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Authors

Pham, Thang

Oh, Sehoon

Stetz, Patrick

et al.

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NANOMATERIALS

Torsional instability in the single-chain limit of a transition metal trichalcogenide

Thang Pham^{1,2,3,4}, Sehoon Oh^{1,2}, Patrick Stetz^{1,2,4}, Seita Onishi^{1,2,4*}, Christian Kisielowski⁵, Marvin L. Cohen^{1,2}, Alex Zettl^{1,2,4,†}

The scientific bounty resulting from the successful isolation of few to single layers of two-dimensional materials suggests that related new physics resides in the few- to single-chain limit of one-dimensional materials. We report the synthesis of the quasi-one-dimensional transition metal trichalcogenide NbSe₃ (niobium triselenide) in the few-chain limit, including the realization of isolated single chains. The chains are encapsulated in protective boron nitride or carbon nanotube sheaths to prevent oxidation and to facilitate characterization. Transmission electron microscopy reveals static and dynamic structural torsional waves not found in bulk NbSe₃ crystals. Electronic structure calculations indicate that charge transfer drives the torsional wave instability. Very little covalent bonding is found between the chains and the nanotube sheath, leading to relatively unhindered longitudinal and torsional dynamics for the encapsulated chains.

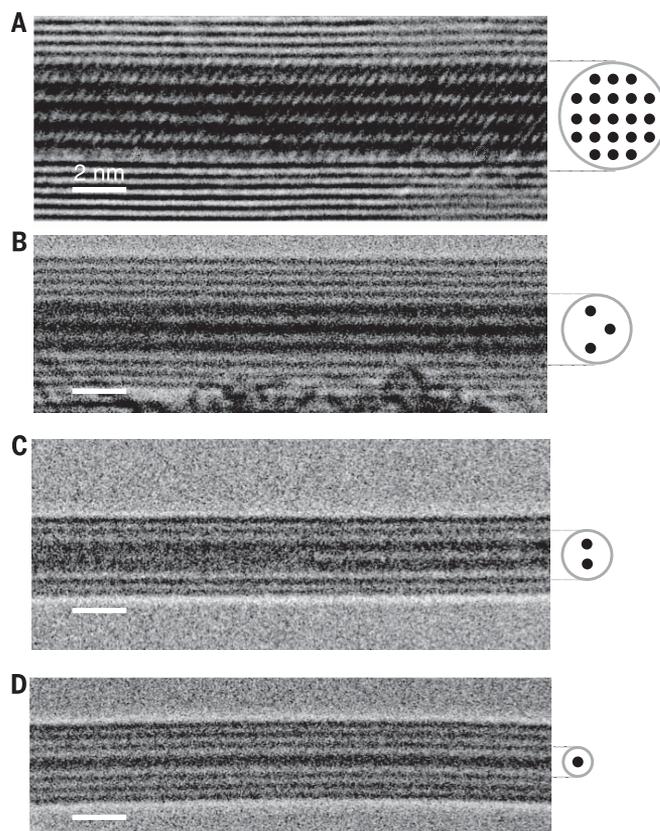
The successful isolation of monolayers of van der Waals-bonded quasi-two-dimensional solids such as graphite (1) and the transition metal dichalcogenides (TMDs) (2) has spurred intense experimental and theoretical interest in these low-dimensional materials. Monolayer or few-layer sheets of graphene or TMDs often display electronic, optical, and structural properties that are markedly different from those of the bulk materials. The thin materials have profound underlying physics and far-ranging applications potential (3). Transition metal trichalcogenides (TMTs) such as NbSe₃ and TaS₃ are closely related van der Waals-bonded quasi-one-dimensional compounds that have been extensively studied in bulk form. These materials can support unusual ground states and collective-mode electronic transport (4). Although some attempts have been made to study thinned TMTs [e.g., NbSe₃ samples have been cleaved down to ~200 chains in width (5)], no experimental or theoretical study has examined TMTs in the single- or few-chain limit. It is far more difficult to isolate and manipulate atomic chains than atomic sheets, and atomically thin samples can be highly air-sensitive (6).

