4. One-dimensional systems

• Contents

• Introduction
• Classification and fabrication techniques
  • 1D metals, polymers
  • Carbon nanotubes
  • Semiconductor wires
  • Metallic wires obtained by MCBJ technique and STM
  • Metallic wires obtained with STEM
  • Nanowires grown on surfaces
  • Other chemical techniques to obtain nanowires
• The Peierls transition and Kohn anomaly
• Cylindrical jellium model of QW
• Transport: quantization of the conductance.
• Quantum size effects
• Other hot topics
• Summary
• Introduction

• Classification:

1) Percolation (type of bonding): polymers, Carbon nanotubes....

2) Confinement effects: etched semiconductor wires, nanowires produced with STM, necks....

• Transverse size comparable to Fermi wave length:

- Confinement in two directions
- Electron structure in subbands
- Characteristic DOS as $\epsilon^{-1/2}$
- Consequence: oscillations in the physical properties.

• Classification and fabrication techniques

<table>
<thead>
<tr>
<th>BreakJunction</th>
<th>Nanotube</th>
<th>Molecular Wire</th>
<th>Quantum Wire</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition</td>
<td>Cu, Ag, Au...</td>
<td>C, N, H, S</td>
<td>GaAs/AlGaAs</td>
</tr>
<tr>
<td>Geometry</td>
<td>?</td>
<td>Tubular</td>
<td>Planar (2-D)</td>
</tr>
<tr>
<td>Width</td>
<td>Atomic</td>
<td>1-20 nmeters</td>
<td>- 1 nm</td>
</tr>
<tr>
<td>Length</td>
<td>1-1000 nm</td>
<td>1-20 μm</td>
<td>few nanometers</td>
</tr>
<tr>
<td>External Connections</td>
<td>Easy</td>
<td>Problematic</td>
<td>Challenging</td>
</tr>
<tr>
<td>Fabrication</td>
<td>Contact Mechanics</td>
<td>Carbon Arc</td>
<td>Test Tube</td>
</tr>
<tr>
<td>Conduction Mechanism</td>
<td>Quasi-ballistic</td>
<td>?</td>
<td>?</td>
</tr>
</tbody>
</table>
Classification and fabrication techniques

One-dimensional metals

- **Requirements:**
  - Strong orbital overlap on neighbouring atoms along a chain and negligible interaction between chains ⇒
  - Part-filled band (1D)

- **Examples:**
  - chain-like bulk systems, KCP: $K_2Pt(CN)_4Br_{0.3}3H_2O$
  - $Pt(CN)^{2-}_{4}$ in square plains forming 1 D stacks, overlap of Pt $5d_{z^2}$ orbitals
  - NC-ligands → insulators between chains
  - $Br^-$ dopants → holes (0.3 holes per Pt atom) ⇒ not filled $5d_{z^2}$ band⇒ metallic behaviour
• 1D metals, polymers

One-dimensional metals

• Average Pt-Pt distance: 2.88 Å (not much larger than in Pt bulk)

Interchain separation: 9.9 Å

Overlap of 5d$_{z^2}$ orbitals

Fig. 8.15 Structure of the 1D metal, KCP (K$_2$Pt(CN)$_4$Br$_{0.3}$H$_2$O), consisting of a stack of square-planar Pt(CN)$_4^{2-}$ clusters with Pt-Pt bonding, via overlap of 5d$_{z^2}$ orbitals, along the chain. (a) side view; (Cox 1987). Electronic Structure and Chemistry of Solids, by permission of Oxford University Press. (b) projection. (Smart and Moore 1992). Solid State Chemistry, Fig. 4.7. with kind permission from Kluwer Academic Publishers)

• 1D metals, polymers

One-dimensional metals

• Anisotropic properties

KCP

Conductivity

Reflectance
plasma-oscillation edge

≈ $10^4 - 10^5$

larger conductivity along chains than $\perp$

Fig. 8.16 Anisotropic electronic behavior of KCP (1D metal) above 200 K: (a) electrical conductivity parallel and perpendicular to the chains. (b) optical reflectivity for light polarized parallel and perpendicular to the chains. (Cox 1987). Electronic Structure and Chemistry of Solids, by permission of Oxford University Press)

T > 200 K: $\sigma$ \parallel $\sim$ T independent

T < 200 K: thermally -activated (associated with Peierls transition)
molecular metals

- 1D metals, polymers

TTF:TCNQ
- Stacks of organic molecules
- Interactions within stack stronger than between stacks.

