TRANSPORT PROPERTIES OF GRAPHENE
IN AND OUT OF THE BULK

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PART I   ELECTRICAL CONDUCTIVITY

PART II   THERMAL CONDUCTIVITY
TRANSPORT PROPERTIES OF GRAPHENE IN AND OUT OF THE BULK

OBJECTIVES – GENERAL

- to show how studies on bulk carbons have paved the way for some physical properties observed now in graphene,

- to stress the similarities and differences observed on a single (or a few) graphene planes, out of the bulk, and a single (or a few) of these planes sandwiched between insulating planes, as in graphite acceptor intercalation compounds (GACs),

- mainly address semi-classical and quantum (non relativistic) aspects of transport.
OBJECTIVES – SPECIFIC

- to show how a 2D (linear) $\mathcal{E}$-$k$ relation with massless fermions (holes) was applied successfully to stage-1 GACs,

- to show that, despite the similarity between the $\mathcal{E}$-$k$ relations in stage-1 GACs and graphene, there are some properties which could not be observed in the bulk material because of intrinsic electron-phonon & defect scattering,

- to show that the *high mobilities* observed up to now in graphene are by no means unique.
TRANSPORT PROPERTIES OF GRAPHENE IN AND OUT OF THE BULK

TOPICS ADDRESSED
Electronic transport
carrier distribution, scattering, disorder and weak localization
Phonons & Thermal conductivity

MATERIALS
Bulk carbons: pristine and intercalated (including with F)
Nanostructured carbons: mainly graphene
CYCLE OF A RESEARCH TOPIC

OUTPUT

very arbitrary units

- Nb of researchers involved
- Nb of papers published
- Hype & excitement
- …
Development of the field of carbon research

Compiled by M.S. Dresselhaus

Number of physics-related publications on Carbon
After 2004: GRAPHENE OUT
One (or a few) supported or free-standing graphene planes:
→ the object of this school

Before 2004: GRAPHENE IN
One (or a few) graphene planes sandwiched between insulating layers:
→ the story of acceptor graphite intercalation compounds (GACs)
2D INTERCALULATION OF GRAPHITE

Graphene layers

Intercalate layer

Graphite quasi-2D

Semimetal \xrightarrow{\text{Intercalation}} Quasi 2D metal (acceptor)
3D anisotropic metal (low-stage donors)
WHY INTERCALATE GRAPHITE?

To develop synthetic electrical conductors* better than copper (~ 1980’s)
- it was never realized and will probably never be realized.

But, in their quest for the Graal, researchers found interest in:
- investigating 2D hole gases (GACs),

and their sponsors in their quest for big money, found interest in:
- developing C-Li batteries (GICs-donors)

* As a result of charge transfer, intercalation increases the hole density, $N$. A decrease in the mobility, $\mu$, is due to the defects introduced by the intercalation process. The net result is a significant decrease in the in-plane electrical resistivity, $\rho$

$$\frac{1}{\rho} = \sigma = q N \mu$$
TRANSPORT PROPERTIES OF GRAPHENE

IN AND OUT OF THE BULK

PART I  ELECTRICAL CONDUCTIVITY

PART II  THERMAL CONDUCTIVITY
## WHAT MODEL FOR THE BAND STRUCTURE

<table>
<thead>
<tr>
<th>Year</th>
<th>Author (s)</th>
<th>Form of Carbon</th>
<th>Dimensionality</th>
</tr>
</thead>
<tbody>
<tr>
<td>1947</td>
<td>Wallace (1)</td>
<td>Virtual graphene</td>
<td>2D</td>
</tr>
<tr>
<td>1957, 1960</td>
<td>SWMC (2)</td>
<td>HOPG</td>
<td>3D</td>
</tr>
<tr>
<td>1980</td>
<td>Blinowski-Rigaux (3)</td>
<td>GACs</td>
<td>2D</td>
</tr>
<tr>
<td>2004- ...</td>
<td><em>Ask the experts</em></td>
<td>Real graphene</td>
<td>2D</td>
</tr>
</tbody>
</table>

