SRC Study on Highly Conductive Polymers (HCP)

Victor Zhirnov, Andrey Kiselev and Ralph Cavin

SRC Forum on Highly Conductive Polymers

October 4, 2007

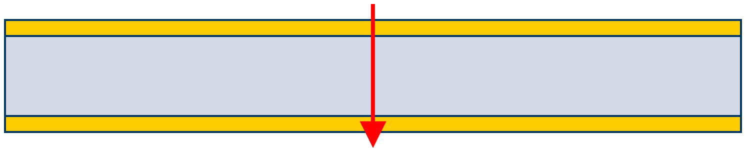
Brief History

- 2005 - SRC upon request of several member companies conducted a preliminary investigation on HCP
  - *Seminar provided by Dr. Kevin Shambrook*
  - Extensive literature survey
    - significant body of literature on the topic of HCP found
  - *No fundamental physics analysis*
  - *2005 SRC Study Report*

Conclusion: More in-depth study is required before one can conclude that there is a real effect

- 2007 – Fundamental Study on Critical Assessments of Highly Conductive Polymers

Very brief summary on HCP



- HCP is produced from a conventional polymer film, e.g. *polypropylene* or *polysiloxanes*

- HCP are reported to exhibit unusual electrical conduction properties
  - The highest measured current through the HCP film is 1700 A from 1cm^2 sample
  - The resistivity of the HCP film in the direction normal to the surface is $\leq 10^{-11}$ Ohm·cm
    - for comparison, the resistivity of bulk Cu is 1.7x 10^{-6} Ohm·cm

- It is believed that a special microstructure is developed in the HCP film
  - Conductive channels of unknown nature

Selected Publications

1989

Institute of Synthetic Polymeric Materials, Moscow, Russia
N. S. Enikolopyan, et al., **Possible Superconductivity near 300-K in Oxidized Polypropylene**, JETP LETTERS 49: 371-375 (1989)

1992

Ioffe Physico-Technical Institute, St.-Petersburg, Russia
A. N. Ionov et al, Low-Resi... Polydipheylene... ...ature, Solid ... (1992)

Metallic bridge formation from electrode material is the cause of low-resistance state

"The main aim of the present work is to verify whether or not the low-resistance state in the above experiments can be explained by the formation either metallic or carbon bridge between the contacts

HV switching
Bridge formation confirmed
Icrit<100mA

1998 *Bar-Ilan University, Israel*
Shlimak I, Martchenkov V, **Switching phenomena in elastic polymer films**, SOLID STATE COM. 107 (1998): 443-446

LV switching
No bridge formation
I_{crit}>2 A

2005-2007

Experiments with superconductive electrodes indicate the non-dissipative transport of charge carriers in the polymers

Ioffe Physico-Techni...
Freie Univer...
A. N. Ionov ...conductivity and Supercurrent in Superconductor-Polymer-Superconductor Systems, Physica B (2005) 506

...Technical Institute, Russia
Freie Universitat Berlin, Germany
A. N. Ionov et al, Local distribution of high-conductivity regions in polyamide thin films, JEPT Lett. (2007) 636

Shlimak I, Martchenkov V, Switching phenomena in elastic polymer films, SOLID STATE COMMUNICATIONS 107 (9): 443-446 1998

"The main aim of the present work is to verify whether or not the low-resistance state in the above experiments can be explained by the formation either metallic or carbon bridge between the contacts

Two switching regimes were found:

High voltage switching

Bridge formation

I_{max}<100mA – limited by bridge melting

Low voltage switching (ultraswitching)

No bridge formation

I_{max}>2 A – limited by electrode burnout

No heating in polymer film

R_{ON}~0.5 Ohm=R_{cont}+R_{film}

Conclusion: "Ultraswitching" (US) is a new effect, which can not be explained in terms of conventional breakdown. Further investigation is needed to throw light on the nature of conducting filaments in the US ON state

Conductivity switching in polymers

- Polymer Memory
  - Vsw=2-5 V
  - Tsw<μs
  - Ron=100-1000 Ohm
  - Switching mechanism not understood

- HCP
  - Vsw~1 V
  - Tsw~30000 s
  - Ron~0.5 Ohm
  - Switching mechanism not understood

Another conductivity switching phenomenon

Cryogenic experiments

A. N. Ionov et al, High Conductivity and Supercurrent in Superconductor-Polymer-Superconductor Systems, Physica B (2005) 506

Experiments with superconductive electrodes indicate the non-dissipative transport of charge carriers in the polymers

A summary of <u>confirmed</u> data:

Low resistance state at RT

What is the RT resistivity?