We present a facile and effective method to prepare low-number chains of NbSe₃ within carbon and boron nitride nanotubes (CNTs and BNNTs). The spatial confinement promotes and

stabilizes the growth of sub-unit cell NbSe₃ down to triple, double, and even single atomic chains. Encapsulation additionally protects the chains from environmental oxidation and facilitates easy handling and characterization. The chains are mobile within the tubes. Unusual helical torsional waves with regular periodicity are observed, even in the single-chain limit. Complete

Fig. 1. Isolation of one-dimensional TMT materials down to single-chain limit.

High-resolution TEM images of (A) ~20 chains, (B) triple chain, (C) double chain, and (D) single chain of prototypical TMT NbSe₃ encapsulated within CNTs [(A) to (C)] and a BNNT (D). The simplified cross-sectional schematics show different numbers of chains encapsulated in tubes of different inner diameters; in this representation, the electron beam impinges horizontally, normal to the tube axis. In (A), atoms appear bright (overfocus); in (B) to (D), atoms appear dark (underfocus). The nanotubes serve as nano-reaction chambers to grow the isolated TMT chains and simultaneously protect them from environmental degradation.



mentary theoretical calculations show that the electronic band structure of NbSe₃ is highly dependent on chain number and orientation, and that the torsional wave instability is driven by charging of the chains. We term this phenomenon a charge-induced torsional wave (CTW).

NbSe₃ chains are directly grown via vapor transport inside the hollow cavity of preformed and open-ended multiwall CNTs and BNNTs (7). Related techniques have previously been used to encapsulate foreign species within nanotubes (8–11). Once the synthesis is complete, the samples can be exposed to air and liquids with no apparent degradation of the encapsulated chains.

Figure 1 shows high-resolution transmission electron microscopy (HRTEM) images of NbSe₃ chains encapsulated within nanotubes. The structure of numerous (~20) chains encapsulated by a CNT of inner diameter 3.86 nm (Fig. 1A) resembles that of the bulk crystal, with signature one-dimensional (untwisted) chains oriented along the axis of the nanotube. By using nanotubes with smaller inner diameter, fewer parallel NbSe₃ chains are isolated, strictly by geometrical constraint, within the cross section of the tube. Shown in Fig. 1, B to D, are triple-, double-, and single-chain NbSe₃ encapsulated within CNTs [(B) and (C)] or BNNTs (D) with successively smaller inner diameters of 2.49 nm, 1.87 nm, and 1.21 nm. This demonstrates that isolated single chains of TMTs can indeed be stabilized. We note that the unit cell of bulk NbSe₃ contains six chains (12), so even the three-chain specimen is well below the single-unit cell limit.

¹Department of Physics, University of California, Berkeley, CA 94720, USA. ²Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA. ³Department of Materials Science and Engineering, University of California, Berkeley, CA 94720, USA. ⁴Kavli Energy NanoSciences Institute, University of California, Berkeley, CA 94720, USA. ⁵Molecular Foundry and Joint Center for Artificial Photosynthesis, Berkeley, CA 94720, USA.

*Present address: Max Planck Institute for Chemical Physics of Solids, 01187 Dresden, Germany.

†Corresponding author. Email: azettl@berkeley.edu

Quantitative chemical analysis of encapsulated TMT chains by means of energy-dispersive spectroscopy (fig. S1) yields 75.65 ± 7.57 atomic percent (at %) Se and 24.35 ± 4.26 at % Nb. Although the NbSe₃ chains in the few-chain limit encapsulated within nanotubes have the same stoichiometry as the bulk material, as well as a similar local trigonal-prismatic atomic structure, the chains do not precisely adopt the internal configuration found in bulk crystals. Rather, the chains are twisted, supporting a static helical torsional wave. This is true even for an isolated single chain. For double or triple chains, the strands additionally twist around each other to form double or triple helices, much like double-helix DNA or the strands in a multiwire steel cable. Figure 2A shows an aberration-corrected phase-contrast TEM (AC-TEM) image of a single NbSe₃ chain inside a double-walled CNT. The atomic model and the corresponding TEM simulation by the multislice method are also shown. The experimental image, model, and simulated image confirm the alternating orientations of the chain (i.e., the twisting of the chain). The wavelength of the associated static torsional wave (i.e., the distance for a full 2π rotation) is approximately 41 nm.