Fig. 8.17 Crystal structure of the 1D metal, charge-transfer organic compound, TTF: TCNQ (the component molecules are shown in the inset) for two projections of the structure. (Cox (1987). Electronic Structure and Chemistry of Solids, by permission of Oxford University Press)

Conjugated polymers

- 1D metals, polymers

C atoms exhibit $sp^2+p_z$ hybridization $\Rightarrow$ involve $p_z\rightarrow\pi$

- bonds intramolecular and $\sigma$ bond between molecules $\rightarrow$

- delocalized electrons

Conjugated polymers

$\sigma-(\pi\sigma)-\sigma-(\pi\sigma)$

e.g.: polyacetylene (CH)$_x$ (PA)
Orbitals of Acetylene

- Two sp hybrid orbitals from each C form sp–sp σ bond
- pz orbitals from each C form a pz–pz π bond by sideways overlap and
  py orbitals overlap similarly

The carbon-carbon triple bond leaves the carbon atoms with two sp hybrid orbitals for sigma bonding, placing all four atoms in the same straight line, with CCH bond angles of 180°.

Conjugated polymers

- 1D metals, polymers
- Polymerized form of acetylene (CH)x: the simplest conjugated polymer

Two conformational isomers of PA: cis and trans

Fig. 8.21 Conformational isomers of polyacetylene (PA): (a) cis-PA; (b) trans-PA (thermodynamically stable at room temperature). (N.B. for simplicity neither the single hydrogen atom bonded to each carbon atom, nor the carbon atoms themselves positioned at the intersections of the bonds, are shown.)
1D metals, polymers

Conjugated polymers

The electronic structure is dominated by $\pi$ electrons

<table>
<thead>
<tr>
<th>Localized $\pi$-electrons</th>
<th>Delocalized $\pi$-electrons</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Localized" /></td>
<td><img src="image2" alt="Delocalized" /></td>
</tr>
</tbody>
</table>

Single bonds $sp^2$ ($\sigma$)

Double bonds ($\sigma$ and $\pi$) overlap $p_z$ neighbour atoms

Fig. 8.22 Two configurations of the bonding in trans-polyacetylene: (a) conjugated system in which the $p_z$-electrons are localized in $\pi$-bonds and $\sigma$- and $\pi$-bonds alternate; (b) delocalized configuration in which the $p_z$-electrons are delocalized along the polymer chain and all bonds are equivalent. A block representation of the bands, and their occupancy by $p_z$-electrons, is also shown for each case.

### Table 8.1 Some representative conjugated polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Chemical name</th>
<th>Monomer</th>
<th>$\pi-\pi^*$ energy gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>t-PA</td>
<td>trans-polyacetylene</td>
<td>![image3]</td>
<td>1.5</td>
</tr>
<tr>
<td>PPP</td>
<td>poly (p-phenylene)</td>
<td>![image4]</td>
<td>3.0</td>
</tr>
<tr>
<td>PPV</td>
<td>poly (p-phenylenevinylene)</td>
<td>![image5]</td>
<td>2.5</td>
</tr>
<tr>
<td>PPy</td>
<td>polypyrrole</td>
<td>![image6]</td>
<td>3.1</td>
</tr>
</tbody>
</table>

- Pure conjugated trans PA is non-metallic
- Doping: e.g. Na (donor), I₂ (acceptor) → metallic, but e⁻'s and holes not in conduction band! ⇒ conductivity increase, e.g. 10⁵ s⁻¹ m⁻¹ at 300 K.
- Change in bond-conjugation phase
  → states in band gap
  → occupation of band gap states by e⁻'s or holes
  ⇒ soliton states delocalized over 10-15 C atoms

It was shown in 1976 that oxidation of this material with iodine results in a 10⁸-fold increase in conductivity. The conductivity of this doped material approaches the conductivity of the best available conductor, silver. This was one of the first known examples of a conductive organic polymer.

The Nobel Prize in Chemistry in 2000 was awarded to Alan J. Heeger, Alan G. MacDiarmid, and Hideki Shirakawa for this work.

Possibility of transitions between s⁻ levels and π* band, apart from π-π* transitions.

- When electronic ground state is not double degenerate, excess charge localized at a particular point in polymer chain: polaron, associated with local distortion of chain.

