Théorie Quantique des Materiaux (TQM)
Institut de Minéralogie et de Physique des Milieux Condensés

M. Calandra, F. Mauri, L. Paulatto, M. Casula

www.graphene-flagship.eu

GRAPHENE FLAGSHIP

TEAM EXPERIENCE

➡ The team has a proven succesful expertise in electronic structure calculation

➡ Strongest fields of research:

- Phonons – IXS, Raman and Infrared spectra (energy, intensity and linewidth)

  A.C. Ferrari *et al., Raman Spectrum of Graphene and Graphene Layers,*
  Phys. Rev. Lett. **97**, 187401 (2006)

  Piscanec *et al., Kohn anomaly and electron-phonon interaction in graphite,*
  Phys. Rev. Lett. **93**, 185503 (2004)

- Electron-phonon interaction (Transport and superconductivity)

  G. Profeta, M. Calandra and F. Mauri, *Phonon-mediated superconductivity in graphene by Li deposition*, Nature Phys. **8**, 131 (2012)

  M. Lazzeri *et al.*, *Electron Transport and Hot Phonons in Carbon Nanotubes*, PRL **95**, 236802 (2005)

- Theoretical prediction and interpretation of spectroscopic data including Raman, INS, IXS, NMR, EPR and core-hole spectroscopy

➡ Methodological developments

French « home » of the QUANTUM-ESPRESSO code.

FLAGSHIP GOALS (TQM)

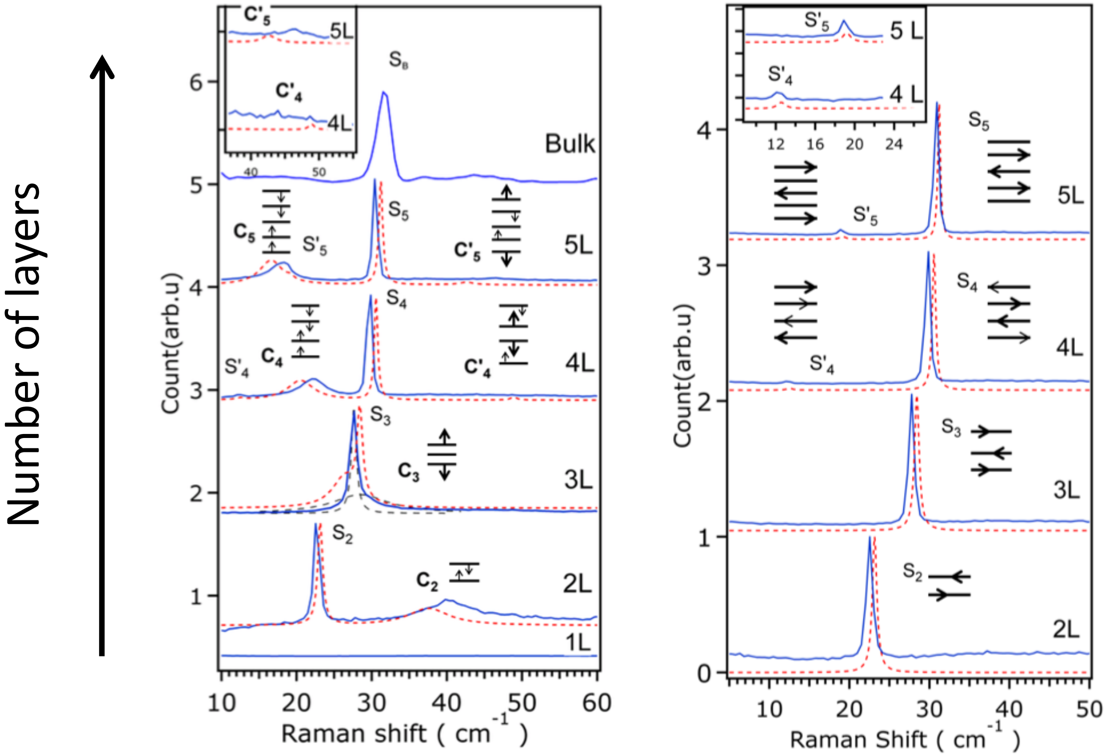
1. Raman (and infrared) characterization of nanolayers
    - First order Raman scattering.
    - Double resonant Raman scattering.

2. Describe transport properties of FET devices (Graphene and transition metal dichalcoenides.
    - Role of the external large applied electric field in FET
    - Intrinsic transport (electron-phonon and electron-electron scattering)
    - Defect Scattering
    - Scattering with the substrate (remote phonon coupling)

3. Intrinsic Thermal transport in 2D nanolayers based devices

GOAL 1 : SAMPLE CHARACTERIZATION BY RAMAN SCATTERING

Ex.: Raman spectroscopy of Ultralow energy shear and compression modes in few layers MoS_2



Exp.

