First Principle Investigation on Thermoelectric Properties of TMDC: Beyond Rigid Band Model
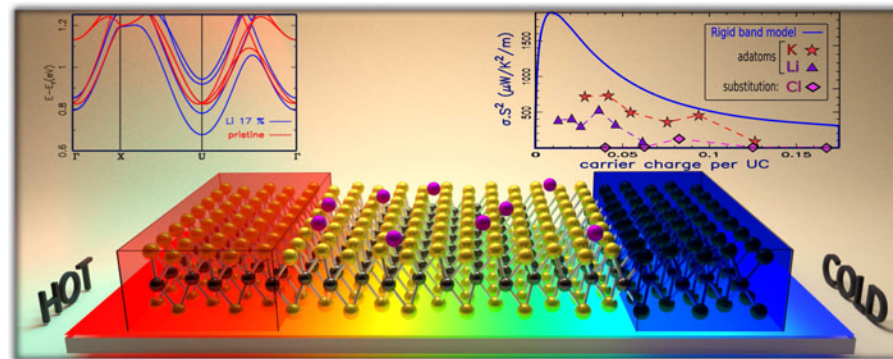
Ch. Adessi, S. Thebaud, R. Bouzerar and G. Bouzerar

Institut Lumière Matière, Université Claude Bernard Lyon 1-CNRS, France

Outlines

- The Basics of the Seebeck Effect

- The structure of TMDCs and the Doping Issue

- Primary Results with Rigid Band Shift Model

- Doped TMDC (ab-$initio$)

- Power Factor using Realistic Doping (w disorder)

- Concluding Remarks

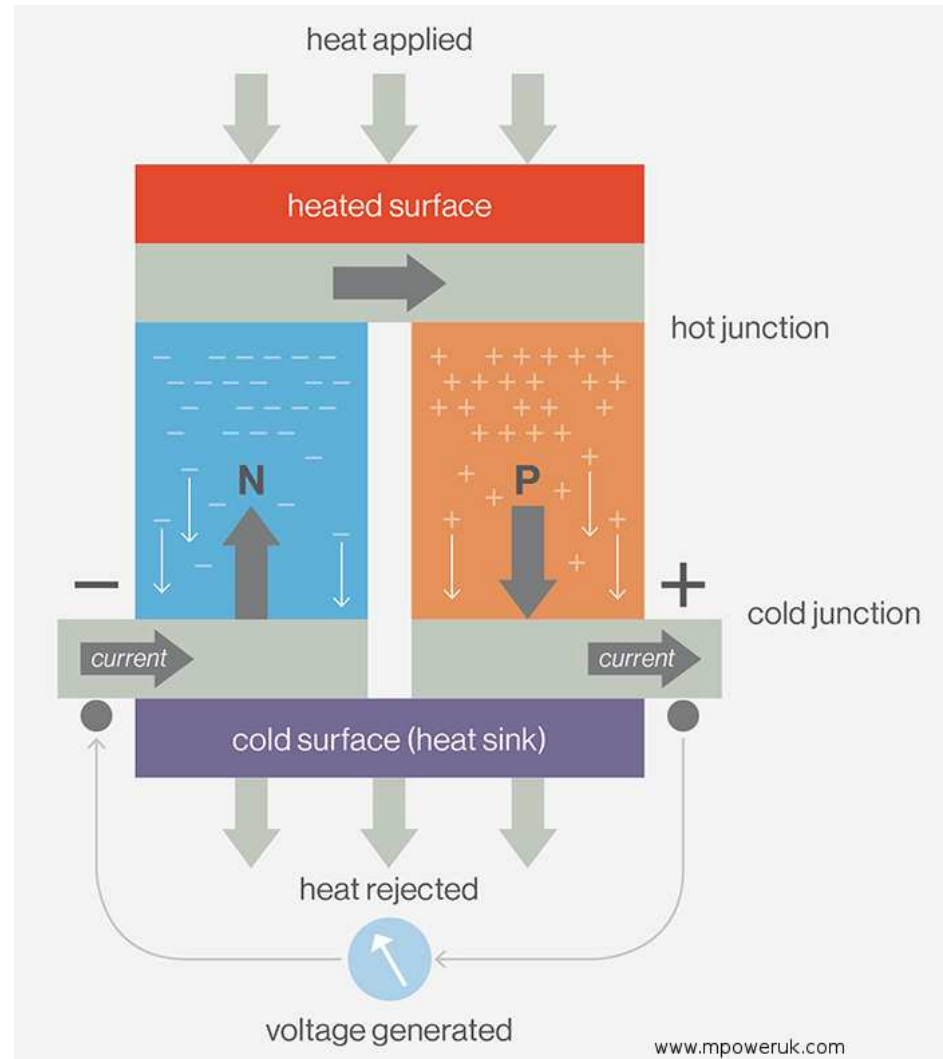Ch. Adessi et $al.$, J. Phys. Chem. C (2017)