SC state at cryogenic temperatures

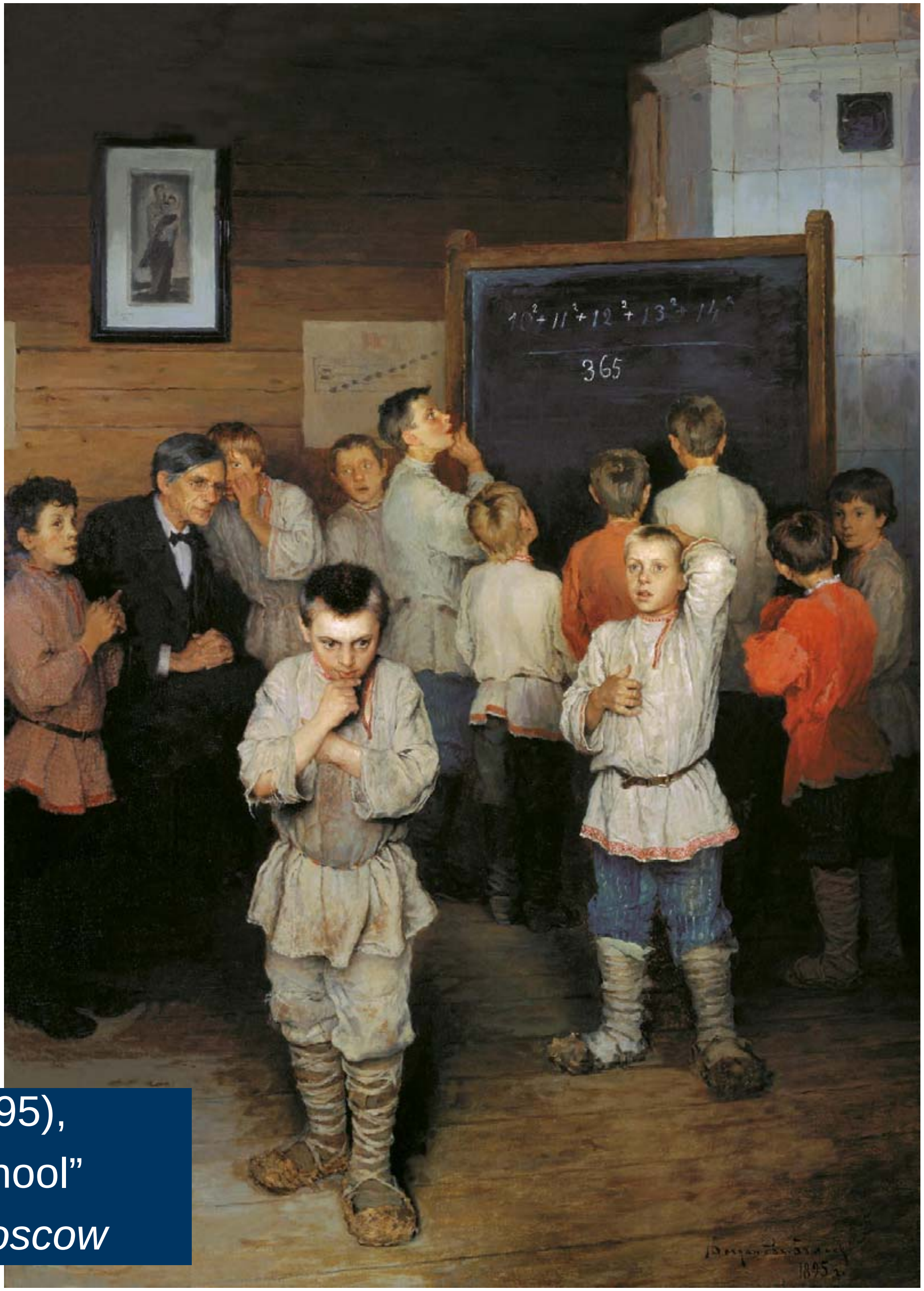
What does physics have to say?

HCP claim: 10^{-11} – 10^{-24} Ohm·cm

Cu: 1.7x 10^{-6} Ohm·cm

The Study Team:

Andrey Kiselev/NCSU
Kevin Shambrook/Sonoma State U
Ralph Cavin/SRC
Harold Hosack/SRC
Dan Herr/SRC
Dale Edwards/SRC
Victor Zhirnov/SRC
Jonathan Dobson



Nikolai Bogdanov-Bel'sky (1895),
“Mental counting in a rural school”
The Tretyakov Gallery, Moscow

Study Group Approach

- Regular FxF meetings with the following objectives:

- To review publications in the field
  - a 'pro et contra' approach

- To review experimental reports
  - summarize quantitative experimental results reported on highly conductive polymers
  - to address alternative interpretations of experimental results
    - the role of electrode materials is unclear
    - contaminations from ambient may contribute to the uncertainty of measurements
    - Conductive bridge formation may be the cause of low-resistance state
    - Bla... bla...

