				
CC-4	1.39	1.46	1.39			
CC-5	1.41	1.44	1.44	1.41		
CC-6	1.39	1.47	1.40	1.47	1.39	
CC-7	1.41	1.45	1.43	1.43	1.45	1.41
CC-∞	1.45	1.45	1.45	1.45	1.45	1.45

where an isolated unpaired C atom exists on the center of the chain with a weak dimerization on the two sides of the chain. Here, the paired C atoms on the two sides of CC-5 and CC-7 has $d_{\text{C—C}}=1.41$, longer than $d_{\text{C—C}}=1.39$ Å in CC-4 and CC-6.

To account for the different bonding features of even- and odd-numbered chains, we study their electronic band structures, together with the charge and spin characters of subbands due to π electrons, so-called dangling-bond (DB) electrons. For CC-2, the charge characters of the DB states, DB$_1$ and DB$_2$, reveal the bonding and antibonding states, respectively [see Figs. 4(a) and 4(c)]. This manifests that the DB$_1$ state gives rise to dimerization. On the other hand, for CC-3, the two lower-lying occupied DB states, DB$_1$ and DB$_2$, show the majority- and minority-spin characters, respectively, mainly localized at the central atom C$_2$, while the highest occupied DB state, DB$_3$, is associated with the majority-spin density at the side atoms C$_1$ and C$_3$ [see Figs. 4(b) and 4(d)]. The sum of these spin densities of DB$_1$, DB$_2$, and DB$_3$ is close to the total spin density [see Fig. 4(e)] which represents a FI spin ordering. Such spin characters of the DB states in odd-numbered chains obviously weaken the C—C bonding, yielding the above-mentioned solitonlike structure [see Fig. 1(f)].

It is noteworthy that the delocalization of π electrons in infinitely long chain is broken as the chain length becomes finite. The resulting localized π electrons in finitely long chains give rise to not only dimerization in even-numbered chains, driven by electron-phonon coupling, but also the FI spin ordering in odd-numbered chains, caused by electron-electron interactions. The former can be described by the Su-Schieffer-Heeger (SSH) (Ref. 9) Hamiltonian which has successfully described dimerization in polyacetylene. Moreover, Hirsch and Grabowski[10] reported the presence of FI spin ordering in odd-numbered polyacetylene chains if the effect of on-site Coulomb repulsion U is included in the SSH Hamiltonian. Thus, it is likely that the physics of the present finitely long chains would be described by the so-called Peierls-Hubbard (PH) (Ref. 17) Hamiltonian. We note that, as the chain length is shorter, U is enhanced due to a more localizing feature of π electrons. In the $U\rightarrow\infty$ limit, the PH can be converted to the Heisenberg SP (Refs. 18 and 19) model defined by

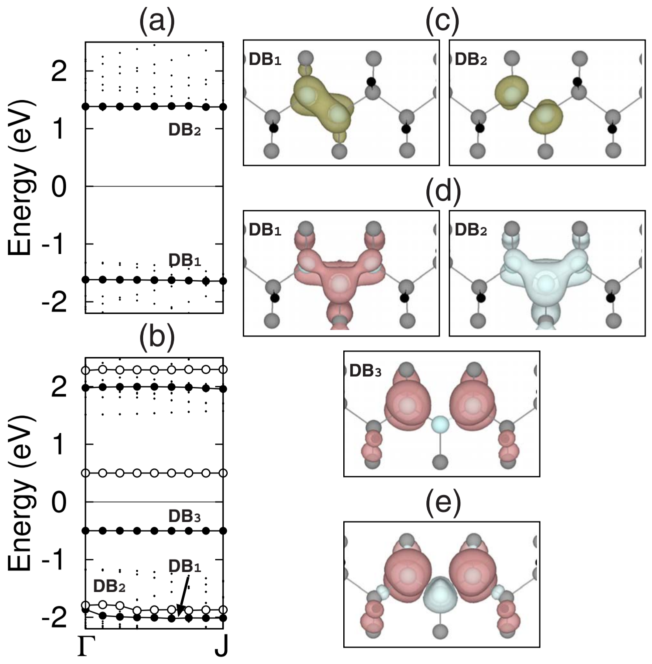

FIG. 4. (Color online) Calculated band structures of (a) CC-2 and (b) CC-3. The energy zero represents the Fermi level. The direction of Γ-J line is along the chain. In CC-2 (NM configuration), the solid circles represent the subbands due to the DB electrons, while in CC-3 (FI configuration), the solid and open circles represent the subbands of majority and minority spins, respectively. The charge and spin characters of subbands at the Γ point are also given in (c) and (d), respectively, where the charge (spin) density isosurface is shown at 0.04(0.02) electrons/Å^3. In (e), the total spin density isosurface is also shown at 0.02 electrons/Å^3.

$$\hat{H} = J\sum_i [1 + \alpha(q_{i+1} - q_i)]\mathbf{S}_i \cdot \mathbf{S}_{i+1} + \sum_i \left[\frac{p_i^2}{2M} + \frac{K}{2}(q_{i+1} - q_i)^2\right],$$

where q_i and p_i are the conjugate displacement and momentum operators for the ith site and α is the displacement-spin coupling constant. This SP Hamiltonian becomes the HH if the spin-Peierls effects are ignored. Thus, we believe that the SP model would reduce the above-mentioned deviations between the HH and DFT results for the ratio of spin moments. The detailed model analysis will be done in our future work.

In summary, for 1D C atomic chains generated on the H-terminated C(111) surface, we found a drastic change from delocalized to localized π-electron states as the chain length becomes finite, thereby giving rise to dimerization in even-numbered chains and the FI spin ordering in odd-numbered chains. These structural and electronic instabilities shown in the present system can also occur for other 1D C chains, which can be fabricated on the H-terminated graphene, graphite, and diamond surfaces.[20,21] Especially, the even-odd effects in various 1D C chains might be a promising perspective for the design of carbon-based devices for storages and processing of quantum information.

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[15] The weakened AF configuration with increasing the chain length can be associated with the decrease in the energy difference ΔE_{DB} between the lowest unoccupied and the highest occupied DB states: we obtain $\Delta E_{\mathrm{DB}}=1.00$ [see Fig. 4(b)], 0.75, and 0.61 eV for CC-3, CC-5, and CC-7, respectively.
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