The Seebeck Effect
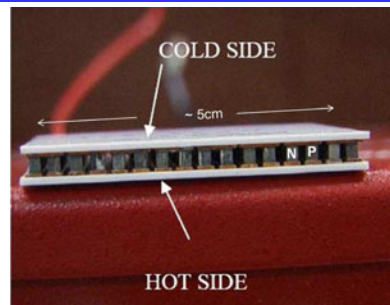
Thomas Johann Seebeck

(1770-1831)

Electromotive force caused by temperature gradient (input) across two dissimilar conducting metals, which form a closed loop.

Seebeck Coefficient:

$$S = \frac{\Delta V}{\Delta T}$$

$\begin{cases} \text{N type} & \Rightarrow & S < 0 \\ \text{P type} & \Rightarrow & S > 0 \end{cases}$

Université Claude Bernard Lyon 1

Device Efficiency

The ability of a given material to efficiently produce thermoelectric power is related to the figure of merit:

$$ZT = \frac{\sigma.S^2.T}{\kappa}$$

$\sigma.S^2$: Power Factor (PF)

κ: Thermal Conductivity

$\Rightarrow$ A good TE material has a large PF and a small κ

- 2D materials (like TMDC) are expected to have a low thermal conductance.

- It is possible to reduce κ by phonon engineering.

- To obtain the largest Power Factor (PF), we need a large σ and a large S.

  - Metal have large σ and poor S.
  - Semiconductor have very poor σ and large S.

- One way to obtain a large PF is to use doped semiconductor.

- We have investigated two technics: substitution and adsorption doping.
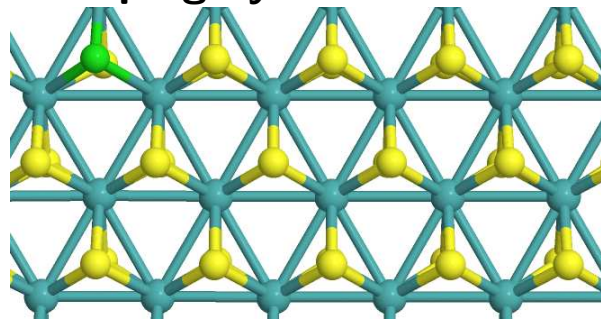
Université Claude Bernard Lyon 1

TMDC's Structure

M (Mo,W) X (S,Se,Te)
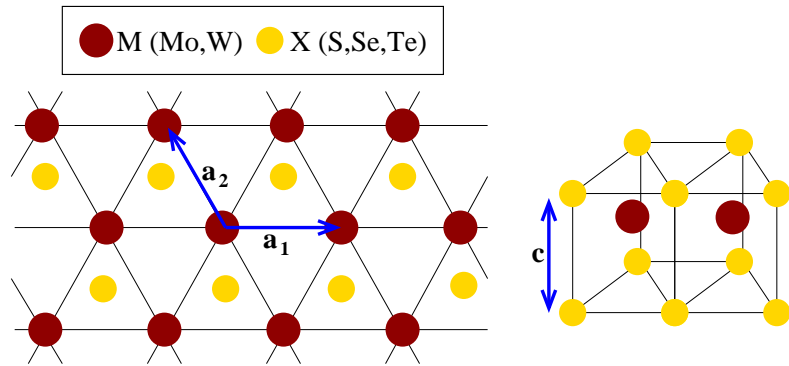
- TMDC (MX_2) $\Rightarrow$ honeycomb structure.
- Made up of layered X-M-X sheets.
- Two hexagonal sheets of X atoms and an intermediate hexagonal sheet of M atoms.
- Monolayer TMDC are semiconductor with direct band-gap.

