Chiral solitons in a coupled double Peierls chain

Sangmo Cheon,1,2 Tae-Hwan Kim,1,2 Sung-Hoon Lee,1,2 Han Woong Yeom1,2*

Chiral edge states are the hallmark of two- and three-dimensional topological materials, but their one-dimensional (1D) analog has not yet been found. We report that the 1D topological edge states, solitons, of the charge density wave system of indium atomic wires self-assembled on a silicon surface have chirality. The system is described by a coupled double Peierls-dimerized atomic chain, where the interchain coupling induces dynamical sublattice symmetry breaking. This changes its topological symmetry from $Z_2 \times Z_2$ to $Z_4$ and ends solitons with a chiral degree of freedom. Chiral solitons can produce quantized charge transport across the chain that is topologically protected and controllable by the soliton’s chirality. Individual right- and left-chiral solitons in indium wires are directly identified by scanning tunneling microscopy.

Topological edge states that exist between two topologically distinct phases play a key role in quantum Hall insulators and topological insulators (1, 2). They are gapless and responsible for edge currents that are chiral in the sense that they propagate in one direction only (3, 4). The direction or chirality of the edge current in quantum Hall insulators depends on the sign of the difference of topological quantum numbers, called Chern numbers (5), of the two phases. The helical edge states of three-dimensional (3D) topological insulators are intrinsically chiral because they consist of two spin-dependent copies of chiral edge states for any transport axis at the surface (6, 7). Although the chirality is the essential feature of the edge states of 2D and 3D topological materials, there is no direct analog in 1D. Peierls-dimerized atomic chains such as polycetylene (8) are prototypical 1D topological materials (9) and have topological edge states, known as Jackiw-Rebbi solitons (10), but they do not have chirality. In fact, “chiral” solitons are difficult to define because currents cannot be defined at the zero-dimensional edges (11). There have been theoretical proposals for nontrivial solitons, such as irrationally charged solitons (13-17), but no efforts have been made to endow solitons with chirality.

Here, we report that the 1D charge density wave (CDW) system of indium atomic wires self-assembled on a silicon surface (18-22) has chiral solitons, where the chirality is defined through dimensional extension by adiabatic phase evolution (23-25). The indium wire is described by a coupled double Peierls-dimerized atomic chain with four degenerate ground phases. The interchain coupling induces dynamical breaking of the sublattice symmetry and results in three types of topological edge states—right-chiral, left-chiral, and nonchiral solitons—each having distinct off-midgap electronic states. The three types of solitons are identified with scanning tunneling microscopy and spectroscopy (STM/STS).

In our system, indium atoms deposited on the Si(111) surface at an elevated temperature self-organize into an ordered array of metallic wires (18). Each wire consists of two zigzag chains of indium atoms (Fig. 1A) (19) and possesses three metallic bands crossing the Fermi level at room temperature (20), as shown in the band structure (Fig. 1B) obtained from density functional theory (DFT) calculations (20, 26). It undergoes a period-doubling CDW transition at around 125 K (18) to form the characteristic hexagon structure (20), mainly through the Peierls dimerization along the two outer indium rows (21). In this CDW state, one of the three surface bands ($S_3$) is lifted up above the Fermi level and the other two bands ($S_1$ and $S_2$) mix to open a band gap (22). The latter two bands play the major role in the CDW and soliton formation, as described below.

To study coupled Peierls chains, we generalized the tight-binding Su-Schrieffer-Heeger (SSH) Hamiltonian for a single Peierls chain (8, 26). In the single-chain SSH model of half-filled $p$ orbitals, a spontaneous Peierls dimerization occurs with two possible dimer configurations (A and B phases in Fig. 1C) to gain electronic energy by opening a CDW gap (27). For a double chain with finite interchain hopping (insets of Fig. 1A), the half-filled band of each chain couples to form two split bands, $S_1$ and $S_2$ (Fig. 1D). The coupled chains also undergo a metal-insulator transition via the Peierls dimerization that occurs simultaneously in both chains. The ensuing structure allows for a mixing of $S_1$ and $S_2$, resulting in a characteristic double Peierls gap. The band structures of this double-chain model (Fig. 1D)

---

1 Center for Artificial Low Dimensional Electronic Systems, Institute for Basic Science (IBS), Pohang 790-784, Korea.
2 Department of Physics, Pohang University of Science and Technology (POSTECH), Pohang 790-784, Korea.
*Corresponding author. E-mail: shlee@ibs.re.kr (S.H.L.); yeom@postech.ac.kr (H.W.Y.)
reproduce the two characteristic bands of indium wires (Fig. 1B) for both metallic and CDW phases. Here, the particular type of the interchain coupling, the zigzag geometry, is crucial to reproduce these electronic structures (Fig. S1).