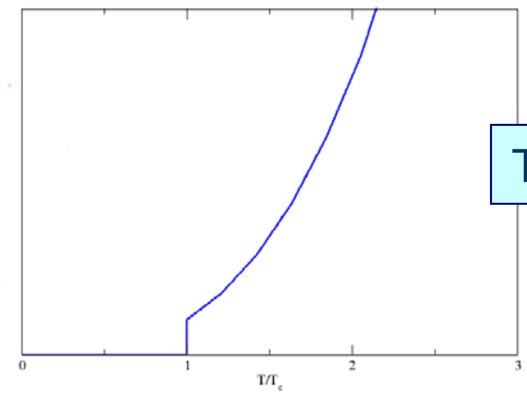
- To explore universal mechanisms of electrical conduction in solids, which are applicable to e.g. both normal conductors and superconductors
  - understanding the fundamentals and developing working hypotheses could help in planning experiments


I'd stay away from such projects-it's a great way to lose your reputation…
Don't believe in this garbage!…
It is impossible!
Can we prove it is impossible?
Well, Maybe…
HCP
$\frac{h}{2e^2}=12.9k\Omega$
$\xi=\frac{\hbar}{\sqrt{2m\alpha}}$
T>300K

What is the minimum possible resistivity?

- The resistivity of the HCP film in the direction normal to the surface is reported to be 10^{-11} – 10^{-24} Ohm·cm
  - for comparison, the resistivity of bulk Cu is 1.7x 10^{-6} Ohm·cm

- What is the *RESISTIVITY* of a superconductor?



Textbook picture of SC

What is the minimum possible resistivity?

Quantum Transport Limit

Heisenberg's Energy-time relation

$$\Delta E \Delta t \geq \frac{h}{2}$$

Plank's constant

h=6.62x10^{-34} Js

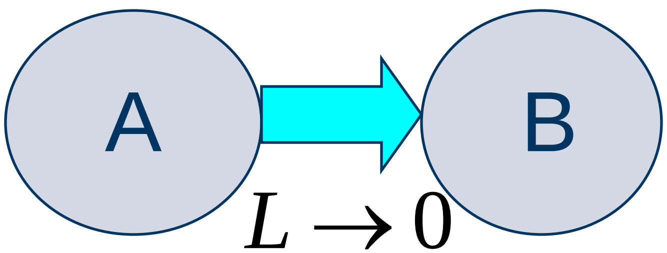
$$\Delta t \geq \frac{h}{2\Delta E}$$

Minimal time of dynamical evolution of a physical system

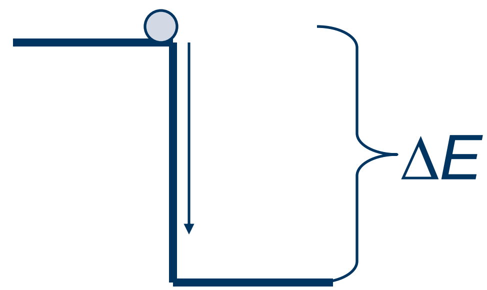
N. Margolus and L. B. Levitin, Physica D 120 (1998) 188

Quantum Resistance

Single –electron Conductance channel



Electron's charge
e=1.6x10^{-19} C



Ohm's Law:

$$V = IR$$

$$V = \frac{\Delta E}{e}$$

$$I = \frac{e}{\Delta t}$$

R-?

$$\frac{\Delta E}{e} = \frac{e}{\Delta t} R$$

$$R = \frac{\Delta E \Delta t}{e^2} = \frac{h}{2e^2} =$$

$$= \frac{6.64 \times 10^{-34} J \cdot s}{2 \times (1.6 \times 10^{-19} C)^2} = 12.9 k\Omega$$

Summary on Quantum resistance

Heisenberg's Energy-time relation

$$\Delta E \Delta t \geq \frac{h}{2}$$

Plank's constant

h=6.62x10^{-34} Js

Ohm's Law:
V=IR

$$R = \frac{h}{2e^2} = 12.9 k\Omega$$

von Klitzing constant

It was experimentally discovered in the 1980s in Quantum Hall Experiments

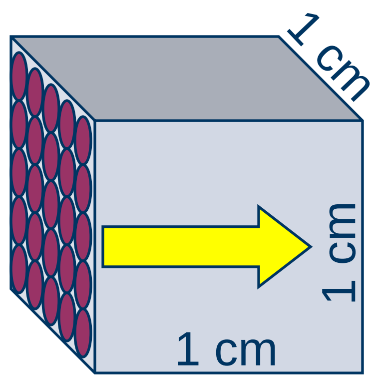
Nobel Prize in 1985

Minimum Resistivity?

$$\sigma_{\max} = \frac{2e^2}{h} \cdot n_{2d} = \frac{2e^2}{h} \cdot \left(n_{at}\right)^{\frac{2}{3}}$$

$$n_{2d} \sim \left(n_{at}\right)^{\frac{2}{3}}$$

Number of atoms in cross-section



$$\rho_{\min} = \frac{1}{\sigma_{\max}} = \frac{h}{2e^2} \left(n_{at}\right)^{-\frac{2}{3}}$$

$n_{Cu} = 8.44 \times 10^{22}$ at/cm^3

$$\rho_{\min} = 6.72 \cdot 10^{-12} \left(\Omega \cdot cm\right)$$

Quantum resistance model vs. experiment

- What is the *RESISTIVITY* of a superconductor?