Doping Issue

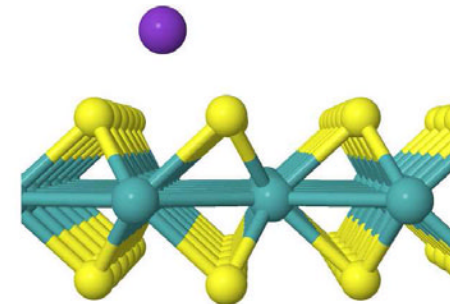**Doping by Substitution:**

Hole doping   Electron doping

15	16	17
P phosphorus 30.97	**S** sulfur 32.06	**Cl** Chlorine 35.45

41	42
Nb Niobium 92.91	**Mo** sulfur 95.96

73	75
Ta Tantalum 180.95	**Re** Rhenium 186.207

Doping by Adsorption:

3	2 1
Li lithium 6.94	

11	2 6 1
Na Sodium 22.99	

19	2 8 8 1
K potassium 39.098	

37	2 8 18 8 1
Rb Rubidium 85.47	

Alkali metals come as e^- donnors

Outstanding Experimental achievement:

N-doping of MoS_2 by surface charge transfer using K.

(Fang *et al.* Nano Letters 2013, 13, 1991-1995)

Université Claude Bernard Lyon 1

A Few Words About Theory

$\Rightarrow$ The PF is obtained using *ab-initio* calculations and Green's function technics (NEGF) on the basis of Landauer-Büttiker formalism

Boltzmann	NEGF
• Semi-classical theory	• Full *ab initio* theory
• Scattering mechanisms described by: Relaxation Time (τ)	• Based on localized basis set (SIESTA)
	• Scattering mechanisms have to be defined
It gathers all scattering mechanisms: (defects, e^- - e^-, e^- - phonons ...)	**Insight on disorder scattering**

S and G are computed using the Transmission:

$$G = -\frac{2e^2}{\hbar} \int_{-\infty}^{+\infty} T(E) \left(\frac{\partial f}{\partial E} \right) dE \,,$$

$$S = -\frac{1}{k_B T} \frac{\int_{-\infty}^{+\infty} (E - E_F) \, T(E) \left(\frac{\partial f}{\partial E} \right) dE}{\int_{-\infty}^{+\infty} T(E) \left(\frac{\partial f}{\partial E} \right) dE} \,.$$

Left Lead   Device   Right Lead

L_z

●:X ●:M ●: adatom
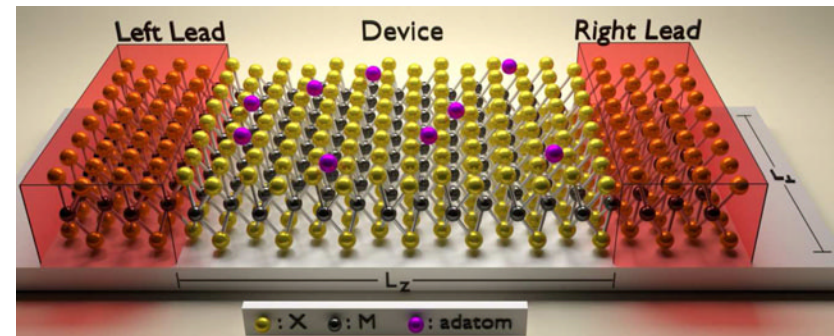
Within this formalisn, it is possible to deal with realistic disordering.

