Layered and 2D materials: electronic properties and structural instabilities from First Principles

Pablo Ordejón

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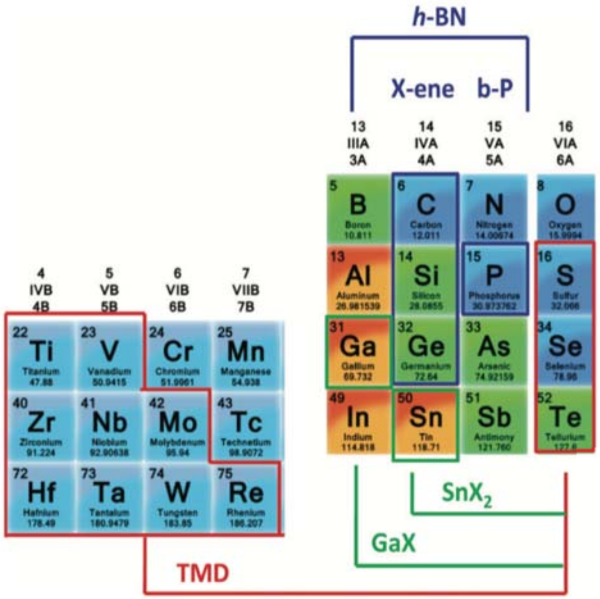
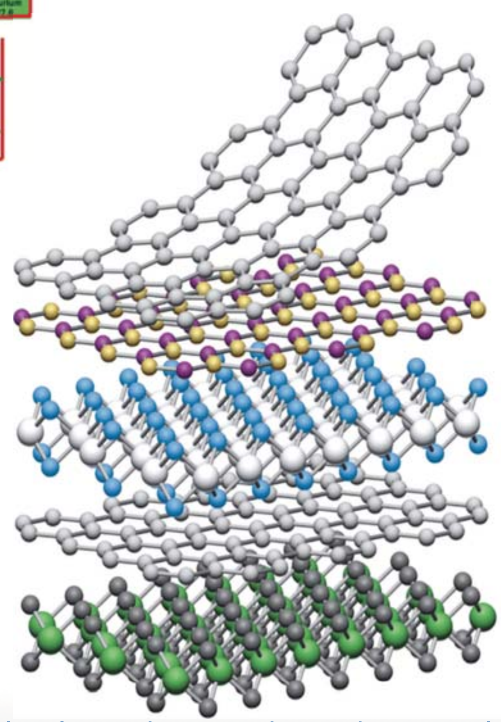
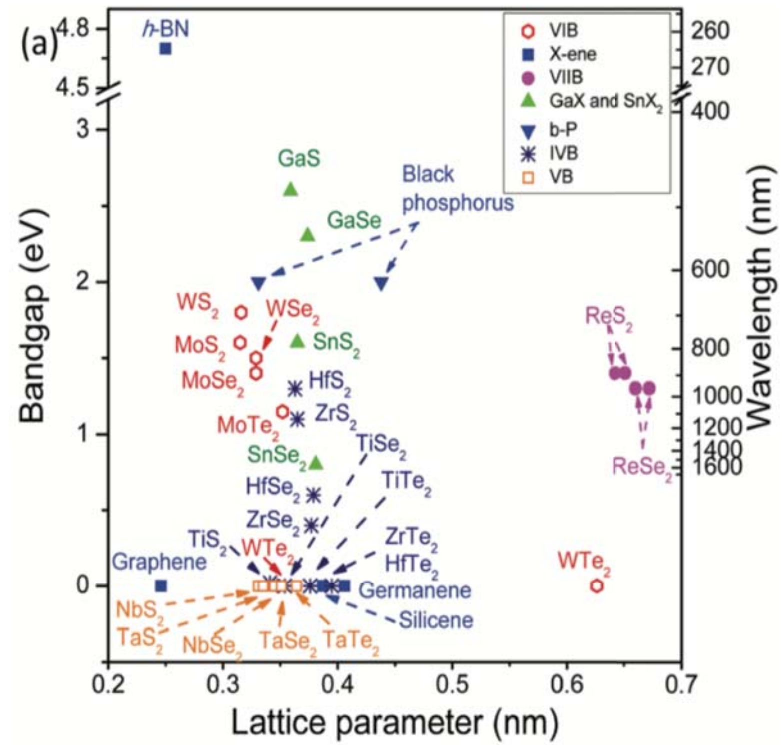
Graphene and 2D materials



Selected 2D materials from the periodic table.





Low dimensional solids

2D materials inherit the rich physics of **<u>tradicional low-dimensional solids</u>** (3D crystals with 1D or 2D electronic behavior and properties)

- Instabilities – CDWs (Peierls or other mechanisms), superconductivity, ...
- Non-Fermi liquid behaviour
- Fluctuations
- Localization
- ...

What new physics arise when the materials are <u>truly</u> 2D?

Charge Density Modulation (waves)

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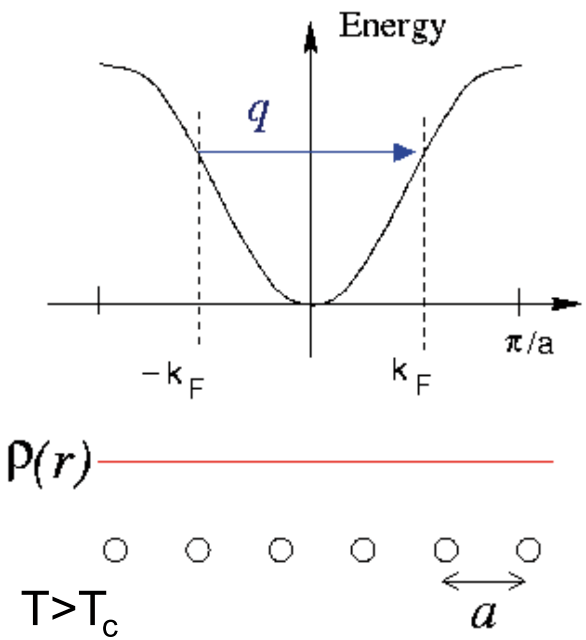
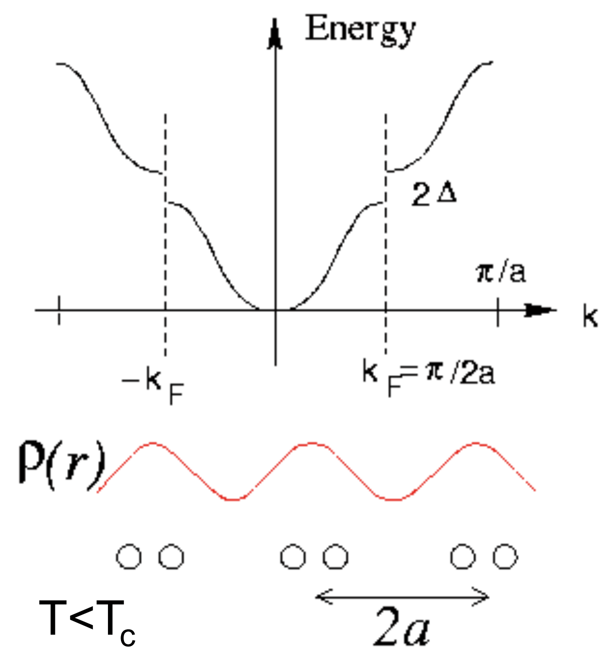
In systems with 1D bands: existence of 'Peierls Instabilities' (similar to Jahn-Teller distortions in molecules)