As a consequence of the dimerization on both chains, the double chain has four degenerate ground phases (Fig. 2A), which are denoted as AA, BA, BB, and AB. This double-chain model describes correctly the fourfold degeneracy of the hexagon structure of the indium wire, which was well established experimentally (20, 21). Without the interchain coupling, the four ground states are simply a trivial product of the degeneracy of the interchain coupling, the four ground states AA, BA, BB, and AB. This double-chain model describes the fourfold degeneracy of the AA, BA, BB, and AB. This double-chain model describes the fourfold degeneracy of the AAB, BAA, BAB, and ABB configurations of four equivalent ground phases (fig. S3). This result and the C4 symmetry indicate that the double Peierls chain has a unique topological band structure with the cyclic Z4 symmetry. Whereas the two degenerate phases of a single Peierls chain result in a pair of soliton and antisoliton, the four degenerate phases dictate 12

Fig. 2. Four degenerate ground phases. (A) Atomic configurations of four equivalent ground phases—AA, BA, BB, and AB—of a coupled double Peierls chain. (B) Total energy surface in the phase space of dimerization displacements of each chain (Δ1, Δ2). (C) Sublattice pseudospin of each Bloch state for each chain, color-coded in the band structure, for the AA and BA phases. The plot labeled by θ describes the polar component of the pseudospin vector—i.e., the direction in the Sx−Sz plane. The sign of Sx is labeled at band edges. The plot labeled by θ describes the polar component of the pseudospin vector—i.e., the Sx value. The sign of Sz is labeled at band edges. (D) Diagram of topological solitons for the double chain. Owing to the fourfold rotational symmetry, 12 solitons are grouped into three types: right-chiral (R), left-chiral (L), and nonchiral (N) solitons.

Fig. 3. Chiral solitons. (A) Schematics of solitons and wave functions of primary soliton states for each type of soliton. Unpaired kink sites are marked by black arrows. The ovals are guides for comparison with the STM images in Fig. 4B. Soliton wave functions are represented by sublattice pseudospin vectors for every pair of atoms. (B) Band structure of a double Peierls chain of a finite length (left), where the momentum (kx) is taken as a parameter for the phase evolution of AA BA AA, and the illustration of corresponding chiral edge currents in the 2D real space of a cylindrical geometry (right), where the y coordinate corresponds to the frequency domain of the phase evolution. The red and cyan bands correspond to localized edge states at left and right edges, respectively. (C) Center of the bonding charges of each phase. The phase evolution of AA BA AA leads to charge pumping from the right edge to the left.
solitons among them (Fig. 2D). They can be categorized into three types owing to the $C_2$ symmetry: right-chiral (R), left-chiral (L), and nonchiral (N) solitons. The chiral nature of the soliton will be elaborated below. Figure 3A shows the schematic structures of three representative solitons and their soliton wave functions in a pseudospin description: $AA \rightarrow BA, AB \rightarrow BB$, and $AA \rightarrow BB$. The unpaired kink site in the right-chiral soliton has a different interchain coupling and thus has a different sublattice potential from that in the left-chiral soliton, and the nonchiral soliton has two unpaired kink sites, one at each chain. The different sublattice potentials are reflected in the wave functions: The sublattice pseudospins along the chain helically rotate in opposite directions in the right-chiral and left-chiral solitons, whereas their direction is fixed for the nonchiral soliton.

The three types of solitons have distinct electronic spectra (Fig. 4A). All solitons have two states within the gap but at different energies: The right-chiral (left-chiral) soliton has both states below (above) the midgap, but the nonchiral one has one below and the other above the midgap. For the nonchiral soliton, the two gap states are simply the bonding and antibonding states of the two soliton states of each chain. For the chiral solitons, consider the right-chiral $AA \rightarrow BA$ soliton as an example. When the interchain coupling $\delta$ is zero, it has a soliton state at chain 1 at zero energy, with a charge of $e$ when occupied (adding contributions from both spins) ($8, 10$). As $\delta$ increases, the energy level is lowered by an induced sublattice potential and the charge state decreases from $e$, similarly to the Rice-Mele model ($13, 14$). On the other hand, the induced sublattice potential of chain 2 exhibits a sign inversion near the kink of chain 1 and produces another soliton state emerging from the valence band edge with a small irrational charge ($26$). Interestingly, the total charge of the two soliton states is conserved to be $e$, regardless of the size of $\delta$, owing to the $C_2$ symmetry. Thus, when the Fermi level is at the midgap, the right-chiral soliton is negatively charged by $e$, and similarly the left-chiral soliton is positively charged, whereas the nonchiral soliton is neutral. This integer charge state has an important consequence in the charge-transfer behavior, as discussed below.