What is wrong with quantum resistance?

Our result:

$$\rho_{\min} = 6.72 \cdot 10^{-12} (\Omega \cdot cm)$$

$$\rho_{Cu} = 1.7 \cdot 10^{-6} (\Omega \cdot cm)$$

D. J. Quinn and W. B. Ittner, 'Resistance in a Superconductor', J. Appl. Phys. 33, 748 (1962):

$$\rho_s \leq 3.6 \cdot 10^{-23} (\Omega \cdot cm)$$

Collective behavior of electrons is a key mechanism for Superconductivity

Electrons participate in conductance process not individually, but collectively

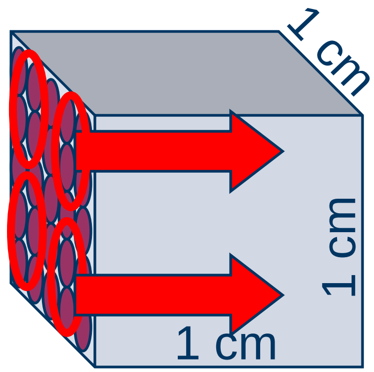
$$\sigma_{\max} = \frac{2e^2}{h} \cdot n_{2D}$$

$$\sigma_{\max} = \frac{2(Me)^2}{h} \cdot N_g$$

N_g - # of groups

Electrons form groups

M - # of electrons in one group



$$N_g = \frac{n_{2D}}{M}$$

$$\sigma_{\max} = \frac{2(Me)^2}{h} \cdot \frac{n_{2D}}{M} = \frac{2Me^2}{h} \cdot n_{2D} = \frac{2Me^2}{h} (n_{at})^{\frac{2}{3}}$$

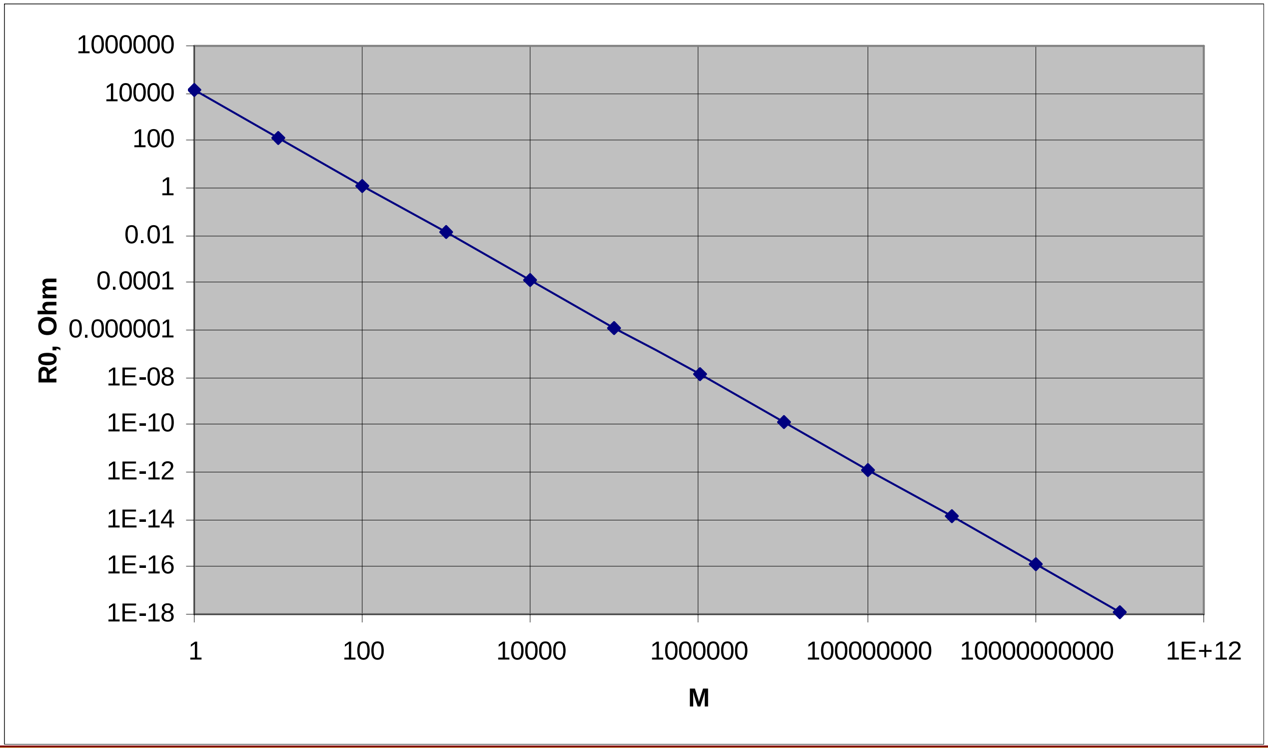
Collective Electron Transport: Size Effects of Resistance