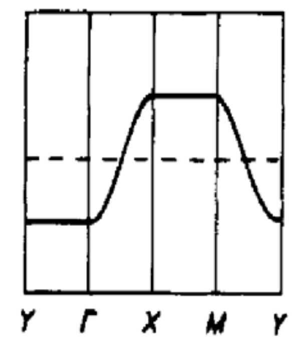
2D & 3D
"Low dimensional materials"

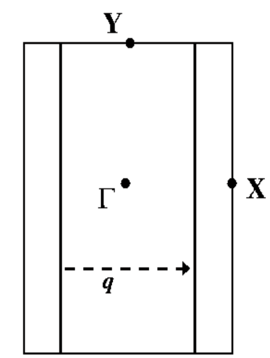


Periodic electron density



Modulated electron density (*Charge Density Wave*)





Fermi Surface "Nesting"

Two materials with electronic instabilities

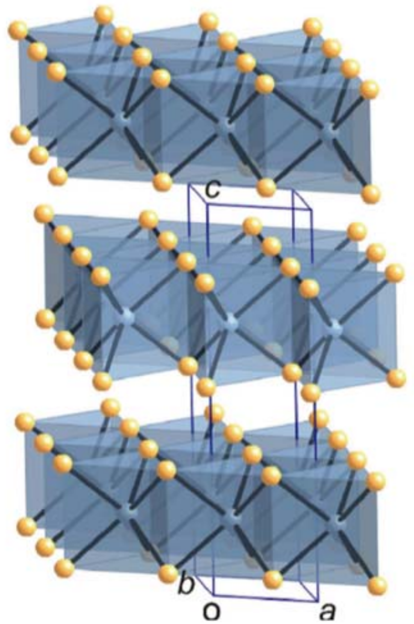
- $NbSe_2$
  - CDW and Superconducting instabilities
  - Two-gap superconductor?
  - STM: Surfaces of 3D crystals AND in the single-layer – open issues

- $TiSe_2$
  - CDW and Superconducting instabilities (as a function of doping)
  - Similar observations in the single-layer (doping with a FET setup)

.... **How can First-Principles calculations help in understanding these materials/properties?**

2H-$NbSe_2$

- Stacking of (Nb-centered trigonal prismatic) layers
- Two layers per unit cell, related by a screw axis symmetry along *c*
- At 30K, it undergoes a CDW transition leading to a (3a x 3a) superstructure.
- Superconducting at T_c ~ 7K, with many controversial aspects
- Two-gap scenario suggested by some experiments
- The interplay between the CDW and the SC state is not yet fully clear

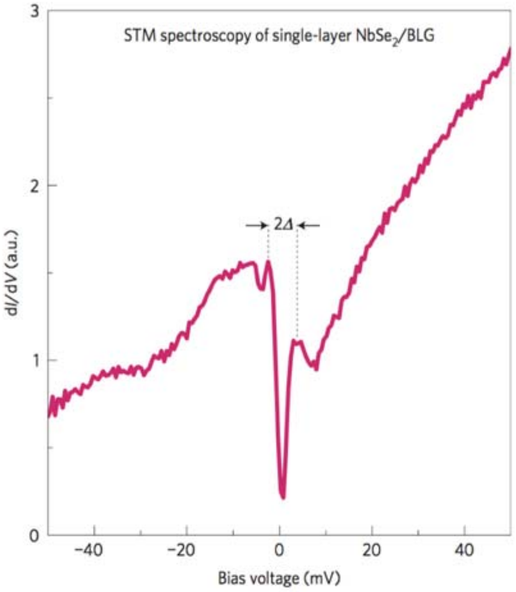


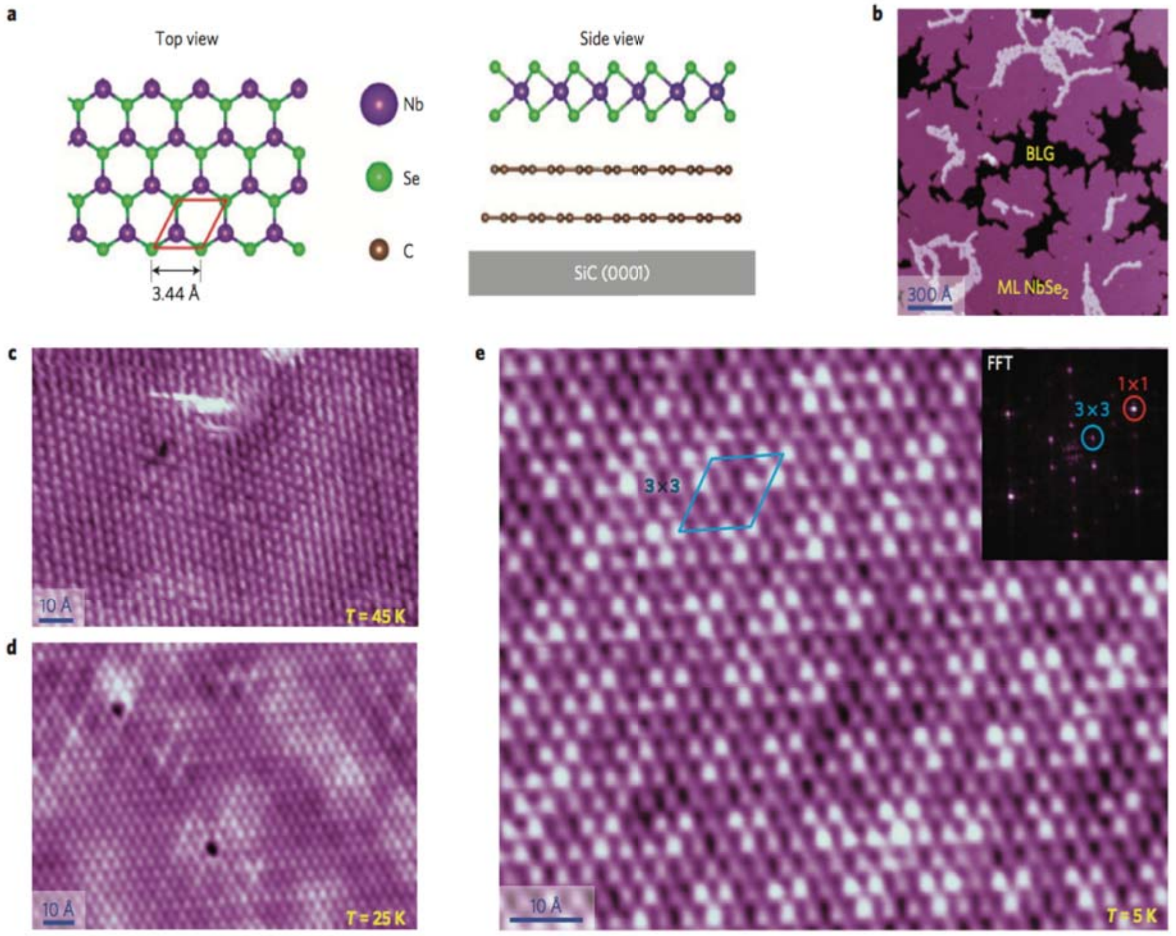
Silva-Guillén, Noat, Cren, Sacks, Canadell, Ordejón
PRB 92, 064514 (2015)