Shown in Fig. 2, B and C, are additional TEM images of the spiraling behavior of double- and triple-chain specimens, respectively. For the double chain (here encapsulated within a BNNT), the additional twisting is not strictly periodic; there are regions where the two strands run parallel without spiraling about each other. On the other hand, for triple chains, we invariably find that the three chains are consistently tightly twisted around each other in a triple-helix fashion. Figure 2D shows an AC-TEM image of such a triple-chain configuration within a CNT. For triple chains, we find a spiraling node-node distance ranging from 1.45 to 1.85 nm within CNTs and 1.90 to 2.30 nm within BNNTs (fig. S2B). (In the simplest interpretation, the full wavelength of the torsional wave in this case is here 6 times the node-node distance, notwithstanding additional complexities of on-chain twisting.)

Stimulation from the TEM imaging electron beam often causes the chains to bodily transport axially along the core of the tube. In addition, the wave itself can propagate along the TMT. For CNTs, charging of the chains, which is key to the torsional wave instability, comes primarily from electron transfer from the CNT to the chain, whereas for BNNTs, the insulating nature of the host tube amplifies charging effects from the TEM beam (either directly from the beam current or indirectly from radiolysis processes of the BN shell or hydrocarbon contaminants nearby) (13, 14) and leads to in situ twisting and untwisting of the chains (as seen in Fig. 2B).

To explore the underlying physics of the above systems, we performed first-principles calculations based on pseudopotential density functional theory (DFT) (15). We first investigated the atomic and electronic structure of single-chain NbSe₃ isolated in vacuum. We constructed three initial candidate structures for the chain using

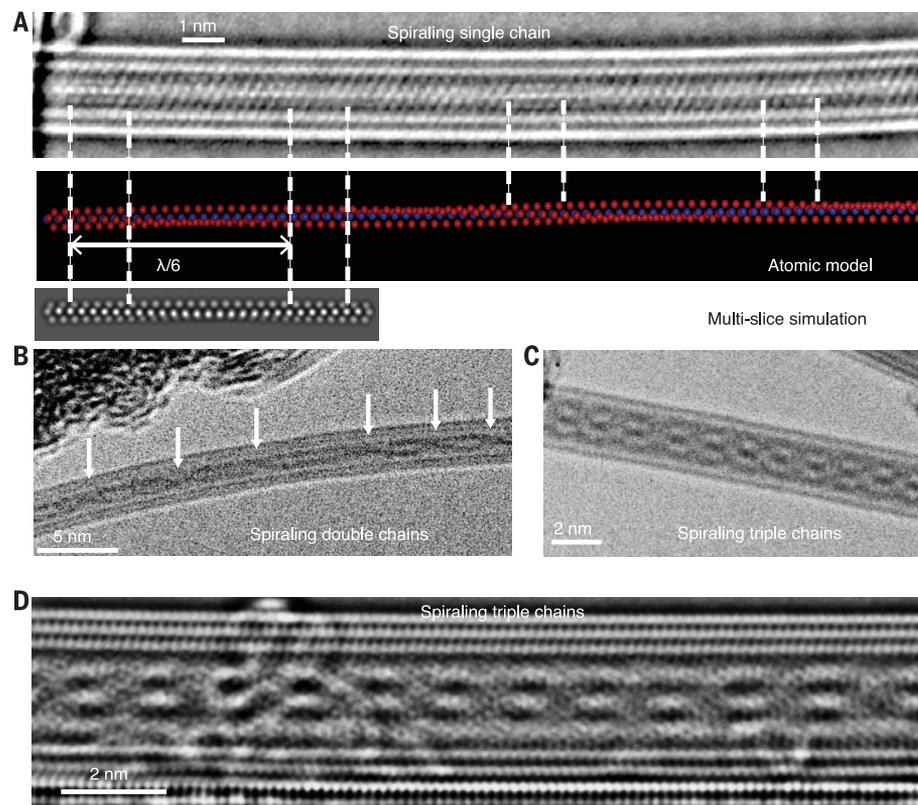


Fig. 2. Torsional waves of TMT chains. (A) Atomic-resolution phase-contrast TEM image of a spiraling single chain of NbSe₃ isolated inside a double-walled CNT. The structure of the single chain contains repeated patterns corresponding to different projected orientations along its length; the dashed vertical lines delineate the repeated patterns. As illustrated in the atomic model (red, Se; blue, Nb) and multislice simulation, the single chain forms spirals with 60° rotation ($2\pi/6$ or $\lambda/6$) every ~ 6.8 nm. (B to D) The torsional waves in higher-order chains (double and triple chains). (B) HRTEM image of spiraling double chains of NbSe₃ within a BNNT. The structure contains several aperiodic twisting nodes, as indicated by the white arrows. (C) HRTEM image and (D) typical AC-TEM image of spiraling triple chains. Triple chains of NbSe₃ exhibit long-range twisting with well-ordered torsional wavelengths. In (A) and (D), atoms appear bright (overfocus); in (B) and (C), atoms appear dark (underfocus).