M	R_0, Ohm	N_g	ρ_{min}	W_{min}, cm	W_{min}, nm
1	12929.69	1.9241E+15	6.71985E-12	2.28E-08	0.23
10	129.2969	1.9241E+14	6.71985E-13	7.21E-08	0.72
100	1.292969	1.9241E+13	6.71985E-14	2.28E-07	2.28
1000	0.01293	1.9241E+12	6.71985E-15	7.21E-07	7.21
10000	0.000129	1.9241E+11	6.71985E-16	2.28E-06	22.80
100000	1.29E-06	1.9241E+10	6.71985E-17	7.21E-06	72.09
1000000	1.29E-08	1924102916	6.71985E-18	2.28E-05	227.97
10000000	1.29E-10	192410292	6.71985E-19	7.21E-05	720.92
1E+08	1.29E-12	19241029.2	6.71985E-20	2.28E-04	2279.74
1E+09	1.29E-14	1924102.92	6.71985E-21	7.21E-04	7209.18
1E+10	1.29E-16	192410.292	6.71985E-22	2.28E-03	22797.43
1E+11	1.29E-18	19241.0292	6.71985E-23	7.21E-03	72091.80

Reported for HCP

Reported for conventional SC

Resistance with Group Electron Transport



The large number in electrons in the group, M, implies minimum width of the conductor to accommodate large M

$$W_{\min} \sim (M)^{\frac{1}{2}} \cdot (n_{at})^{-\frac{1}{3}}$$

Minimum Resistivity of a SC

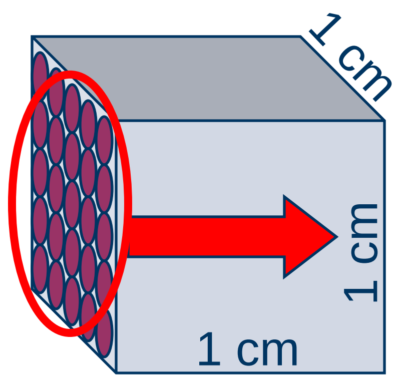
$$\sigma_{\max} = \frac{2(Me)^2}{h} \cdot \frac{n_{2D}}{M} = \frac{2Me^2}{h} \cdot n_{2D} = \frac{2Me^2}{h} \left(n_{at}\right)^{\frac{2}{3}}$$

$$\rho_{\min} = \frac{1}{\sigma_{\max}} = \frac{h}{2Me^2} \left(n_{at}\right)^{-\frac{2}{3}}$$

$$\rho_{bal}\left(M = N\right) = \frac{h}{2e^2} \frac{n^{-\frac{4}{3}}}{A}$$

$$M_{\max} = N = n_{at} \cdot A$$

Total number of electrons in cross-section



Electrons form groups

M - # of electrons in one group

Connection between Ballistic Conductance Model and canonical theory of SC

Electrons participate in conductance process not individually, but collectively

$$\sigma_{\max} = \frac{2e^2}{h} \cdot n_{2D}$$

$$\sigma_{\max} = \frac{2(Me)^2}{h} \cdot N_g$$

Electrons form groups

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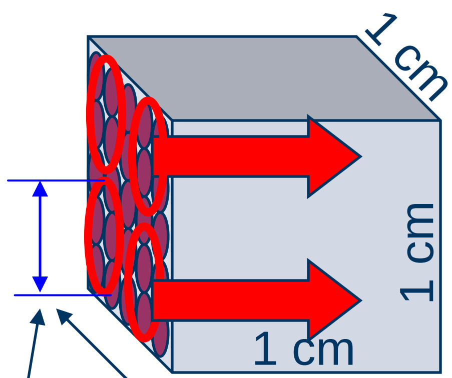


The conductive state has a characteristic size of the group (size of quasiparticle):