Single layer $NbSe_2$

M. Crommie's group:
Ugueda et al., Nat. Phys. 12, 92 (2016)

- (3x3) CDW remains in 2D
- SC transition at 1.9 K
- STS reveals several features for the CDW state, including a narrow quasigap at Ef





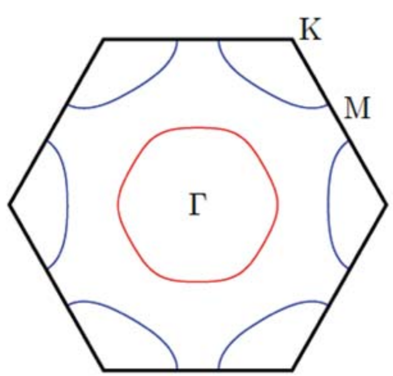
Single layer $NbSe_2$ - DFT Calculations

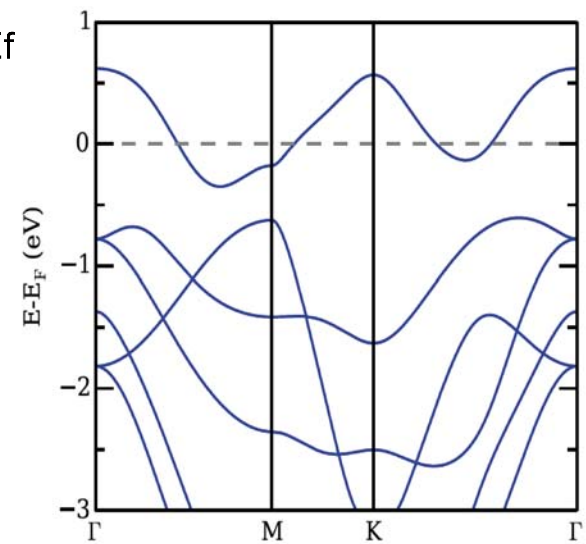
Silva-Guillén, Ordejón, Guinea, Canadell, 2D Mater. 3 (2016) 035028

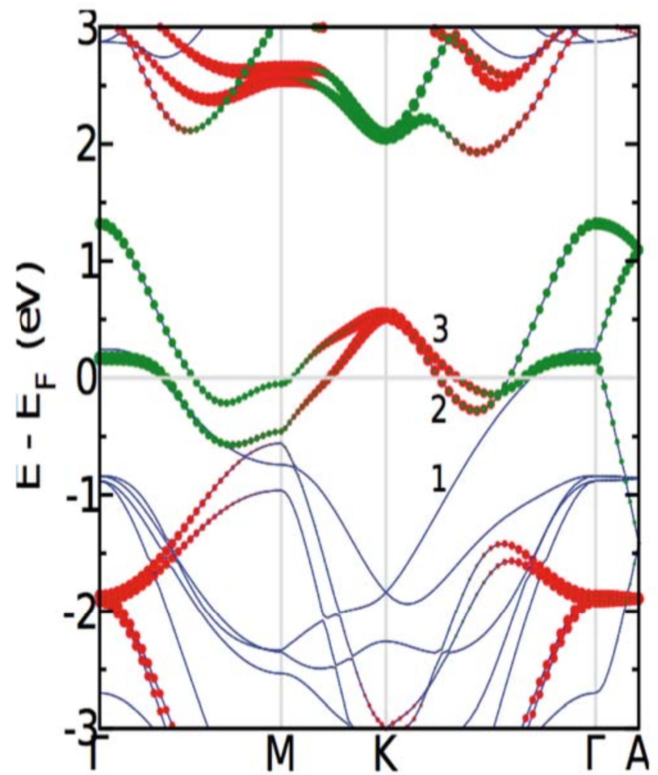
We impose the experimental structure of the (3x3) CDW in the bulk phase for the single-layer, and explore the effects on the electronic structure to compare with the experiments (above the SC temperature)

Non-modulated phase: comparison with the bulk:

- Bands are not folded
- Only one band at Ef
- Lower, Se-based band below Ef
- Fermi surface: only one Γ and one K cylinder







Single layer $NbSe_2$ - DFT Calculations

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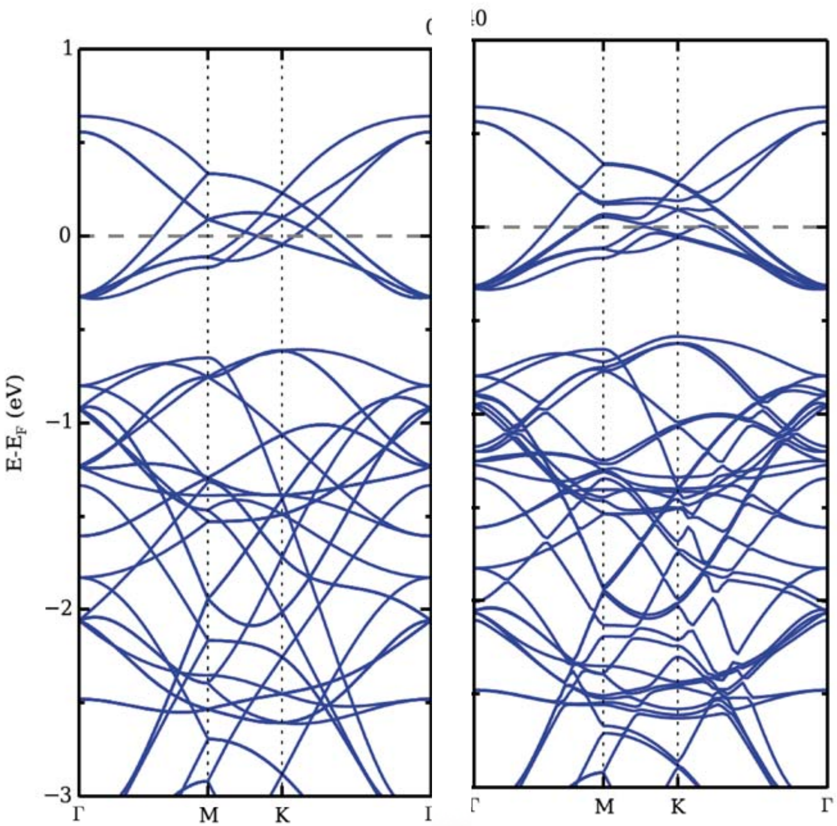
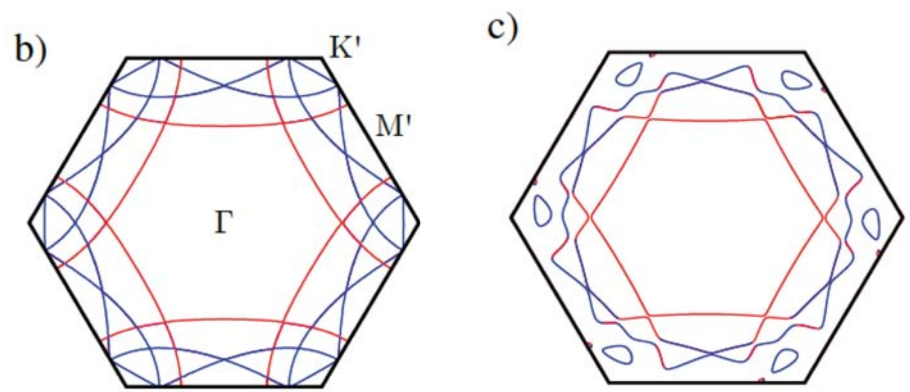
1x1 (non modulated) 3x3 CDW