the atomic positions of the three different types of chains comprising the bulk solid (16) (fig. S5). The atomic positions for the candidate structures were fully relaxed by minimizing the total energy. All three candidates relaxed into the same atomic structure (Fig. 3A), whose corresponding band structure is shown in Fig. 3B with two bands (Ψ_1 and Ψ_2) crossing the Fermi energy.

We investigated the atomic and electronic structures for the untwisted single-chain NbSe₃ encapsulated inside an (8,8) CNT (indices chosen for convenience) (Fig. 3C). The separately relaxed atomic positions of single-chain NbSe₃ isolated in vacuum, and those of the empty CNT, were used. Further relaxation was not performed. We calculated the binding energy E_b of a single-chain NbSe₃ (fig. S6), which is defined as $E_b = E_{\text{NbSe}_3} + E_{\text{CNT}} - E_{\text{NbSe}_3/\text{CNT}}$, where E_{NbSe_3} and E_{CNT} are the total energies of separated single-chain NbSe₃ and CNT isolated in vacuum, and $E_{\text{NbSe}_3/\text{CNT}}$ is the total energy of the joint system of single-chain NbSe₃ encapsulated inside the CNT. The calculated binding energy of the chain is 1.36 eV per NbSe₃ formula unit (f.u.). This large binding

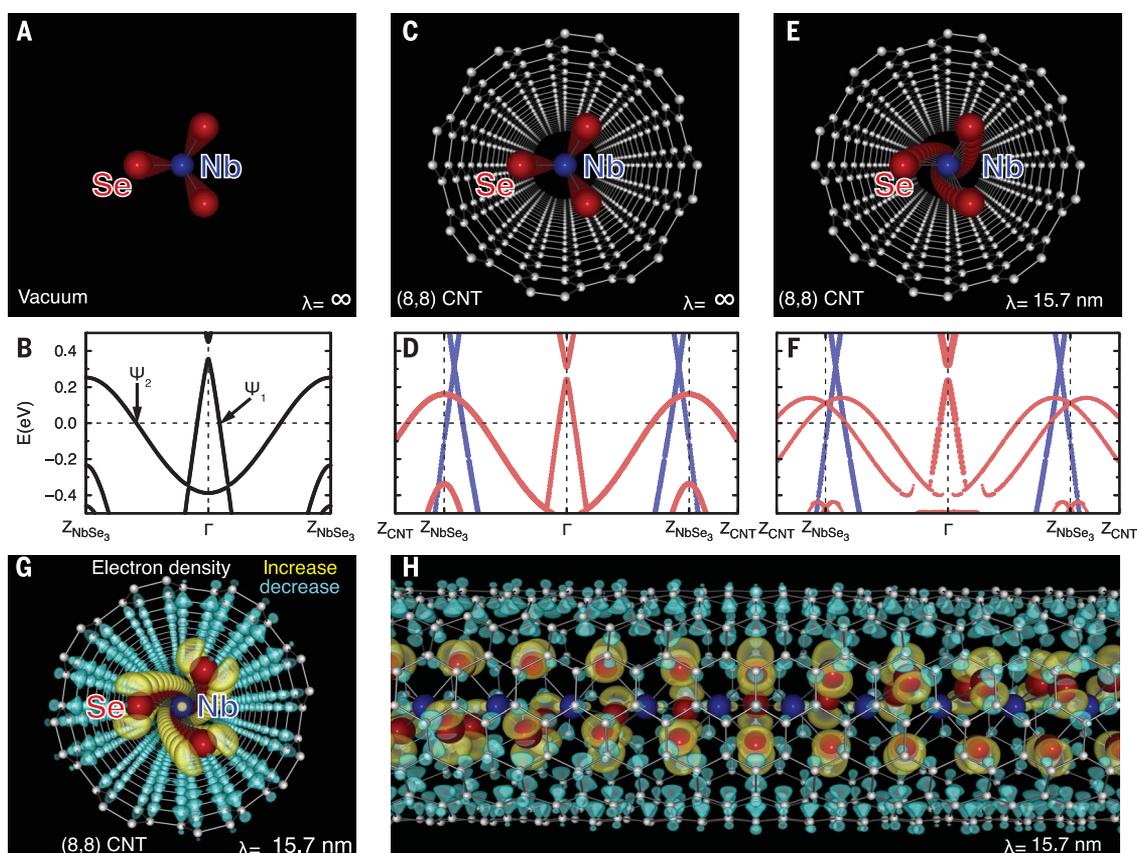
energy accounts for the stability of single-chain NbSe₃ encapsulated inside CNTs. Figure 3D shows the electronic band structure of the chain inside the CNT. Confinement does not alter the states near the Fermi energy appreciably, except for the charge transfer. Charge (0.23 e/f.u.; i.e., 0.08 e per Se atom) is transferred from the CNT to the NbSe₃ chain (fig. S7), driven by the work function difference. We found no appreciable amount of covalent bonding between the chain and CNT (Fig. 3, G and H, and figs. S7E and S8), which explains the high mobility of the chain inside the CNT.