**References:**

P.R. Wallace, Phys. Rev. 71, 622 (1947)
The dispersion relation for a stage-1 compound is:

$$-\varepsilon_v(k) = \varepsilon_c(k) = \frac{3}{2} \gamma_0 b k$$

$\gamma_0$ → nearest in-plane overlap energy

$b$ → in-plane nearest neighbor distance
COMPARE THE DISPERSION RELATIONS FOR GRAPHENE AND GACs

The figures for graphene are from: Terrones et al., Nano Today 5, 351 (2010)
ELECTRICAL CONDUCTIVITY
WHAT DO WE MEASURE?

GRAPHENE OUT

One (or a few) supported or free-standing graphene planes
Direct access to the graphene sheets by means of nanopropes.

CARBON NANOTUBE

Direct access to the nanotube
Graphene


Carbon nanotube

ELECTRICAL CONDUCTIVITY
WHAT DO WE MEASURE?

GRAPHENE IN (GACs)

One (or a few) graphene planes sandwiched between insulating layers.

Macroscopic probes on the bulk, but...
Representation of stage-1 graphite-FeCl$_3$ compound showing the graphene layers sandwiched between intercalate layers.

Red arrows indicate *graphene planes* and the blue ones the *intercalate layers*. Note that the intercalate layers maintain the bulk FeCl$_3$ structure.

As regards electrical conduction, one may consider *graphene conductors* in parallel, insulated from each other by the *intercalant*.
<table>
<thead>
<tr>
<th>STAGE 1</th>
<th>STAGE 2</th>
<th>STAGE 3</th>
<th>STGDE 4</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Diagram" /></td>
<td><img src="image2" alt="Diagram" /></td>
<td><img src="image3" alt="Diagram" /></td>
<td><img src="image4" alt="Diagram" /></td>
</tr>
</tbody>
</table>

**Graphene plane**

**Intercalate (K) plane**

**STAGING PHENOMENON IN GRAPHITE-POTASSIUM DONOR COMPOUNDS FOR STAGES 1 TO 4**
ELECTRICAL RESISTIVITY OF GACs

The graphene layers (red arrows) act as 2D resistances in parallel: $R_1, R_2, \ldots, R_i$

\[
\frac{1}{R_{tot}} = \sum_i \frac{1}{R_i}
\]

or

\[
C_{tot} = \sum C_i
\]

*R is for electrical resistance and C for conductance*
MODELS APPLICABLE FOR TRANSPORT PROPERTIES

BULK CARBONS
- only semiclassical (until the mid-1980’s),
- quantum (since the mid-1980’s): weak localization effects,
- massless fermions (stage-1 GACs).

NANOSTRUCTURED CARBONS
- NANOTUBES
  - non relativistic quantum mechanics (NRQM) to describe most of its properties
  - weak localization, Universal Conductance Fluctuations,
  - ballistic transport.

- GRAPHENE
  - relativistic quantum mechanics (RQM) or quantum electrodynamics (QED),
  - massless Dirac fermions,
  - ballistic transport.
Intercalation compounds of graphite*

M. S. DRESSELHAUS† and G. DRESSELHAUS‡
Massachusetts Institute of Technology, Cambridge, MA 02139, USA

[Received 29 July 1980]

*This article was originally published in Advances in Physics, volume 30, 1981. It had attracted 876 citations by October 2001, and is ranked 11 in the index of articles attracting more than 100 citations.
As a result of charge transfer, intercalation increases the hole density, $N$. A decrease in the mobility, $\mu$, is due to the defects introduced by the intercalation process. The net result here is a significant decrease in the in-plane electrical resistivity, $\rho$.