1x1 (non modulated) 3x3 CDW

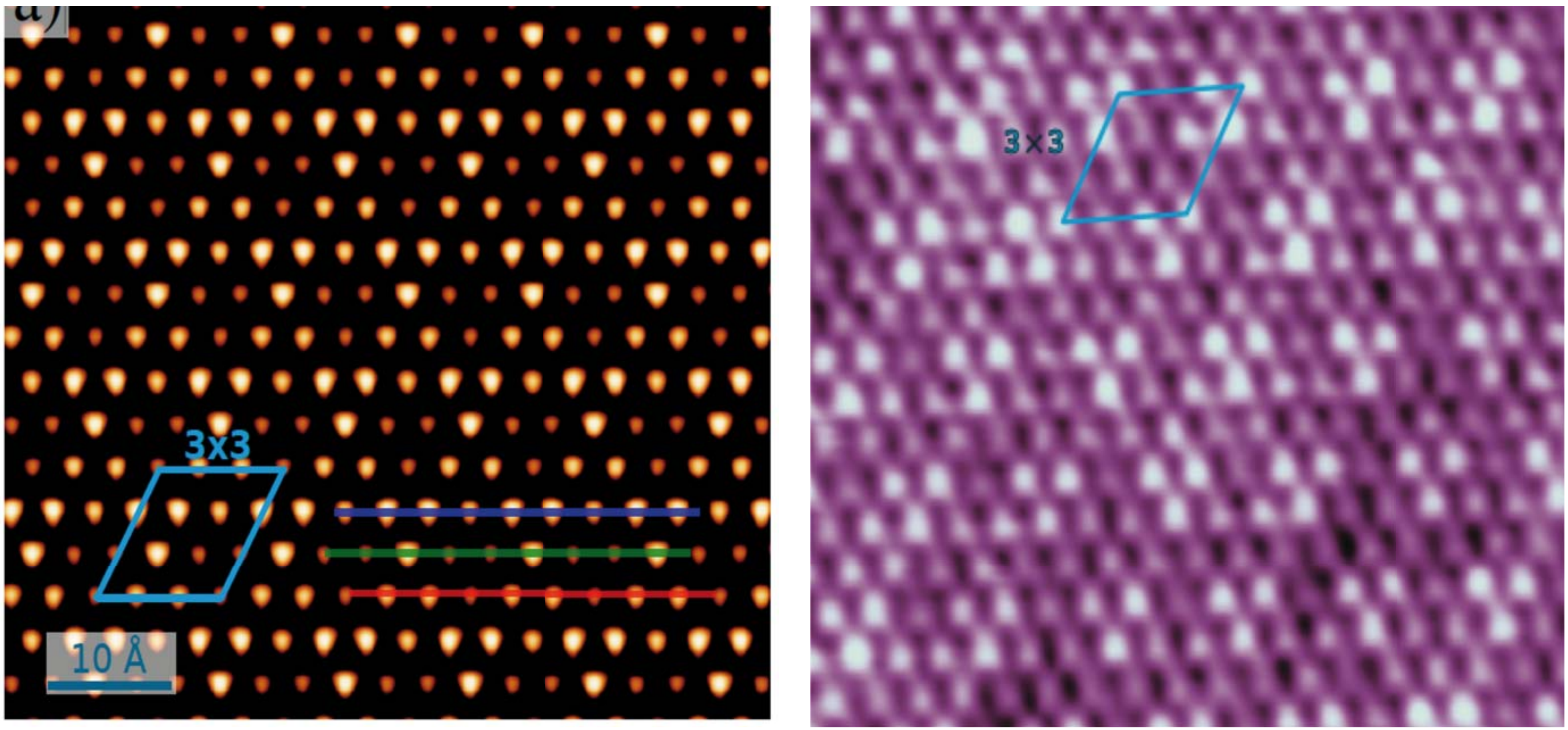


Some smalls gaps open, but the FS is mainly unaffected → CDW is not or Peierls origin (nesting)