TNT 2017 Trends in NanoTechnology Dresden (Germany), June 05-09, 2013

Université Claude Bernard Lyon 1

Transport Using Rigid Band Shift

Rigid shift of the fermi-level $\Rightarrow$ Carrier doping by field effect.
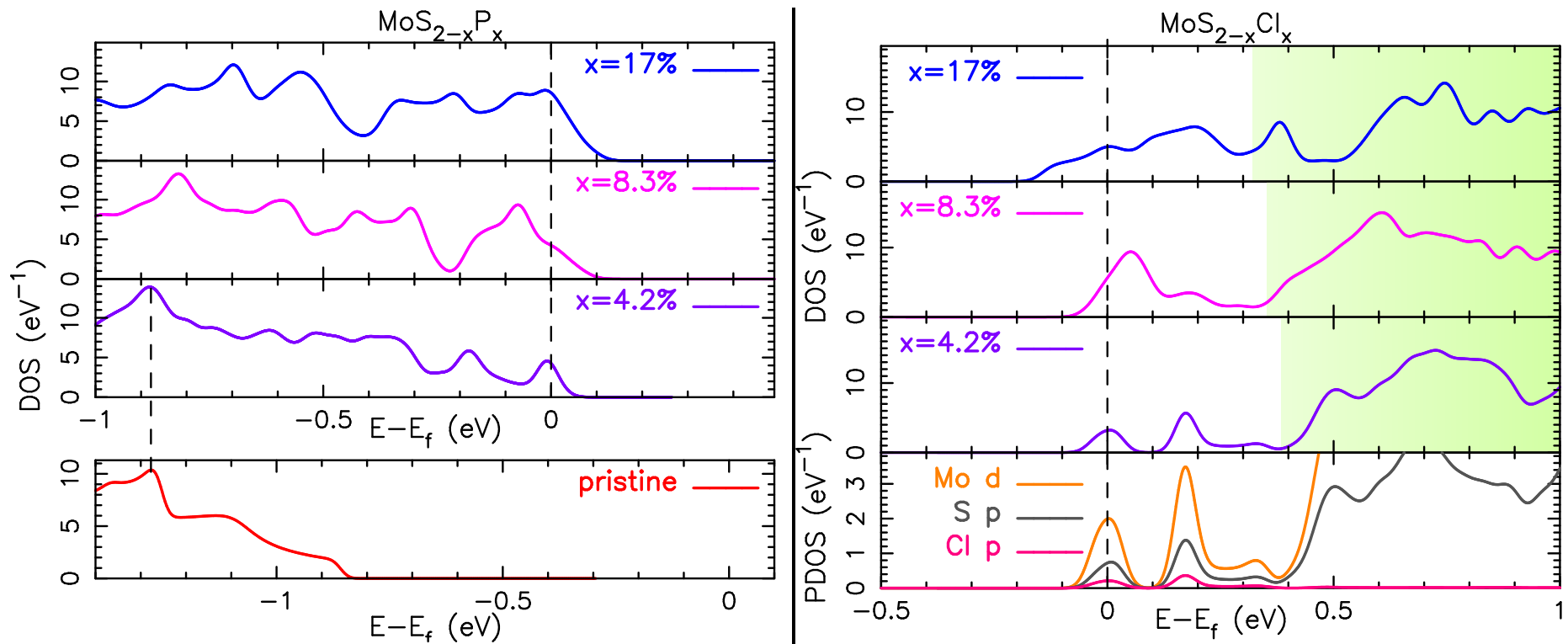
- PF$_{max}$ linked with 2 opposite trends
  - $\sigma \nearrow$ with $|E_f|$
  - $S \searrow$ with $|E_f|$
- Aim: To access the largest PF with a doping technique.

	$S(\mu V/K)$	$\sigma(\mu S/\text{Å})$	PF $(\mu W/K^2/m)$	carrier charge per UC $\times 100$
MoS_2	$-157.$	$8.$	1888	$+1.$
$MoSe_2$	$-87.$	$20.$	1480	$+9.$
WS_2	$-86.$	$16.$	1193	$+6.5$
WSe_2	$-173.$	$7.$	1968	$+1.5$