$$\frac{1}{\rho} = \sigma = qN\mu$$

*Electrical resistivities are in $\Omega\cdot cm$.*

*From: Chieu, Dresselhaus, Endo & Moore, PRB 27, 3686 (1983)*
For a group $j$ of charge carriers:

$$\sigma_j = q N_j \mu_j$$

and, for more than one type of charge carriers:

$$\sigma = \sum \sigma_j$$
MATTHIESSENS’ RULE

\[
\rho = \rho_r + \rho_i
\]

- **total resistivity**
- **ideal resistivity**
  - varies with temperature \(\rightarrow e-p\) interaction
- **residual resistivity**
  - does not vary with temperature \(\rightarrow\) static defects (defect scattering)
- **weak localization effects**
IDEAL & RESIDUAL RESISTIVITIES OF GACs WITH VARIOUS HOST GRAPHITES

Residual resistivity

Ideal resistivity at 300 K

All resistivities are in units of $10^{-6}\Omega\cdot\text{cm}$

From: Piraux & Issi (1986)
This diagram shows clearly the **lower bound** for the room temperature electrical resistivity of GACs, i.e. around $3.4 \times 10^{-6} \ \Omega \cdot cm$, since it is the intrinsic value due to electron-phonon large-angle scattering at this temperature.
Even at RT, the resistivity of pristine carbons is dominated by boundary scattering up to about 1 µm crystallite size.

<table>
<thead>
<tr>
<th>Material</th>
<th>Remarks</th>
<th>Carrier mobility (cm²/V.s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td></td>
<td>~ 4.2K ~ 77K 300K</td>
</tr>
<tr>
<td>Si (bulk)</td>
<td>For electrons (holes = 450)</td>
<td>1,450</td>
</tr>
<tr>
<td>GaAs</td>
<td>Heterostructure -2DEG</td>
<td>36 10⁶ 3 10⁵ 5 10³</td>
</tr>
<tr>
<td>Bismuth</td>
<td>Single crystal, large size, high purity</td>
<td>43 10⁶ 6.4 10⁵ 3.2 10⁴</td>
</tr>
<tr>
<td>HOPG</td>
<td>Heat treated above 3,000 C</td>
<td>6.7 10⁴ 1.2 10⁴</td>
</tr>
<tr>
<td>Graphene</td>
<td>Reference and T to be verified</td>
<td>~10⁶ ??</td>
</tr>
</tbody>
</table>
From: Schlom & Pfeiffer (private communication)
WHY ARE MOBILITIES LOW IN METALS AND HIGH IN SEMIMETALS AND SEMICONDUCTORS?

<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>HIGH TEMPERATURE</th>
<th>LOW TEMPERATURE</th>
</tr>
</thead>
<tbody>
<tr>
<td>METALS</td>
<td>large-angle scattering with large number of high energy interacting phonons.</td>
<td>small-angle scattering with small number of interacting low-energy phonons.</td>
</tr>
<tr>
<td>(high carrier densities)</td>
<td>LOW MOBILITY</td>
<td>HIGH MOBILITY</td>
</tr>
<tr>
<td>SEMIMETALS</td>
<td>large-angle scattering with small number of interacting low-energy phonons.</td>
<td>large or small-angle scattering with small number of interacting low-energy phonons.</td>
</tr>
<tr>
<td>(for small charge carrier densities)</td>
<td>HIGH MOBILITY</td>
<td>VERY HIGH MOBILITY</td>
</tr>
<tr>
<td>SEMICONDUCTORS</td>
<td>large-angle scattering with small number of interacting low-energy phonons.</td>
<td>large or small-angle scattering with small number of interacting low-energy phonons.</td>
</tr>
<tr>
<td>(for small charge carrier densities)</td>
<td>HIGH MOBILITY</td>
<td>VERY HIGH MOBILITY</td>
</tr>
</tbody>
</table>
SMALL AND LARGE-ANGLE ELECTRON-PHONON SCATTERING

efficient scattering > change of direction

a small decrease
FORBIDDEN TRANSITION
(SEMIMETALS)

\[ \hbar k_F + \hbar q > \hbar k_F' \]
\[ \frac{\varepsilon(k_F)}{\varepsilon(k_F')} \sim \frac{\varepsilon(k_F)}{\varepsilon(k'_F)} \]
2D WEAK LOCALIZATION OBSERVED IN GACs

WHAT HAPPENS WHEN WE INTERCALATE FLUORINE?