Fig. 8.25 Schematic illustration of the formation of a negatively charged soliton state, S⁻, on a chain of trans-PA following the introduction of an excess electron into the π* conduction band. The soliton is associated with the change in phase of bond conjugation (and actually extends over 10-15 C atoms, rather than being localized at one as shown here). The soliton-electronic energy level lies at midgap between the π and π* bands and is doubly occupied; the state is negatively charged. Midgap optical absorption involving occupied soliton states is possible in addition to the normal π-π* transitions.

Fig. 8.26 Two different, non-degenerate senses of bond alternation in PPV: (a) benzenoid; (b) quinoid (higher energy).

Fig. 8.27 Excess negative charge on a PPV chain, represented as a region of local quinoid character.
Carbon nanotubes

C-nanotubes
(with C nanostructures, last lecture)

Rolled 2D sheets, but 1D character, e.g. in DOS

Metallic or semiconducting


Single-walled nanotube
(usually concentric multi-walled nanotubes)

Produced in DC-arc struck between two carbon electrodes (Iijima 1991)

Fig. 6.29 Illustration of a chiral, single-shell carbon nanotube, diameter $d = 10.36 \text{ Å}$, based on an icosahedral $C_{190}$ fullerene, sections of which form the two ends. The chiral vector is $e_{15} = (15, 7)$, with helix angle $\theta = -30.11^\circ$. (After Sato et al. 1992. Reprinted with permission from Appl. Phys. Lett. 60, 2004. © 1992 American Institute of Physics)

(More on CNs in last lecture on C nanostructures)
- Semiconductor wires

Etching of semiconductor heterostructures → 1D-wire on the interface or

Electrostatic confinement in a 2DEG at semiconductor interface → electrodes separated by a narrow gap and placed over the 2DEG.

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**Fig. 8.32** Methods of confining a 2D electron gas to form a 1D quantum wire. (a) Formation of a 2D electron gas at the interface between an undoped GaAs layer and an n-type doped AlGaAs layer, itself in contact with a metal gate electrode where a Schottky junction is formed. The bending of the electron bands (at one representative k-point) as a function of distance, z, through the modulation-doped heterostructure is shown; this results from the electrostatic potential due to the ionized donors in the AlGaAs layer (shown as +). The 2D degenerate electron gas forms in a well in the conduction band resulting from the band bending of the GaAs conduction band and the (repulsive) 0.3 eV conduction-band discontinuity at the interface with the AlGaAs. (b) Restriction of the 2D gas to a 1D channel by means of the etching of the n-type AlGaAs layer to form a linear mesa (extending into the page). The confined 1D electron gas is shown by the thick black line. (c) Use of a split gate, biased negatively, to confine the 1D gas by electrostatic means. In both (b) and (c), the + signs refer to positively charged ionized donors in the AlGaAs layer, and the hatched layer is an undoped AlGaAs spacer layer to reduce scattering of the 1D gas by the ionized donors. (Benakker and van Houten (1991). Reproduced by permission of Academic Press, Inc.)

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**Metallic wires obtained by MCBJ technique and STM**

**Metallic nanowires or point contacts**

STM/AFM-tip

Mechanically-controlled break junction
• Metallic wires obtained by MCBJ technique and STM


STM

Fig. 4. Conductance curves of a gold nanowire at low temperature (42 K) using a stable STM. Two complete consecutive cycles of approach-retraction are shown. The lower and higher curves correspond to approach and retraction, respectively.

• Metallic wires obtained by MCBJ technique and STM

Simultaneous force and conductance measurement.

STM and AFM

• Metallic wires obtained by MCBJ technique and STM

**Au forms chains before breaking**

![Fig. 49. Snapshots of atomic configurations from MD simulations of Au contacts. The pictures show, from two different viewpoints, the final configuration just before rupture of three different contacts: (a) Au[111], (b) Au[110], and (c) Au[100]. Reprinted with permission from [279]. © 1998 American Physical Society.](image)

• Metallic wires obtained by MCBJ technique and STM

**Mechanically-controlled break junction**

**MCBJ**

![Image of MCBJ setup](image)

E.Scheer et al. PRL 78, 3535 (1998)
• Metallic wires obtained by MCBJ technique and STM

Interesting review

Quantum properties of atomic-sized conductors

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• Metallic wires obtained with STEM

Gold nanowires

Y. Kondo et al., PRL 79, 3455 (1997)

Gold Nanobridge Stabilized by Surface Structure

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(Received 18 March 1997)

We fabricated gold nanowires using electron-beam lithography in an SEM using a local electron microscope. The dimensions of these nanowires were 2-3 nm in diameter and 3-10 nm in length. The nanowires showed strong reflectivity. We propose a nanowire model for a nanowire with a thickness of 2 nm. The model is represented by a hexagonal prism, the surface layer of the prism has a hexagonal plane, and the core of the prism has a cross-sectional cavity structure. The nanowire is considered to be stabilized by the capillary action of the medium.