The three types of solitons are indeed observed in indium wires. Figure 4B displays STM images of indium wires with different solitons. The left and right sides of these wire segments correspond to different ground phases with kink sites at their interfaces. The CDW crests are translated or flipped across the kink sites. The nonchiral soliton was analyzed previously ($27$) and can largely be understood by two normal solitons at each chain. However, for the chiral solitons, the detailed STM line profiles indicate a distinct structural property (Fig. 4C). Whereas the chain with a kink shows a typical soliton profile of a hyperbolic tangent function, the other single-phase chain exhibits a small double-dip amplitude modulation. These structural features are well reproduced by the calculated atomic displacement fields of the double Peierls chain model (Fig. S8). Beyond the structures, the STS revealed distinct local density of states (LDOS) for three different solitons (Fig. 4A). The right-chiral (left-chiral) soliton sites show strong LDOS enhancements near the bottom (top) of the band gap but the nonchiral solitons near both the bottom and top of the gap. This agrees reasonably well with the model calculations, considering the limited resolution of the STS data.

The concept of the “chiral” soliton that we propose is inherited from the chiral edge states of 2D quantum Hall systems. Consider a cyclic phase evolution of the 1D system along $AA \rightarrow BA \rightarrow BB \rightarrow AB \rightarrow AA$. This evolution corresponds to transporting four right-chiral solitons sequentially through the chain from the right edge to the left. It is topologically nontrivial in the sense that it encircles the origin in the $(\delta_1, \delta_2)$ space (Fig. 2D), where the origin is singular with a zero band gap. An effective 2D Hamiltonian of the system, with the second dimension in the momentum space being the cyclic evolution ($25$), represents a Chern insulator with a Chern number of $-2$ ($26$), corresponding to a double sheet of the Haldane’s honeycomb lattice model for the quantum Hall effect ($4$). Figure 3B shows the band structure of a finite-length chain under the cyclic evolution. There are four topologically protected edge states crossing the zero energy, two localized at the left edge and the others at the right edge.

**Fig. 4. Experimental observation.** (A) (Left) Calculated eigenvalue spectra of each type of soliton. All solitons have two in-gap states. (Center) LDOS obtained by STS measurements at the center of each soliton site (solid lines), in comparison with that at a CDW ground state (dashed lines). (Right) Position-dependent LDOS data. The blue region of low LDOS represents the energy band gap. The center position of each soliton is marked by an arrow at the top. $a_x$ is the “x1” period along the chain (3.84 Å). (B) STM images of each type of soliton. The red and blue triangles are guides for local phases at each chain. A and B, respectively. The short lines on the right indicate where the line profiles of Fig. 4C are taken. (C) STM line profiles along the upper (chain 1) and lower (chain 2) parts of an indium wire. The STM line profiles (black) were band-pass filtered and corrected to include the effect of lattice modulation and Friedel oscillation (fig. S7). The cyan lines are fitted soliton profiles convoluted with the CDW modulation. The red and blue lines are fitted soliton profiles, with the color indicating the local phase.
Finding optimal surface sites on heterogeneous catalysts by counting nearest neighbors

Federico Calle-Vallejo, Jakub Tymoczko, Viktor Colic, Quang Huy Vu, Marcus D. Pohl, Karina Morgenstern, David Loffreda, Philippe Sautet, Marcus D. Pohl, Karina Morgenstern, David Loffreda, Philippe Sautet, Aliaksandr S. Bandarenka

A good heterogeneous catalyst for a given chemical reaction very often has only one specific type of surface site that is catalytically active. Widespread methodologies such as Sabatier-type activity plots determine optimal adsorption energies to maximize catalytic activity, but these are difficult to use as guidelines to devise new catalysts. We introduce “co-ordination-activity plots” that predict the geometric structure of optimal active sites. The methodology is illustrated on the oxygen reduction reaction catalyzed by platinum. Sites with the same number of first-nearest neighbors as (111) terraces but with an increased number of second-nearest neighbors are predicted to have superior catalytic activity. We used this rationale to create highly active sites on platinum (111), without alloying and using three different affordable experimental methods.

Slight changes in the surface structure of catalytic materials can have large impacts on the products and energetics of chemical reactions (1, 2). However, not all sites at catalytic surfaces have the same activity or selectivity, which gives rise to the concept of structure sensitivity (3–5). Generally, identification of active sites is a challenging task that requires the combination of several approaches (6, 7). A rational way of designing catalysts should first identify the optimal active sites and then engineer surfaces with the presence of such sites is maximized. Modern computational screening techniques can provide the atomic-scale insight needed to elaborate simple catalyst design rules (2, 6). Such rules are the starting point to engineer target active sites on catalytic surfaces (9–12). The connection between these two steps must be straightforward and clear, which is not trivial in practice. The difficulties originate from an important detail: Existing computational techniques outline optimal energetic properties, which can be met by countless materials. Therefore, it is desirable to create procedures that generate more precise design rules.

Consider the specific case of the oxygen reduction reaction (ORR), \( \text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O} \), a