$$W_{\min} \sim (M)^{\frac{1}{2}} \cdot (n_{at})^{-\frac{1}{3}}$$

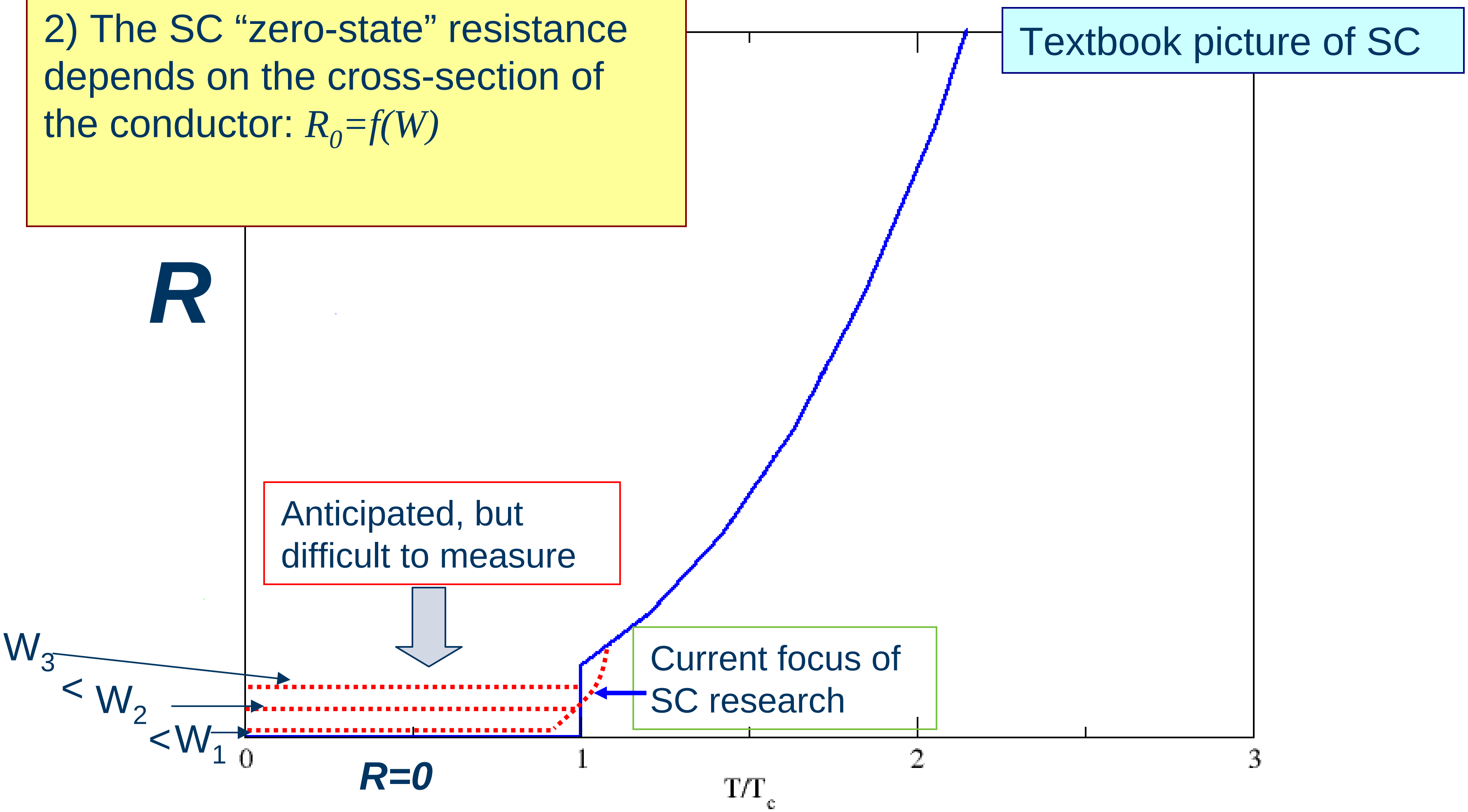
The **coherence length** *in the* Ginzburg-Landau theory of SC

$$\xi = \frac{\hbar}{\sqrt{2m\alpha}}$$

Immediate predictions from the ballistic model

1) The resistance of SC state is a very small but finite value R_0

2) The SC "zero-state" resistance depends on the cross-section of the conductor: $R_0=f(W)$



Very brief summary on HCP

- HCP is produced from a conventional polymer film (e.g. *polypropylene* or *polysiloxanes*

- HCP are reported to exhibit unusual electric... nduction properties
  - The highest measured current through th... m is 1700 A from $1 cm^2$ sample
  - The resistivity of the HCP film in th... n normal to the surface is $\leq 10^{-11}$ Ohm·cm
    - for comparison, the resistivi... Cu is $1.7x\ 10^{-6}$ Ohm·cm

- It is believed that a sp... microstructure is developed in the HCP film
  - Quasi-one-dimensional conductive paths of unknown nature

The reported data doesn't seem to contradict to the fundamental physics

Connection between Quantum Conductance Model and canonical theory of superconductivity

- The ballistic model corresponds to temperatures much lower than critical temperature, $T << T_c$
  - temperature does not appear in the model
- In the ballistic model, the group of *M* electrons (quasiparticle) has an characteristic size
  - the equivalent characteristic size in the canonical theory of superconductivity is the Landau-Ginzburg coherence length

A direct test of the applicability of the ballistic model to superconductivity

The resistivity of the superconducting lead film was reported to be $\rho \sim 3.6 \times 10^{-23}$ Ohm-cm.

D. J. Quinn and W. B. Ittner, Resistance in a Superconductor JAP 33 (1962) 748

→ *Superconductivity: Fundamentals and Aplications,* by W. Buckel and R. Kleiner (2004 WILEY-VCH)

Material: Pb, $n_{Pb}=3.3 \times 10^{22}$ at/cm^3

$$\rho_{bal}(M = N) = \frac{h}{2e^2}\frac{n^{-\frac{4}{3}}}{A}$$

Pb film thickness: 1.2 μm;

Width of the cross-section: ~3cm

$\rho_{bal}=3.4 \times 10^{-23}$ Ohm-cm

Almost exactly the experimental number!