- Hole doping leads to lower PF.
- Largest PF for MoS_2 and WSe_2 for moderate carrier doping.
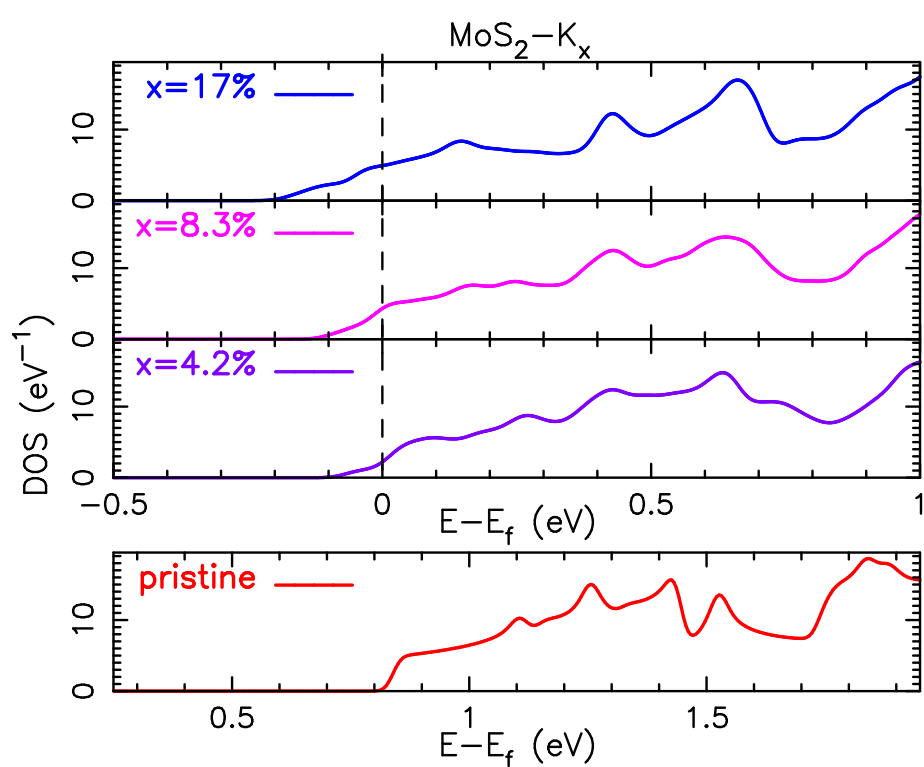- Armchair transport direction leads to similar results.
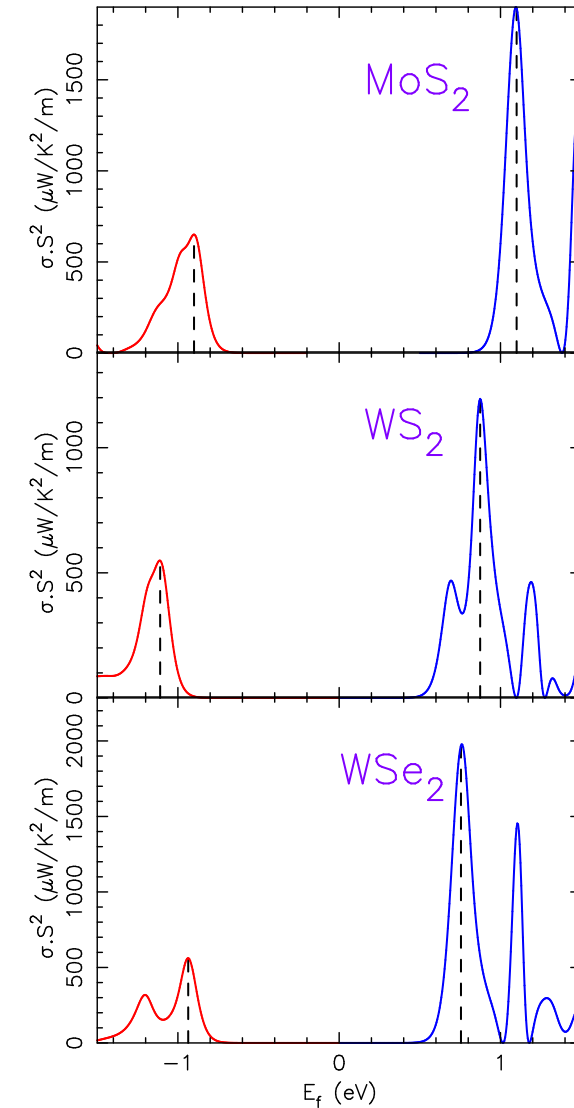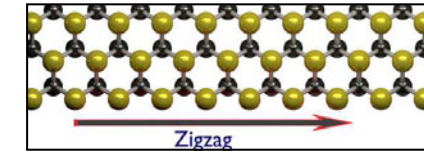
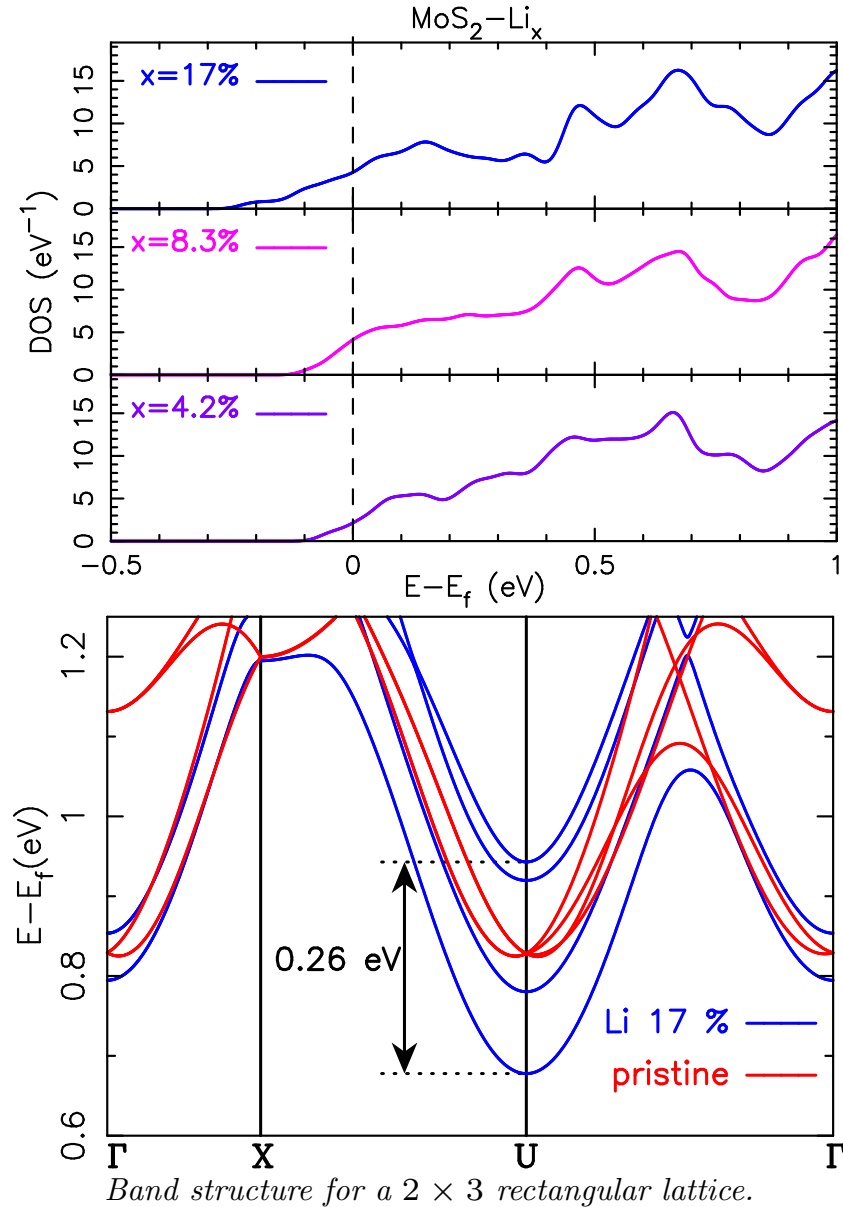# *Ab initio* Calculations
For Substitution Doping