Theory

Boukicha, Calandra et al.
arXiv:1304.4122
PRB sous press.

Theory completely *ab initio*, position, intensity, linewidth (phonon-phonon scattering)

Unusually large anharmonicity of compression modes: impact on thermal transport.

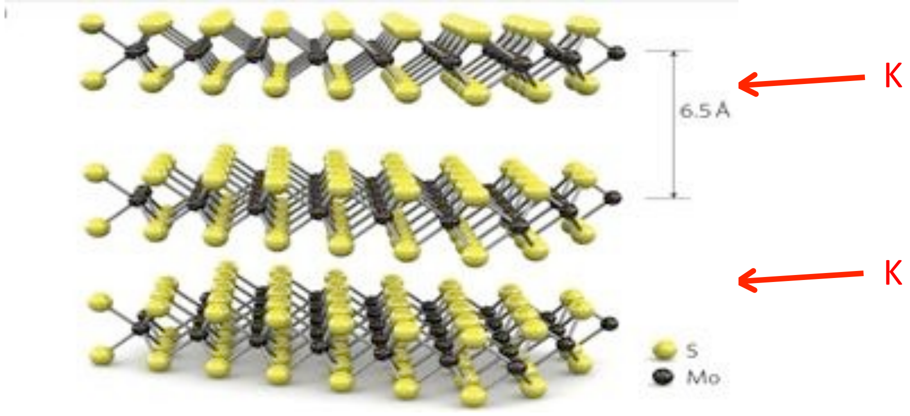
Note: Theory + Samples + 0.5 Measurements @ IMPMC

What about other TMD or multilayer 2D crystals ?

GOAL 2: ELECTRIC TRANSPORT IN 2D CRYSTALS (GRAPHENE AND BEYOND)

Tunable transport properties = tunable number of carriers.

Chemical doping or intercalation

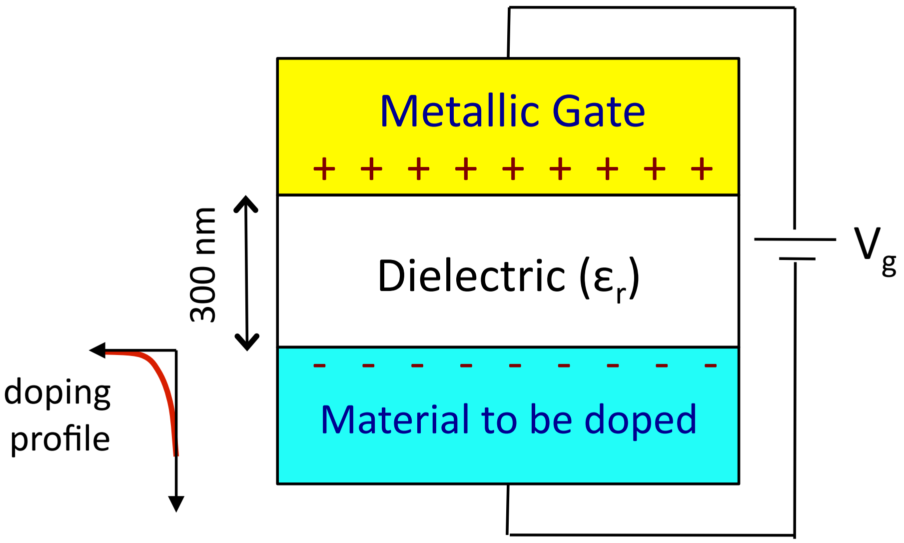


Ex. MoS_2

Radisavljevic, B *et al.* Nature Nanotech. **6**, 147 (2011).

- ✔ Large number of carriers injected.
- ✗ Doping can be non-uniform.
- ✗ Not always possible.