Conclusions from the model

- If many-electron coherent transport could be achieved, it would yield conductivity in the range reported for Highly Conductive Polymers

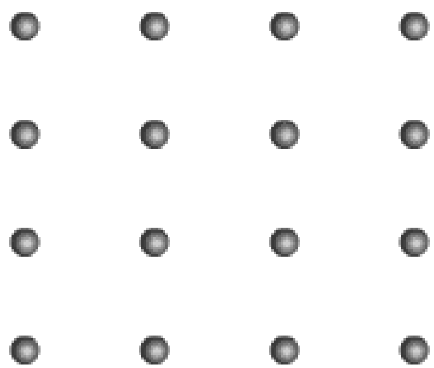
- The result of this model doesn't guarantee the validity of the existence of highly conductive polymers.
  - Nevertheless, it sends an encouraging message that such systems are in principle possible.

- There remain many questions including
  - The structure of the material
  - Theoretical basis of expectations

Classical Superconductivity

No complete theory on superconductors as yet exists. Bardeen-Cooper-Schriffer (BCS) theory help establish a mechanism for superconductors.

- Current in a superconductor is made up of electron pairs
- Each lattice atom is positively charged
- The first electron pulls the lattice atoms together, making them vibrate coherently. That, in turn, pulls the following electron
- Interaction between coherent atom vibrations (phonons) and electrons causes superconductivity



1911	**Hg**	**4.2 K**
1941	**NbN**	**16.1 K**
1953	**V_3Si**	**17.5 K**
1973	**Nb_3Ge**	**23 K**
1986	**$(La_{1.85}Ba_{.15})CuO_4$**	**30 K**
1987	**$YBa_2Cu_3O_7$**	**92 K**
1994	**$Hg_{0.8}Tl_{0.2}Ba_2Ca_2Cu_3O_{8.33}$**	138 K 164?
2???	**???**	**??? ?**

Room-Temperature superconductivity?

Possible theoretical basis

- There is an established theory of high-temperature superconductivity in polymers developed by Little and followed up by Ginzburg and others and it is based on an exciton mechanism
  - the original paper by Little has a very large number of citations

PHYSICAL REVIEW VOLUME 134, NUMBER 6A 15 JUNE 1964

Possibility of Synthesizing an Organic Superconductor*

W. A. LITTLE
Department of Physics, Stanford University, Stanford, California
(Received 13 November 1963; revised manuscript received 27 January 1964)

London's idea that superconductivity might occur in organic macromolecules is examined in the light of the BCS theory of superconductivity. It is shown that the criterion for the occurrance of such a state can be met in certain organic polymers. A particular example is considered in detail. From a realistic estimation of the matrix elements and density of states in this polymer it is concluded that superconductivity should occur even at temperatures well above room temperature. The physical reason for this remarkable high transition temperature is discussed. It is shown further that the superconducting state of these polymers should be distinguished by certain unique chemical properties which could have considerable biological significance.

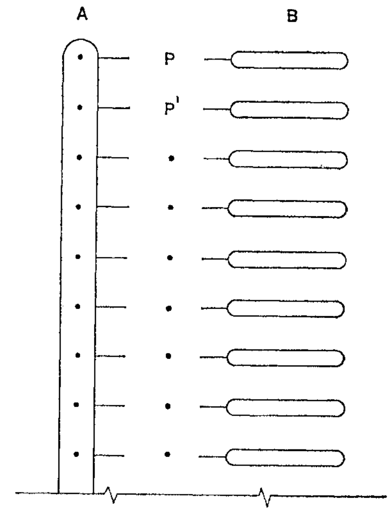


FIG. 1. Proposed model of a superconducting organic molecule. The molecule A is a long unsaturated polyene chain called the "spine." The molecules B are side chains attached to the spine at points P, P′, ⋯.

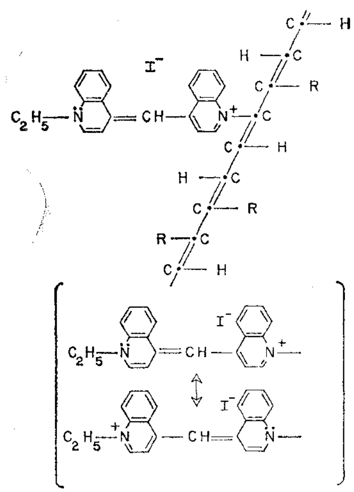


FIG. 3. Chemical structure of the proposed superconducting organic polymer. At each point *R* on the spine a similar side chain to the one shown is attached. These side chains are resonating hybrids of the two extreme structures shown in the inset. The positive charge resonates between the two nitrogen sites as illustrated.