- Subtitution doping by P and Cl is leading to donnor states at the Fermi level.
- This is also observed with F, Br and Re.
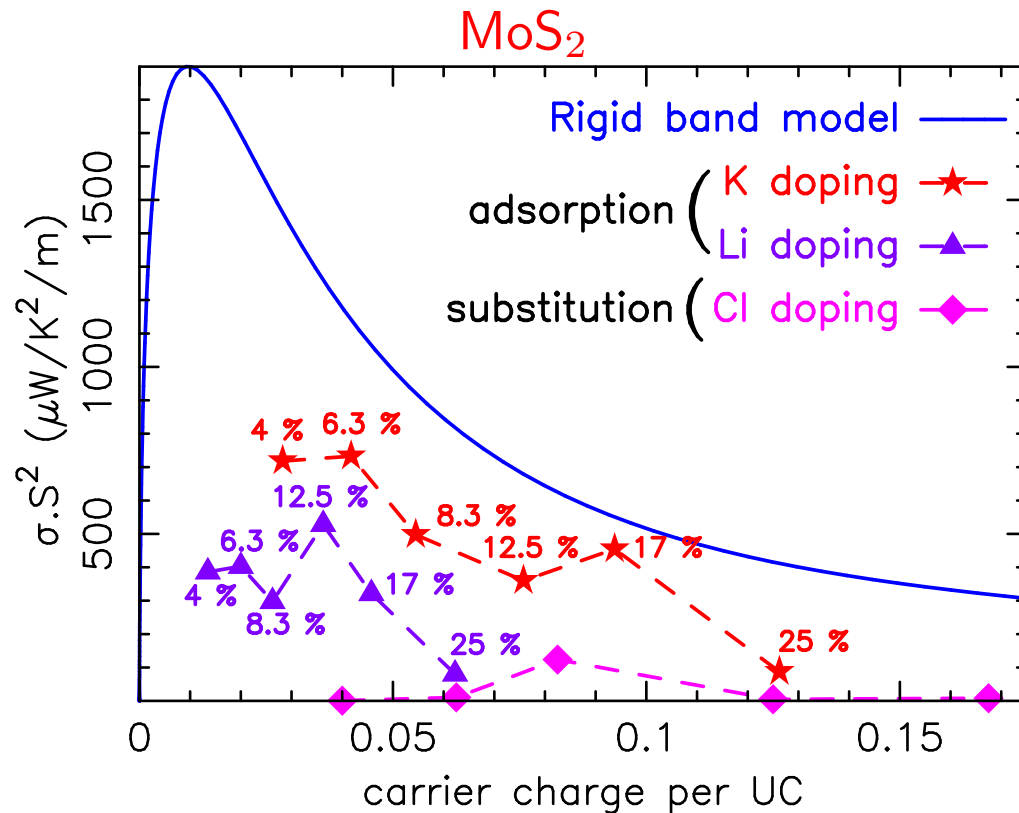- These states lead to almost flat bands at low doping concentration.