Single layer $NbSe_2$ - DFT Calculations

Silva-Guillén, Ordejón, Guinea, Canadell, 2D Mater. 3 (2016) 035028

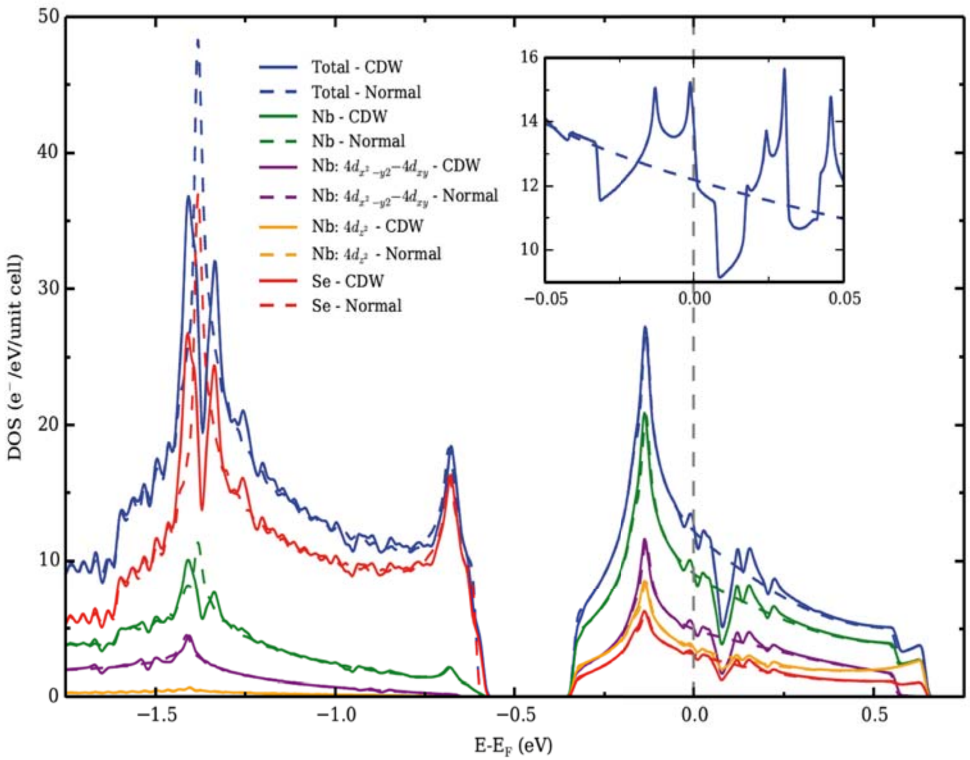
STM images



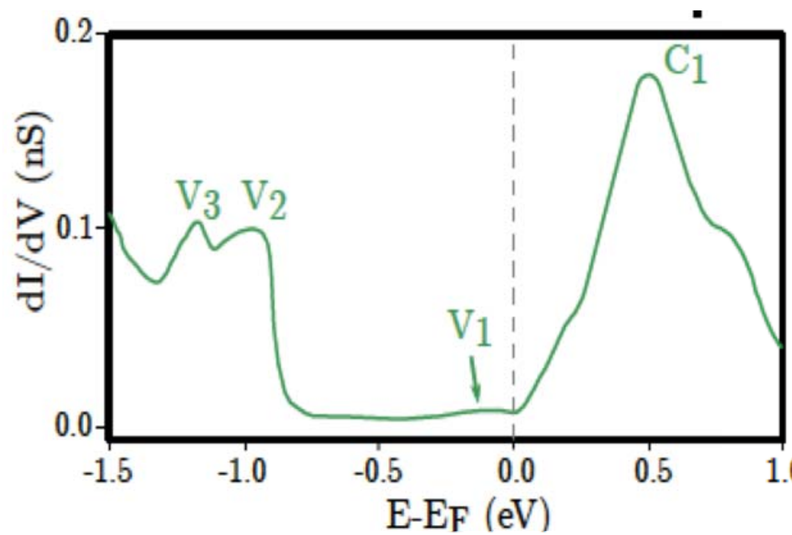
Single layer $NbSe_2$ - DFT Calculations

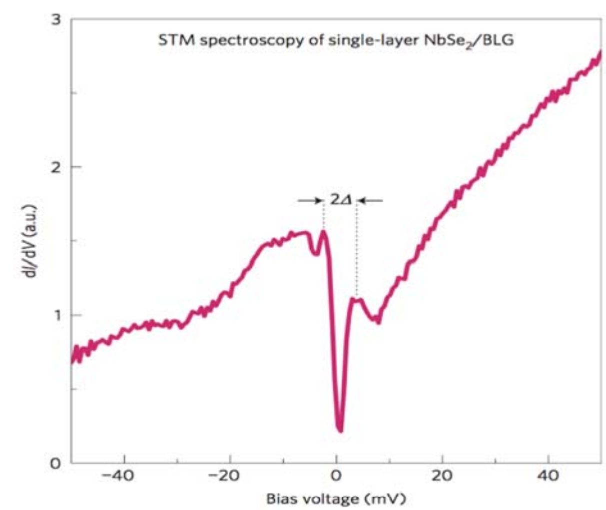
Silva-Guillén, Ordejón, Guinea, Canadell, 2D Mater. 3 (2016) 035028

Computed DOS



Experimental STS





Single layer $NbSe_2$ - DFT Calculations

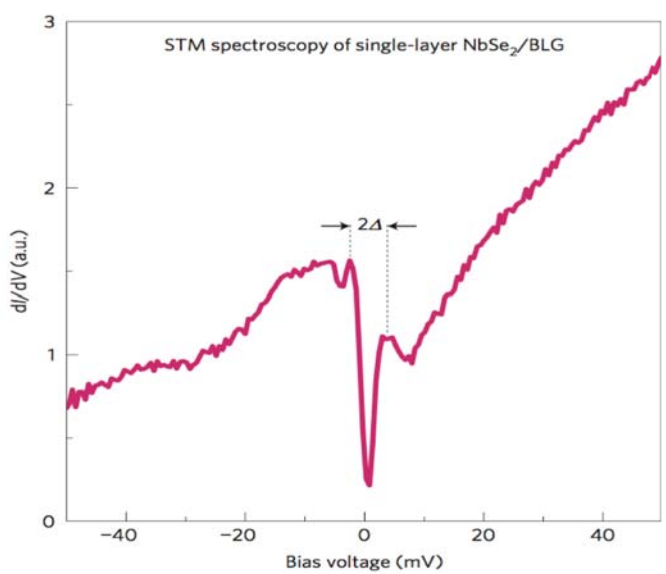
Silva-Guillén, Ordejón, Guinea, Canadell, 2D Mater. 3 (2016) 035028

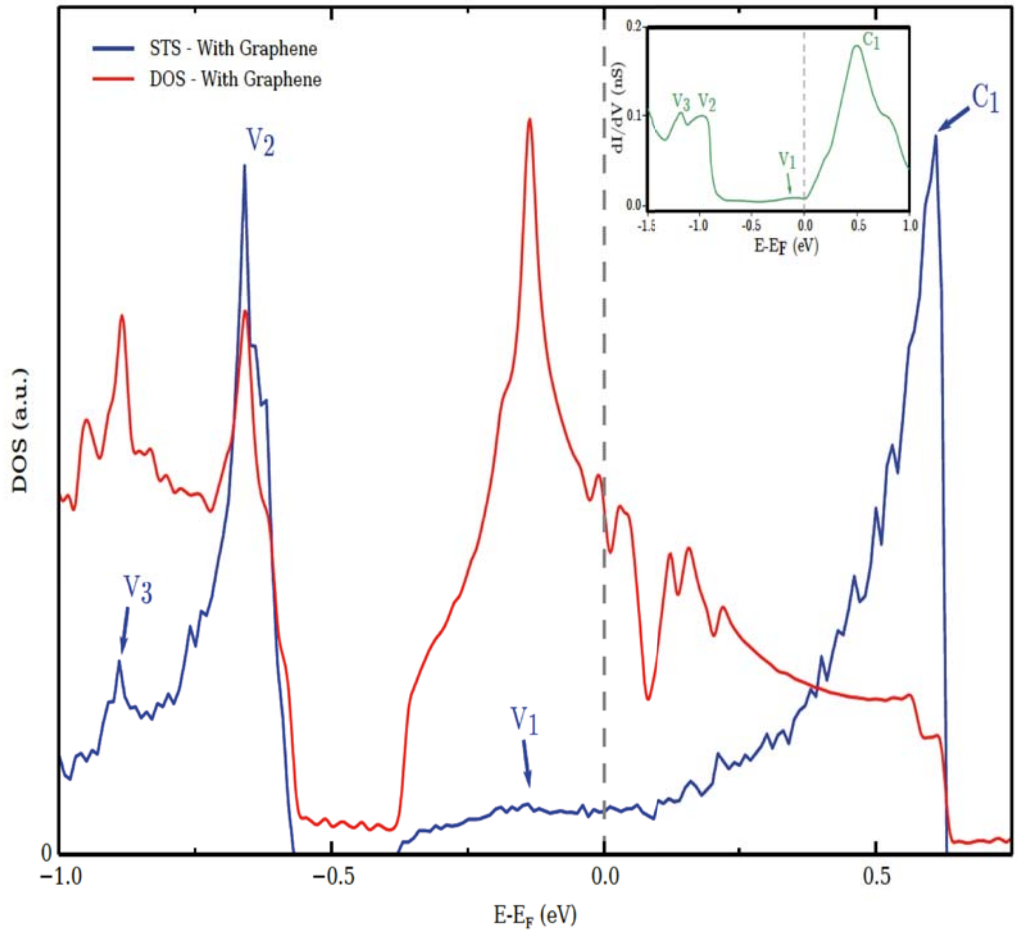
$$I \propto \frac{e^2}{\hbar} \int_0^{eV} dE \rho_s(\vec{r}, E) \rho_{tip}(E - eV) T(E, V, z)$$