Motivated by the experimentally observed torsional wave in single-chain NbSe₃, we investigated the atomic and electronic structures for the twisted single chain encapsulated inside a CNT with a variable torsional wavelength λ . Figure 3, E and F, shows the atomic and electronic structures of the twisted single chain with $\lambda = 15.7$ nm (7). The torsional wave shifts Ψ_2 by $\pm 6\pi/\lambda$, whereas Ψ_1 is not affected appreciably. The torsional wave does not change the binding energy and the charge transfer appreciably,

Fig. 3. Calculated atomic and electronic structures of single-chain NbSe₃. (A, C, and E) Atomic structures and (B, D, and F) corresponding electronic band structures of single-chain NbSe₃ isolated in vacuum [(A) and (B)],

untwisted single-chain NbSe₃ encapsulated inside an (8,8) CNT [(C) and (D)], and twisted single-chain NbSe₃ with $\lambda = 15.7$ nm within the (8,8) CNT [(E) and (F)].

In the axial views of the atomic structures, blue, red, and white spheres represent Nb, Se, and C atoms, respectively. In the band structures, the Fermi energy is set to zero and marked with a horizontal dashed line. In (D) and (F), the band structures represented by red dots are projected onto the chain and unfolded with respect to the first Brillouin zone of the unit cells of the untwisted chain, where Z_{NbSe_3} denotes the zone boundaries for the chain; structures represented by blue dots are projected onto the CNT and unfolded with respect to the first Brillouin zone of the unit cells of the CNT, where Z_{CNT} denotes the zone boundaries for



the CNT. Γ denotes the center of the Brillouin zone ($k = 0$). (G and H) Electron density transferred from the CNT to the chain with $\lambda = 15.7$ nm [axial (G) and lateral (H) views]. Isosurfaces for increased and decreased values are shaded in yellow and cyan, respectively.