WHY IS THE RESULTING GAC SO DIFFERENT THAN ITS COUSINS?
Profund physical modifications, which are more pronounced with increasing fluorine.

- Charge transfer
  modifies the electronic parameters
  by increasing charge carrier density first, then decreasing it:

  **SEMIMETAL > METAL > POOR CONDUCTOR > INSULATOR**

- Distortion of graphene planes
  increases the disorder experienced by the hole & phonon gases
  > Weak to strong localization of holes

- Dimensionality
  Transition from 3D to quasi-2D to 3D system

*A unique situation*
IMPACT ON PHYSICAL PROPERTIES

Electrical resistivity at 4.2K

With increasing fluorine concentration

INSULATOR > POOR CONDUCTOR > METALLIC > SEMIMETALLIC

stronger disorder > strong disorder > weak disorder

strong localization > localization > weak localization

3D > Quasi-2D > 3D

Resistivity (mΩ.cm)

$k_F l$

Pristine C
LOW TEMPERATURE WEAK LOCALIZATION EFFECTS IN $C_xF$ COMPARED TO GICs METAL CHLORIDES

Piraux et al., (MIT, Shinshu, Kyoto, ICMCB, LLN)

Note that for high fluorine concentration, the effect is two orders of magnitude larger in $C_xF$ than in other GACs
For low fluorine concentrations, the effect of charge transfer is comparable to that for other acceptor GICs, i.e. it increases the density of the hole gas, but holes mobilities are lower in F-GICs (stronger defect scattering) and so are the electrical conductivities.
ELECTRICAL CONDUCTIVITY OF PRISTINE SWNT BEFORE AND AFTER FLUORINATION

**EFFECT OF FLUORINATION ON THE ELECTRICAL CONDUCTIVITY OF GRAPHENE**

*In lightly fluorinated graphene*

The fluorine atoms can be attached and removed from the graphene plane reversibly without creating vacancies.

*In heavily fluorinated samples*

The reduction process no longer restores pristine graphene, suggesting damage to the sp2 carbon network.

The temperature-dependent resistivity of fluorinated graphene exhibits insulating behavior, which can be described by variable range hopping in 2D at low carrier densities but deviates from this model at high carrier densities.

**A SITUATION COMPARABLE TO THAT IN BULK F-GACS**

*From: Cheng, S.-H.; Hong, X.; Zhu, J. APS March Meeting 2010*
SCATTERING AND WEAK LOCALIZATION

Since large-scale defects limit the scattering length in HOPG and GACs, many interesting effects observed in graphene cannot be observed in HOPG & GACs.

The other side of the coin

GACs are ideal systems to study 2D weak-localization effects and C-C interaction by varying the degree of disorder, in addition to that of the Fermi level (charge transfer) to a limited extent.
**Band structure**
When we consider a single graphene sheet, Wallace is always right.

**Mobilities**
There are materials with higher mobilities than graphene, where there is still room (at the top) for increase. But who cares about mobilities, once in the ballistic regime.

**Fluorine**
The particular case of fluorine in the bulk gives a clear indication for the nanostructured carbons.
Researchers in carbons have long fantasized about graphene. Now it is there. Enjoy it.

Theorists wake up earlier than experimentalists, but if they want to see their predictions confirmed, they have to wait till the experimenters wake up.

Fortunately, you cannot predict everything and this allows science to keep going and the younger generations to have fun.

Thanks to:
J-C Charlier, UCL,
M.S Dresselhaus, MIT,
L. Piraux, UCL,
J. Heremans, OSU.