$NbSe_2$ on Graphene

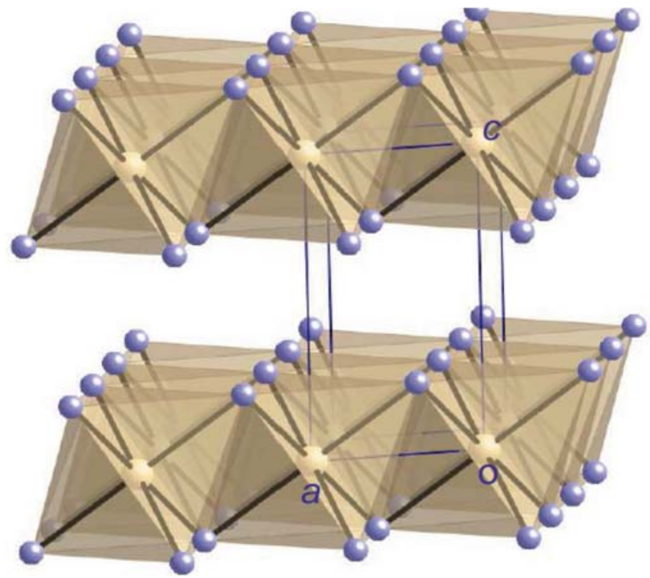
DOS and simulated STS (including tunneling selectivity)

Open issue: the origin of the small gap at Ef for the CDW state





1T-$TiSe_2$



Octahedral layers

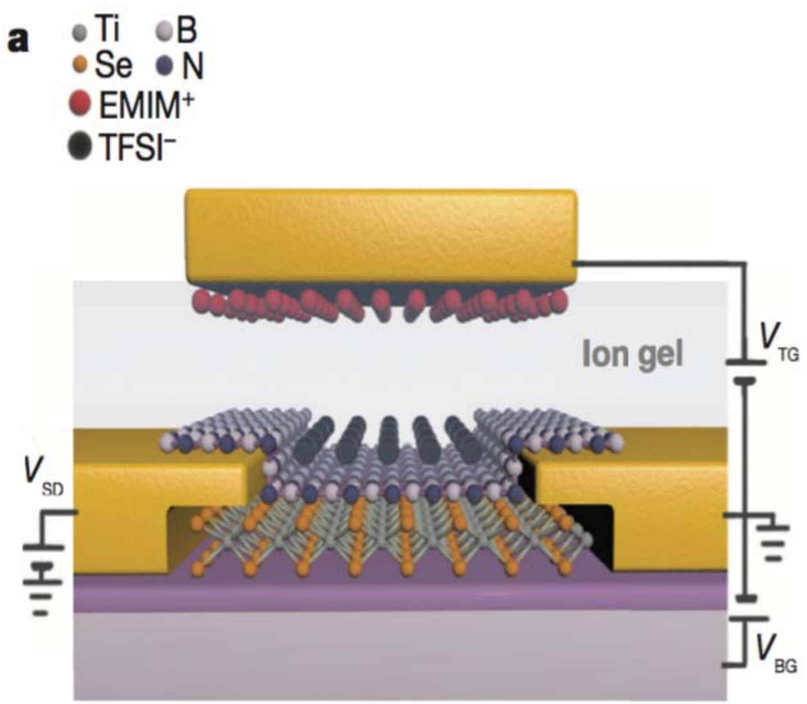
Rich phase diagram

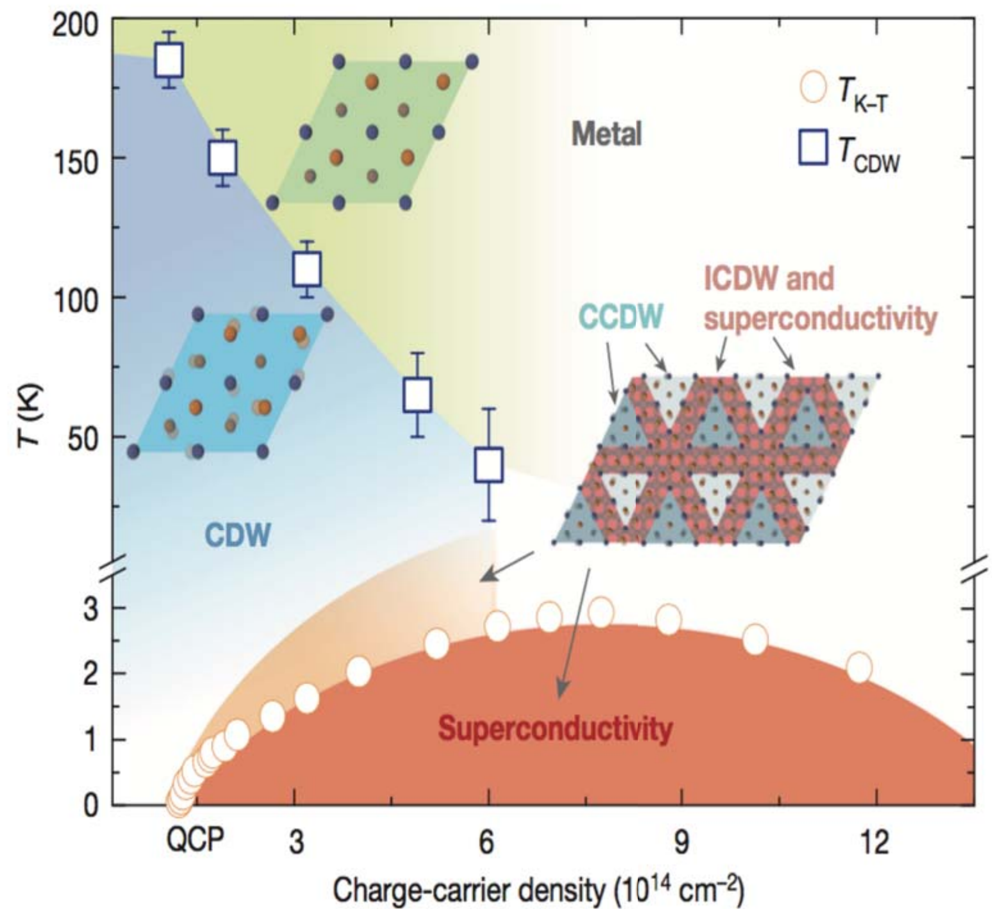
- Commensurate 2x2x2 CDW below 200K
- No SC transition in the pure compound, but SC appears with doping or pressure (which suppresses the CDW)