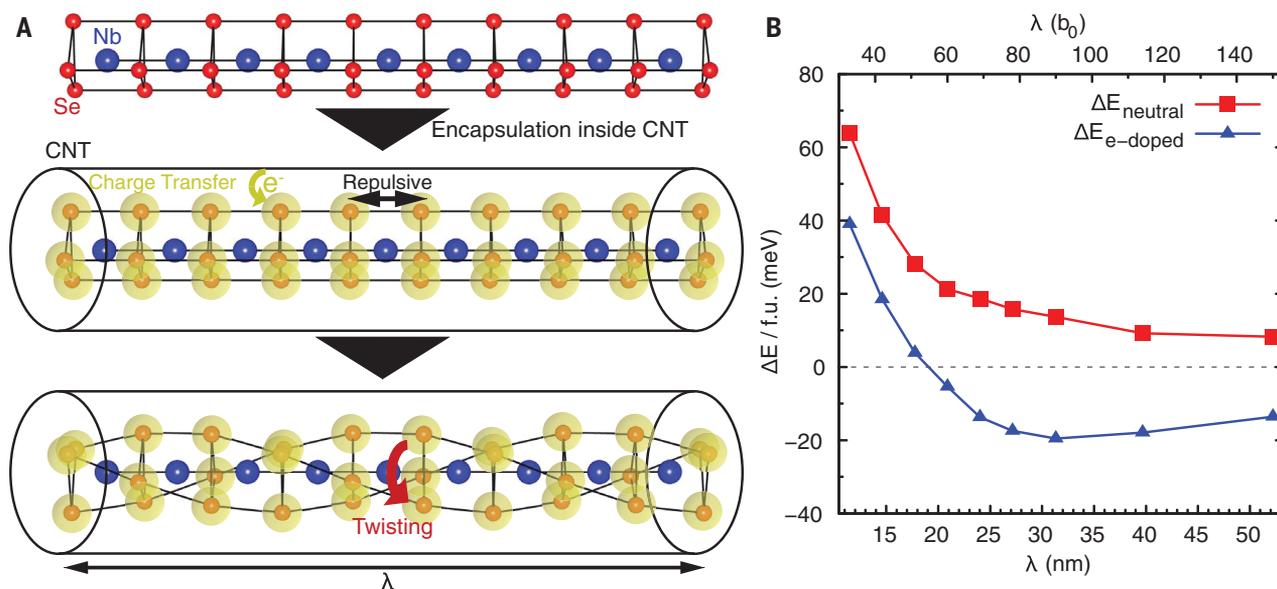


Fig. 4. Charge-induced torsional waves (CTWs) in single-chain NbSe₃. (A) Schematic showing the proposed mechanism of CTW formation in single-chain NbSe₃ inside a CNT. (B) Total energies for neutral and electron-doped single-chain NbSe₃ isolated

in vacuum as functions of λ . $E(\infty)$ is set to zero and marked by a horizontal dashed line; $b_0 = 3.4805$ Å is the distance between the adjacent Nb atoms. Negative ΔE means that a CTW is favored.

and the calculated binding energies are 1.35 to 1.36 eV/f.u. with an electron transfer of 0.23 e/f.u. for all the calculated λ s, as for the untwisted chain.

What drives the torsional wave? There are two main contributions. The torsional wave increases the elastic energy by twisting the orbital configuration of the Nb atoms, but this is offset by a reduction in Coulomb energy between negatively charged Se atoms. To quantify these effects, we calculated the total energies of a twisted single-chain NbSe₃ isolated in vacuum with and without additional electron doping. To obtain the energy increase by twisting, we calculated the total energy difference $\Delta E_{\text{neutral}}$ of a twisted single chain isolated in vacuum as a function of λ , defined as $\Delta E_{\text{neutral}}(\lambda) = E_{\text{NbSe}_3}(\lambda) - E_{\text{NbSe}_3}(\infty)$, where $E_{\text{NbSe}_3}(\infty)$ is the total energy of the untwisted single chain isolated in vacuum. As shown in Fig. 4B, $\Delta E_{\text{neutral}}$ increases as λ decreases. We also obtained the energy difference $\Delta E_{\text{e-doped}}$ for an electron-doped single chain isolated in vacuum as a function of λ by performing the same calculation with additional electron doping, where we added 0.23 e/f.u. to match the encapsulated situation. For $\lambda > 20$ nm, $\Delta E_{\text{e-doped}}$ is negative and the wave distortion is favorable. Within a device configuration, it should be possible to fur-

ther control the charge transfer to the TMT chain(s), allowing external control of the torsional wave and thereby its optical and electronic transport properties.

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SUPPLEMENTARY MATERIALS

www.sciencemag.org/content/361/6399/263/suppl/DC1
Materials and Methods
Supplementary Text
Figs. S1 to S8
References (17–25)

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Oscillating one-dimensional chains

The confinement of materials to nanoscale dimensions often reveals properties not seen in bulk materials. Pham *et al.* confined NbSe₃ within carbon nanotubes (a conductor) or boron nitride nanotubes (an insulator). Transmission electron microscopy revealed an oscillatory motion of the confined chains not observed in bulk crystals. Electronic structure calculations showed that charge transfer drives the torsional wave instability, and the limited covalent bonding between the chains and the nanotube sheath allows unhindered dynamics. Application of an external potential applied to the nanotube should directly affect the torsion and thus lead to different optical and electron transport properties.

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