Adsorption Doping

MoS$_2$–K$_x$

x=17%

x=8.3%

x=4.2%

pristine

DOS (eV^{-1})

E–E$_f$ (eV)

MoS$_2$–Li$_x$

x=17%

x=8.3%

x=4.2%

DOS (eV^{-1})

E–E$_f$ (eV)

0.26 eV

Li 17 %

pristine

E–E$_f$(eV)

Γ X   U Γ

Band structure for a 2×3 rectangular lattice.

- Alkalies are creating states at much more higher energies than the first conduction band.

- They act almost as perfect donnors (band shifting).

- however they affect a bit the dispersion of the bands and remove some degeneracies.

TNT 2017
Trends in NanoTechnology
Dresden (Germany),
June 05-09, 2013

Université Claude Bernard Lyon 1

Power Factor Under Real Doping

MoS$_2$

Chloride

- Very poor PF for Cl
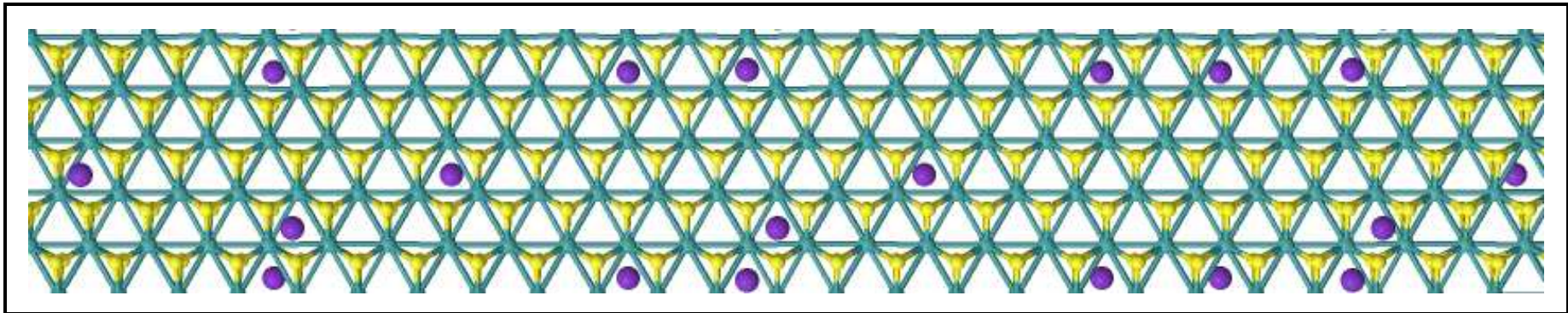- At low concentration $\Rightarrow$ Poor σ