Field-effect doping (FET)



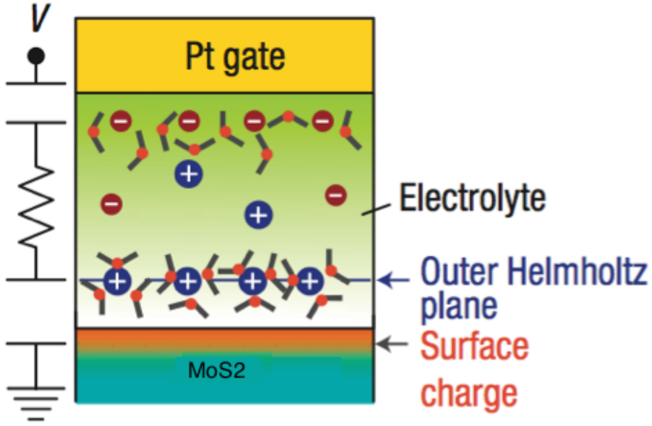
- ✔ Uniform doping
- ✗ Low number of carriers injected (Dielectric breakdown)

Maximum surface charge-density ≈ 10^{12}-10^{13} cm^{-2}

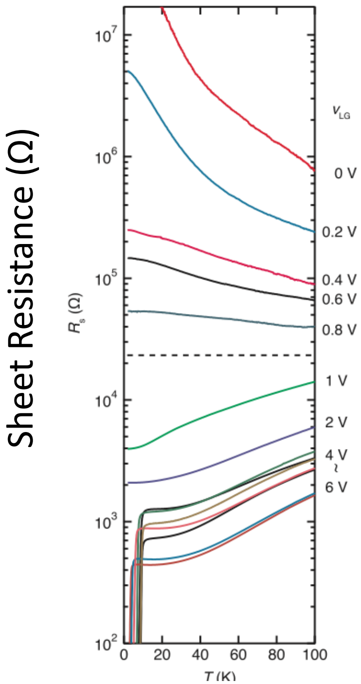
BREAKTHROUGH (2009): ELECTROCHEMICAL DOPING

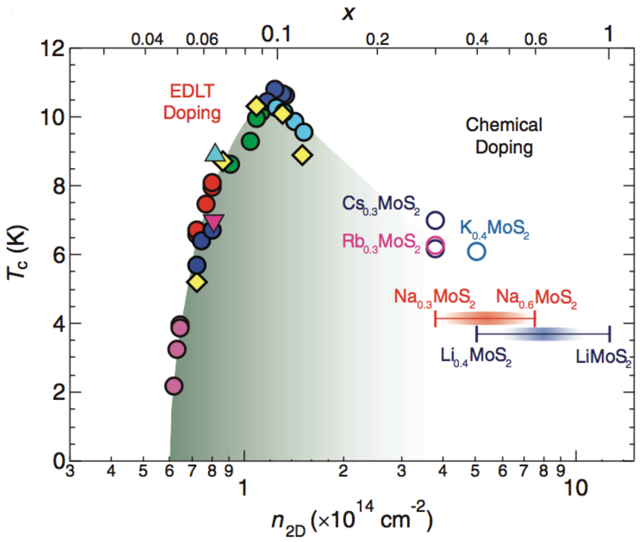
Ionic liquid based field-effect transistors: The best of both worlds.

Ex.: electrochemical doping of few layer thick MoS_2 nanolayer.



Ye *et al.* Science **338**, 1193 (2012)





Maximum surface charge-density achieved ≈ 10^{14}-10^{15} cm^{-2}
(100 times larger than in oxydes FETs)

Doping as easy as turning a knob !

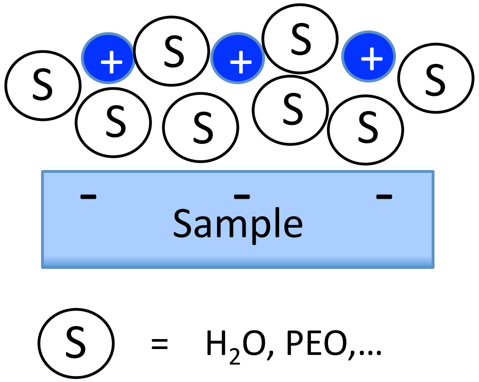
No modeling of electrochemical doping in literature on these substrates!

ELECTRIC TRANSPORT

MODELING OF ELECTROCHEMICAL DOPING

Step 1: Role of the electric field on chemistry and physics

Step 2: Role of the electrolyte : double layer capacity,
chemisorption/physisorption

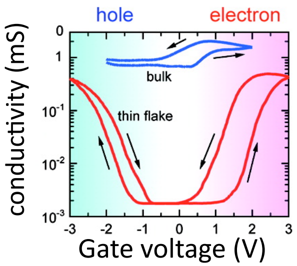


S = H_2O, PEO,…

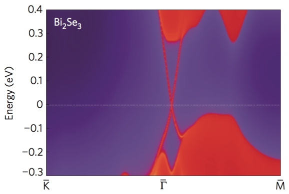
TRANSPORT AND SUPERCONDUCTING PROPERTIES

Step 3: Electron-phonon interaction from first principles
Application to electrochemically doped nanolayers

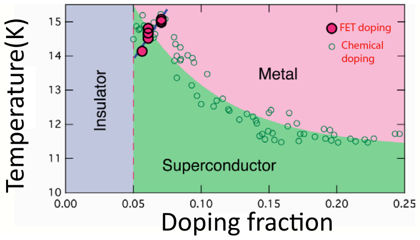
Step 4: Electron-defect scattering effects on mobility.