FIG. 2. Transmission electron micrographs of an Nb 2 nm thick, obtained at the focus of (a) 55 mm and (b) 55 mm. Note the square lattice in (a) and hexagonal one in (b).
Nanowires grown on surfaces

- Atomic chains on insulators
e.g. Au atoms absorbed on the steps of the vicinal Si surfaces

- Segovia et al., Nature 402, 504 (1999)
- Losio et al. PRL 85, 808 (2000)

Continuous Transition from Two- to One-Dimensional States in Si(111)-(5 \times 2)-Au

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(Received 7 February 2001)

A strong, gold-induced surface state is found on single-domain Si(111)-(5 \times 2)-Au at low temperatures. Its band structure is one dimensional near the Fermi level $E_F$ and gradually becomes two dimensional towards the bottom of the band, thus providing a model for a continuous transition in dimensionality. A Fermi-level gap is observed in the one-dimensional portion of the band near $E_F$.

Ferromagnetism in one-dimensional monatomic metal chains

P. Gambardella\textsuperscript{a, b}, A. Balatsky\textsuperscript{a}, K. Mulli\textsuperscript{a}, M. E. Malnou\textsuperscript{b}, W. Eberhardt\textsuperscript{a}, K. Kreiss\textsuperscript{a}, \& G. Carboni\textsuperscript{b}

Nature 416, 301 (2002)

Figure 1 STM topographies of the Pt(997) surface. a, Periodic step structure (each white line represents a single step). The surface has a 6.45° miscut angle relative to the (111) direction; repetitive step interactions result in a narrow terrace with distribution centered at 20.2 Å with 2.0 Å standard deviation. b, Co monatomic chains decorating the Pt step edges (the vertical dimension is enhanced for better contrast). The monatomic chains are obtained by evaporating 0.13 monolayers of Co onto the substrate held at $T = 260$ K and previously cleaned by ion sputtering and annealing cycles in ultrahigh vacuum (UHV). The chains are linearly aligned and have a spacing equal to the terrace width.
Other chemical techniques to obtain nanowires

Template assisted nanowire growth

- Create a template for nanowires to grow within based on aluminum's unique property of self-organized pore arrays as a result of anodization to form alumina ($\text{Al}_2\text{O}_3$)
- Very high aspect ratios may be achieved
- Pore diameter and pore packing densities are a function of acid strength and voltage in anodization step
- Pore filling - nanowire formation via various physical and chemical deposition methods

The Peierls transition and Kohn anomaly

Peierls distortion: breakdown of metallic behaviour: structural transition

1D-metal $\rightarrow$ 1D semiconductor with $E_g$

Consider a half-filled band...

Fig. 8.18 Illustration of the origin of the Peierls distortion in a 1D chain of atoms resulting in the opening of a bandgap at $E_F$ in a partially filled 1D band. For the case of half-filling, as shown here, (a) a distortion giving a doubling of the spatial periodicity of the chain leads to (b) gap opening up in the band structure at $k = 2\pi/2a = \pi/a$. (c) The corresponding redistribution of the density of states. (Cheetham and Day (eds.) (1992). Solid-State Chemistry: Compounds, by permission of Oxford University Press).
• The Peierls transition and Kohn anomaly

- Static distortion: dimerization
- New lattice constant $2a$
- New BZ boundary at $k=\pi/2a$
- For a metallic chain with half-filled band $k=\pi/2a$
  \[ \Rightarrow \text{energy gap } \varepsilon_g \text{ at } \varepsilon_F \]  (c.f. nearly free electron model)

Lowering of occupied levels $\Rightarrow \varepsilon_{\text{tot}} \downarrow$
\[ \Rightarrow \text{stable distortion} \]

due to strong coupling between electrons and phonons of particular wave vectors

• The Peierls transition and Kohn anomaly

Metallic chain with band filled to $1/n$
$n \geq 2 \Rightarrow$ Peierls-distortion

\[ k_F = \frac{n}{na} \]