Single-layer and few-layer $TiSe_2$ have been prepared and studied

$1T\text{-}TiSe_2$

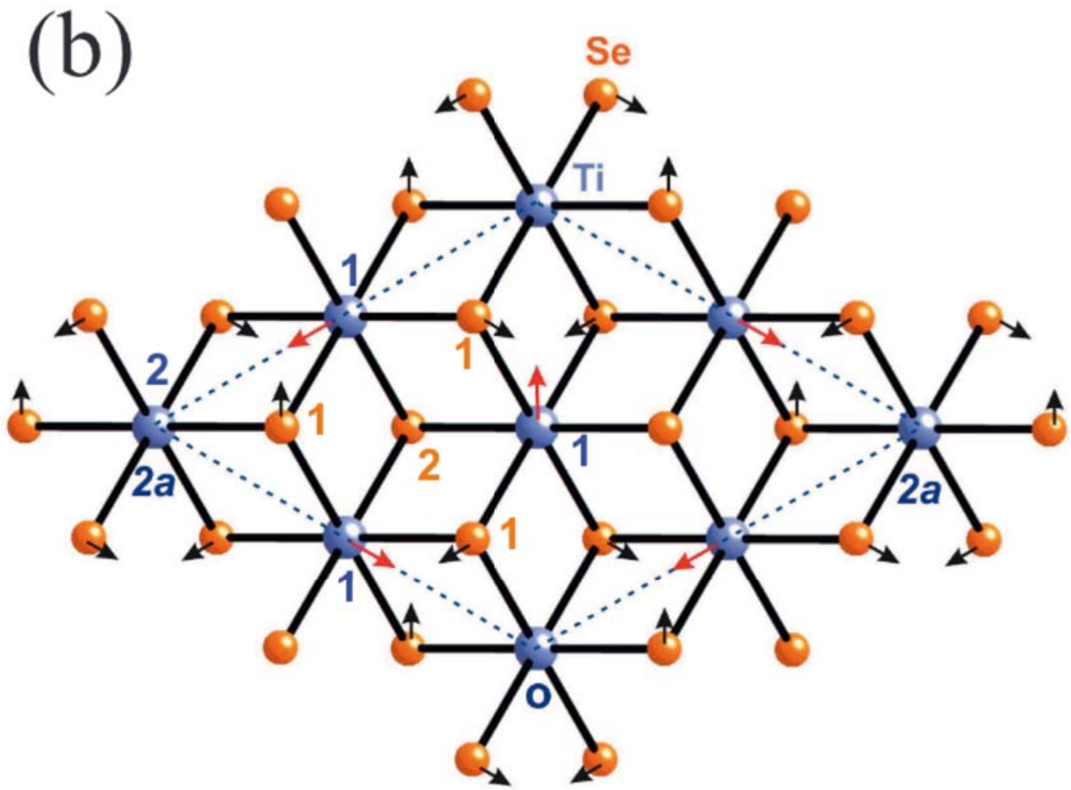
Castro-Neto's group (Nature 529, 185 (2016) have achieved doping of few-layers $TiSe_2$ by means of the electric field in a FET setup, and studied the phase diagram



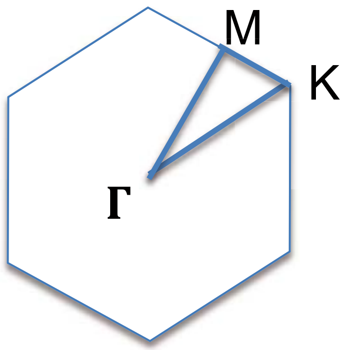


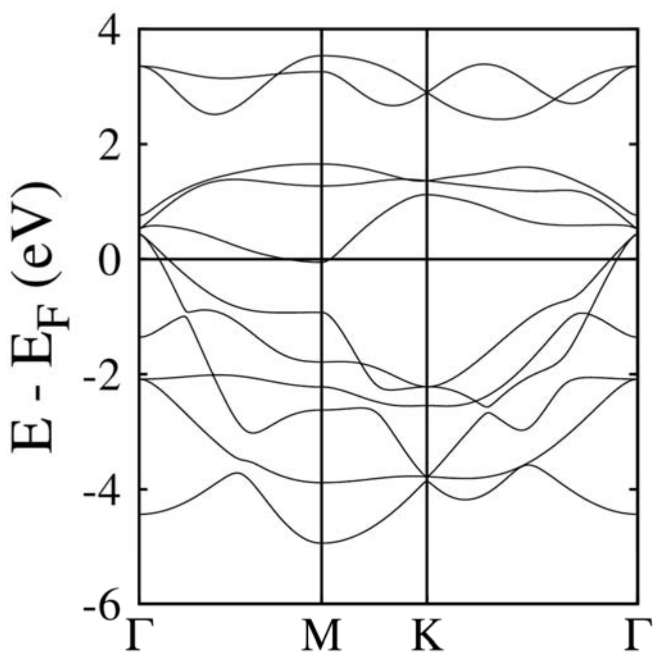
CDW in 1T-$TiSe_2$

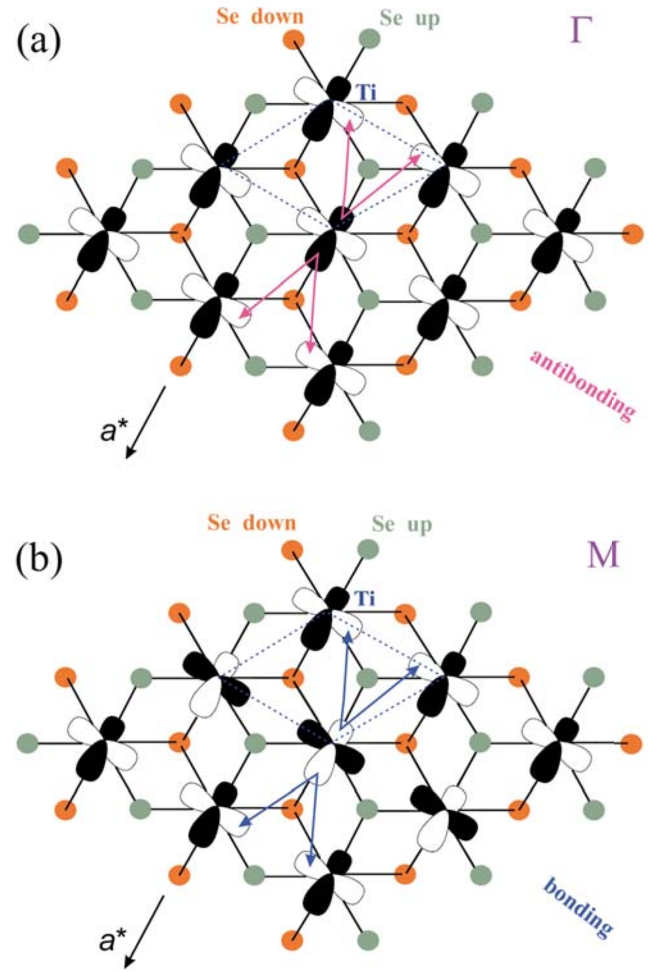
- Bulk: 2x2x2 CDW
- Monolayer: 2x2 CDW
  X.Y Fang, H. Hong, P. Chen, T.-C. Chiang, PRB 95, 201409(R) (2017))