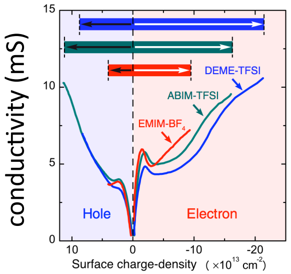
Charge density wave
Materials



Topological
Insulators



Superconductors

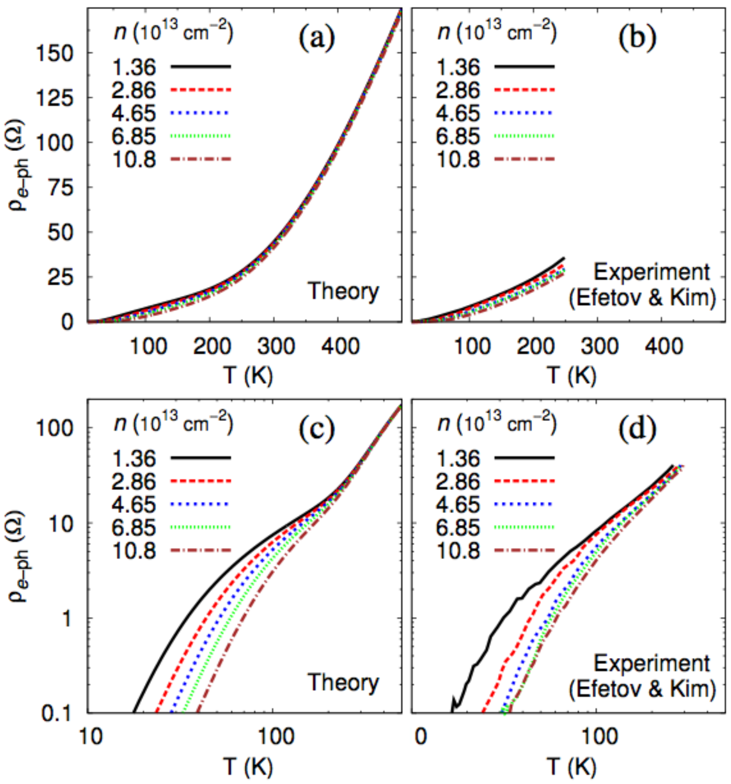


Materials for
nanoelectronics

INTRINSIC ELECTRIC TRANSPORT (INTERMEDIATE TO HIGH T)

- electron-phonon scattering rates from density functional theory + GW
- Mobility/conductivity/resistivity from Boltzmann equation

Example: The intrinsic resistivity of graphene (FET doped)



Previous works: DFT resistivity more then 10 smaller then experiments… WRONG

DFT+GW excellent agreement with Experiments

GW correction (30%)

Collaboration with EPFL Lausanne
(N. Marzari, A. Kis)