Alkali

- Much closer to the Rigid band model.
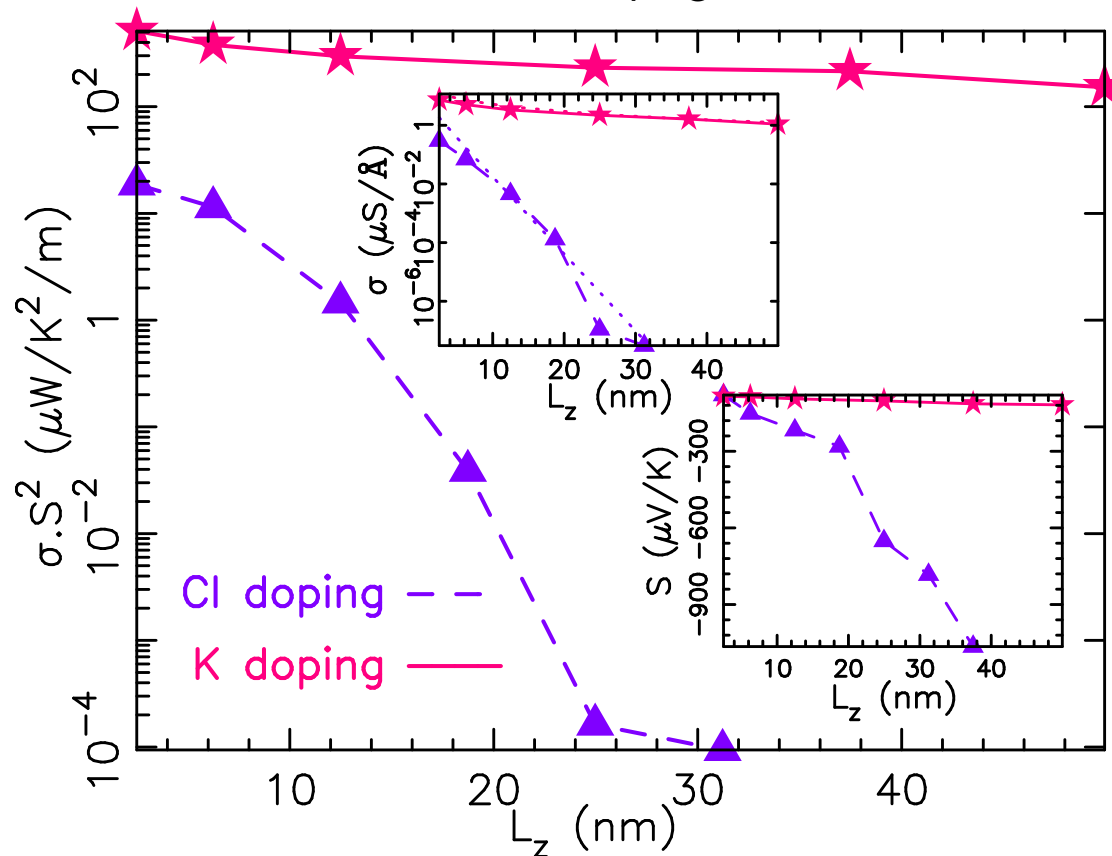- Large atoms (K or Rb) are better candidates than the smaller one (Li or Na).

- Lower conductance for Li and Na.
- Lower PF for MoSe$_2$ and WS$_2$
- MoS$_2$ and WSe$_2$ are the best candidates

4.2%		$\sigma(\mu S/\text{Å})$	S($\mu V/K$)	PF($\mu W/K^2/m$)
MoS$_2$	Na	2.	−105.	200.
	Rb	6.	−113.	728.
MoSe$_2$	K	5.	−79.	289.
WSe$_2$		4.	−150.	929.

Université Claude Bernard Lyon 1

Scattering by Disorders

12.5% doping

Chloride

- The conductivity decay is not compensated by the Seebek increase with the length.
- Anderson Localization

Potassium

- The PF variation is only one order of magnitude for a 50 nm length system.

Coherence length (L_c)

$$\rho(L) \propto e^{2L/L_c} - 1$$

- Cl $\Rightarrow$ 3.5 nm
- K $\Rightarrow$ 1.5 μm

Université Claude Bernard Lyon 1

Concluding Remarks

- Rigid band model should be handled with care

- Cl and P lead to donnor states at the FL

- Chloride leads to an Anderson localization

- Alkalies act almost as perfect e^- donnors

Thanks for your attention!

Université Claude Bernard Lyon 1