Periodicity $D=na$

- $n \in$ integer $\Rightarrow$ commensurate distortion
- $n \notin$ integer $\Rightarrow$ non-commensurate distortion

0-D system, molecules: Jahn-Teller distortion
1-D system: Peierls distortion

Ionic displacements = electron-phonon interaction
Effects at high $T$

For example, for KCP, $D=6.67a$
The Peierls transition and Kohn anomaly

When $T$ increases, the vibrational amplitude of the atoms increases and the static displacement characteristic of the Peierls distortion is washed up $\Rightarrow$ metallic state.
• The Peierls transition and Kohn anomaly

• Kohn anomaly

The response function for electron screening in 1D electron gas diverges at $q = 2k_F$

$$\rho^{\text{ind}}(q) = \chi(q) \phi(q)$$

Singularities in the phonon dispersion curves (Kohn anomalies) above the Peierls transition temperature

$$\chi(q) = -e^2 n(\epsilon_F) \ln \left| \frac{q + 2k_F}{q - 2k_F} \right|$$

Fig. 8.20 Acoustic-phonon branches in deuterated KCP at room temperature measured by inelastic neutron scattering (Renken and Comès (1975)). A Kohn anomaly is evident along the line $q = 2k_F = 0.3 \pi/c$. Reproduced by permission of Plenum Publishing Corp.

• Cylindrical jellium model of QW

Metallic nanowires (circular section)

• Most properties are due to the narrowest part of the neck.

• Approximation: infinite cylinder

Jellium Model

• Two parameters: $R$, $r_s$

The ions are spread forming an homogeneous positive background
• Cylindrical jellium model of QW

\[ \Psi(r, \varphi, z) = A R_{mn}(r) e^{im\varphi} e^{ik_z z} \]

\[ A = \frac{1}{\sqrt{2\pi L}} \]

• Radial wave function verifies radial Schrodinger equation. For just free electrons, Bessel equation:

\[ -\frac{\hbar^2}{2m} \left( \frac{d^2}{dr^2} + \frac{1}{r} \frac{d}{dr} - \frac{m^2}{r^2} \right) R_{mn}(r) = \epsilon_{mn} R_{mn}(r) \]

\[ R_{mn}(r) = J_m \left( \frac{z_{mn} r}{R} \right) \]

Bessel functions \( z_{mn} \) zeros of Bessel functions

\[ n = 1, 2, 3, \ldots \]

37

• Cylindrical jellium model of QW

• Beyond free electrons,

Density Functional Theory

(Local Density Approximation)

\[ V_{\text{eff}}[n(r)] = V_{\text{Coul}} + V_{\text{xc}} \]

Consider interactions with the ions and electron-electron interactions

Kohn-Sham equations to solve a many-body problem (Schrödinger equation)

The density is calculating by solving one-particle equations in an effective potential

\[ \frac{\hbar^2}{m} \left\{ -\frac{1}{2} \nabla^2 + V_{\text{eff}}(r) \right\} \psi_i(r) = \epsilon_i \psi_i(r) \]

• The one-particle energies:

\[ \epsilon_{m,n,k_z} = \epsilon_{mn} + \frac{\hbar^2 k_z^2}{2m} \]
• Cylindrical jellium model of QW

The electron density

\[ n = n_- = \frac{1}{2\pi^2} \sum_{m,n} R_{mn}(r) \left| \frac{1}{2} \sqrt{2(\epsilon_F - \epsilon_{mn})} \right|^2 \]

Neutrality condition:

\[ N_z = \frac{2}{\pi} \sum_{m,n} \sqrt{2(\epsilon_F - \epsilon_{mn})} = n^+ \pi R^2 \]

Density Of States (DOS)

\[ DOS(\epsilon) = \frac{1}{\pi^2 R^2} \frac{2m^{1/2}}{\hbar} \sum_{m,n} (\epsilon - \epsilon_{m,n})^{-1/2} \]

(per unit volume)
Cylindrical jellium model of QW

- Oscillations in Fermi energy, work function, total energy of the system, surface energy, elongation force...as the radius increases, magic radii

- The oscillations are in correlation with the peaks in the density of states at the Fermi level (obtained self-consistently from neutrality condition)