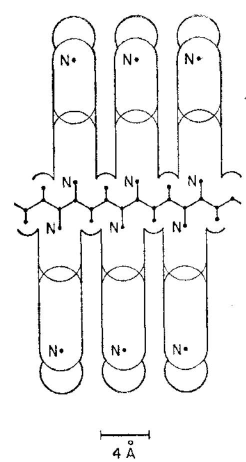


FIG. 4. Approximate scale drawing of the proposed superconducting organic polymer. The plane of the benzene rings in the side chains are oriented at right angles to the spine. The two nitrogen sites on each side chain are indicated, but the iodine site has been omitted for the sake of clarity.

PHYSICAL REVIEW B VOLUME 13, NUMBER 11 1 JUNE 1976

Proposed model of a high-temperature excitonic superconductor*

D. Davis,† H. Gutfreund,‡ and W. A. Little

Physics Department, Stanford University, Stanford, California 94305

(Received 16 October 1975)

We present a detailed calculation of the transition temperature of a model filamentary excitonic superconductor. The proposed structure consists of a linear chain of transition-metal atoms to which is complexed a ligand system of highly polarizable dyelike molecules. Calculations of the electronic properties and experimental data on related materials are used to estimate the strength of the excitonic interaction, Coulomb repulsion, and band structure. From this the superconducting transition temperature was calculated by numerical integration of the gap equation. For the particular structure proposed, transition temperatures of several hundred degrees are calculated. However, we find superconductivity only in those systems where the excitonic medium is within a covalent bond length of, and completely surrounds, the conductive spine. This imposes severe constraints on the structure of any excitonic superconductor. We show that for the structure proposed the momentum dependence of the exciton interaction results in the superconducting state being favored over the Peierls state and in vertex corrections to the electron-exciton interaction which are small.

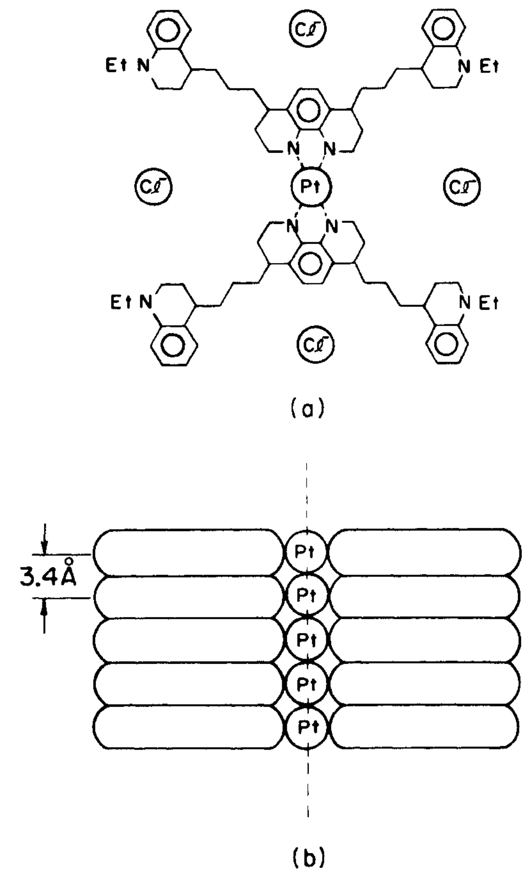


FIG. 1. Proposed model of the structure of an excitonic superconductor. (a) Top view of square planar phenanthroline-dye ligands complexed to Pt. Double bonds in the chromophore are omitted for simplicity. Et stands for ethyl. (b) Side view of chain.

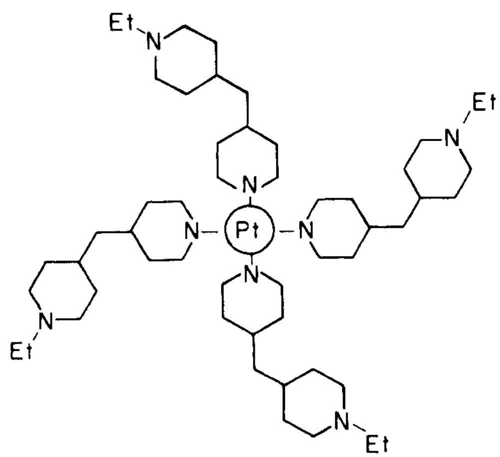


FIG. 2. Simplified version of structure of Fig. 1 for which detailed calculations are presented in this paper.

My personal earlier misconceptions about superconductivity

- Room temperature superconductivity violates the Laws of Physics

- The higher T_c superconductors have lower critical current density J_c
  - $T_c \rightarrow 300$ $J_c \rightarrow 0$

These perceptions were not true

CONCLUSIONS

- **Confirmed data:**
  - **Low resistance state at RT**
  - **SC state at cryogenic temperatures**

- **Unconfirmed data**
  - **SC state at RT**
- **Experimental Challenge:**
  - **RT resistivity measurements**

- **There is an established theory of high-temperature superconductivity in polymers**
  - Little, Ginzburg...

Comments from an authoritative independent expert in superconductivity

"HCP concepts in view of the science of superconductors"

by Andrey Sergeev, SUNY/Buffalo