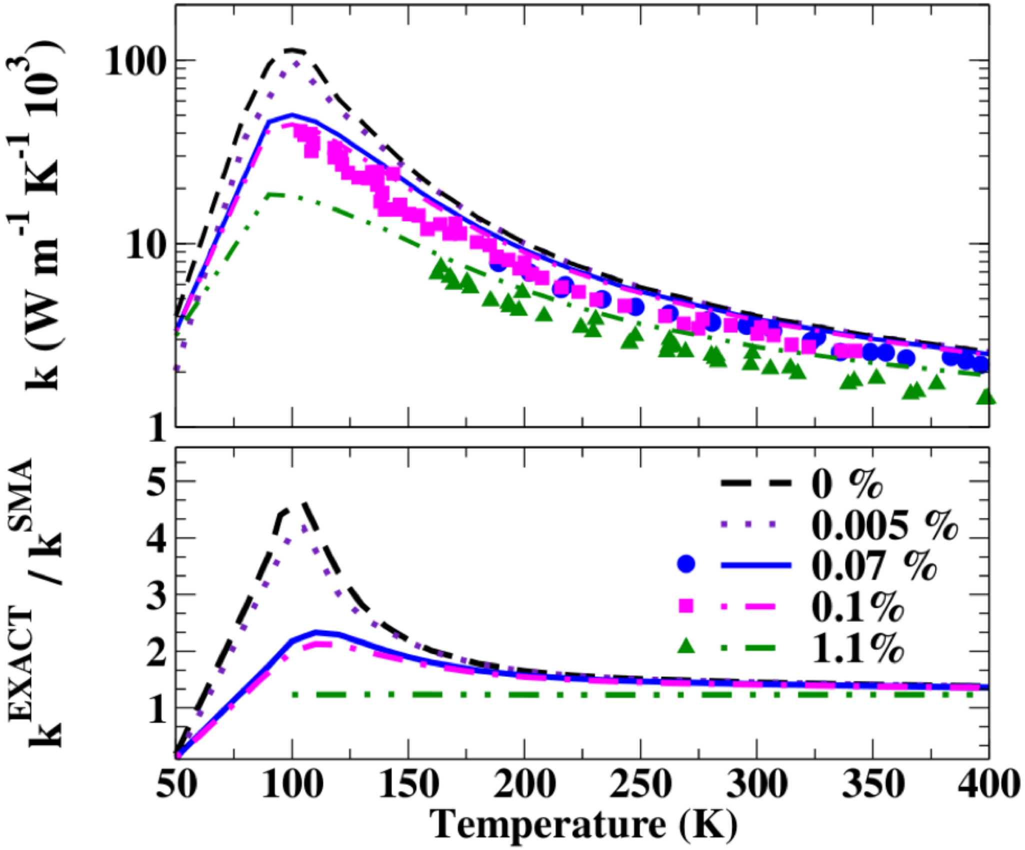
Park *et al.* , In preparation

What about dichalcogenides ?

Thermal Transport

- Anharmonic phonon-phonon scattering rates from firs principles
- Thermal conductivity from Boltzmann equation

Ex. thermal conductivity of isotopically enriched diamond (Graphene, MoS_2 under way)



Fugallo *et al.* arXiv:1212.0470

The method works, what about its application to 2D crystals ?

ORIGINALITY AND IMPACT OF OUR APPROACH

TEAM

Leading team in electronic structure calculation, particularly focused on graphene and understanding properties of low dimensional nanostructures (2D crystals).

ORIGINALITY OF THE APPROACH

We treat electron-phonon, phonon-phonon and electron-electron interactions on equal footing without any empirical parameters (DFT, QMC, GW).

Spectroscopic properties from first principles (IXS, INS, Raman, Infrared, NMR, EPR, core-hole spectroscopy).

Calculation of transport properties in field-effect configuration.

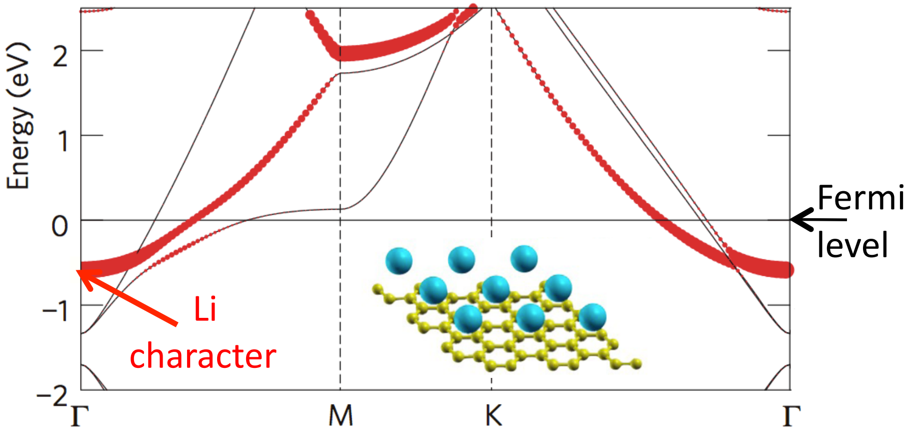
IMPACT IN DIFFERENT FIELDS OF KNOWLEDGE

Surface physics, Nanoelectronics, Solid state physics, Superconductivity, Electrochemistry.

GOAL: LOW T TRANSPORT AT HIGH DOPING -SUPERCONDUCTIVITY

Electrolyte ions can dope the surface (Electrochemically induced reconstructions)

Ex.: Li on top of graphene



Adatom states at the Fermi level!

Partial charge transfer !

G. Profeta, M. Calandra *et al.*, Nature Physics (2012)

Superconductivity induced by adsorbed atoms ?

What happens in electrochemically doped TMD ?