Single Layer $TiSe_2$ – DFT Calculations

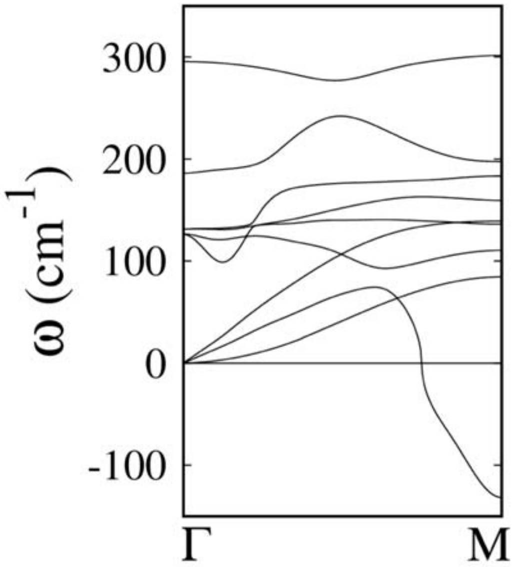


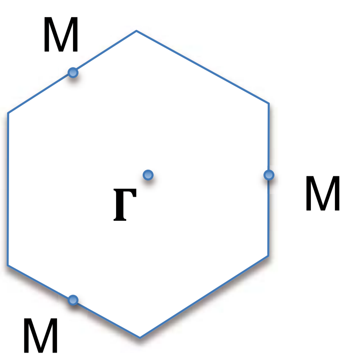


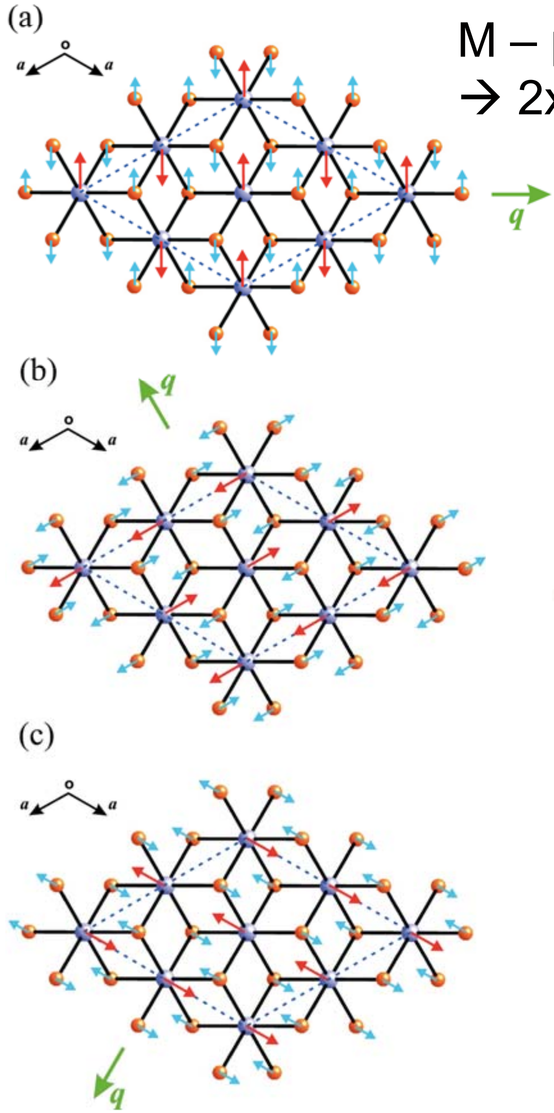


Guster, Canadell, Pruneda and Ordejón, 2D Mater. DOI: https://doi.org/10.1088/2053-1583/aab568

Single Layer $TiSe_2$ – DFT Calculations
Phonons

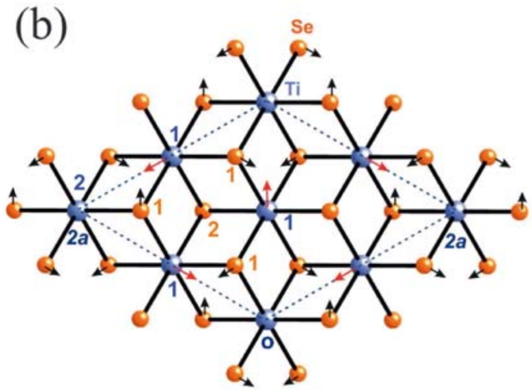






M – phonon
→ 2x1 pattern

"3Q" combination
→ 2x2 pattern



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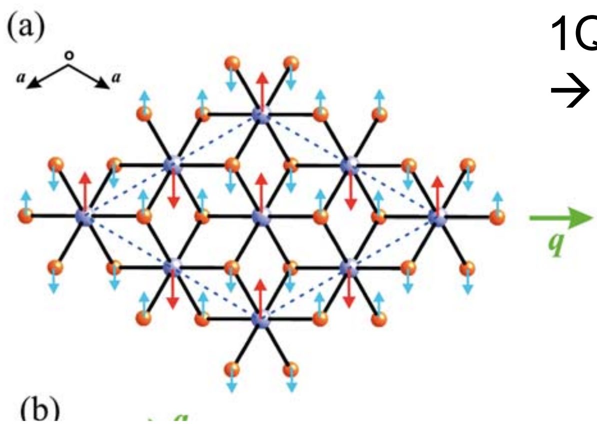
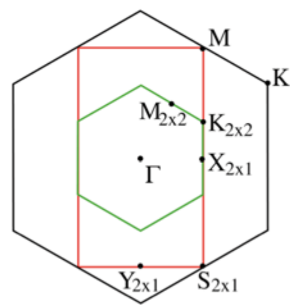
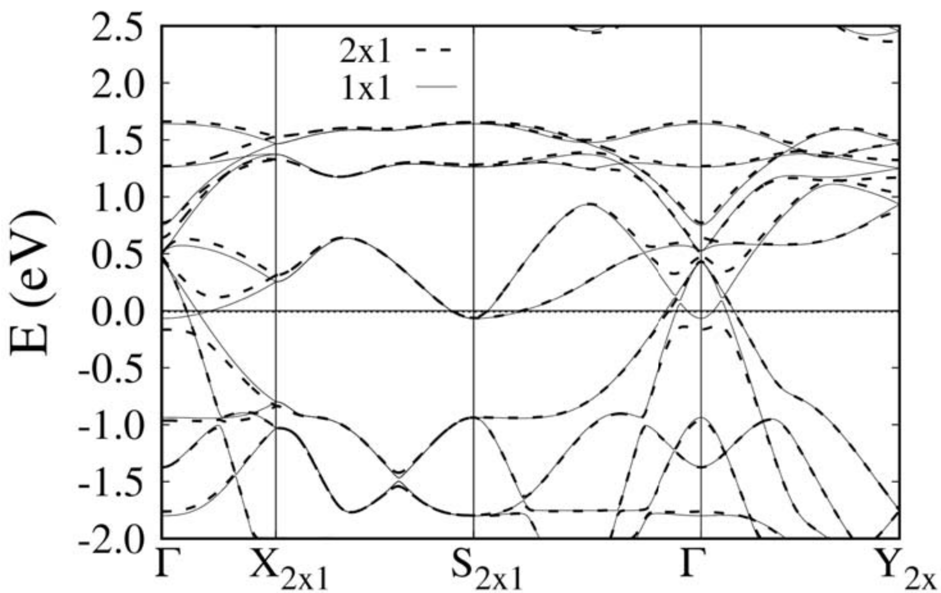
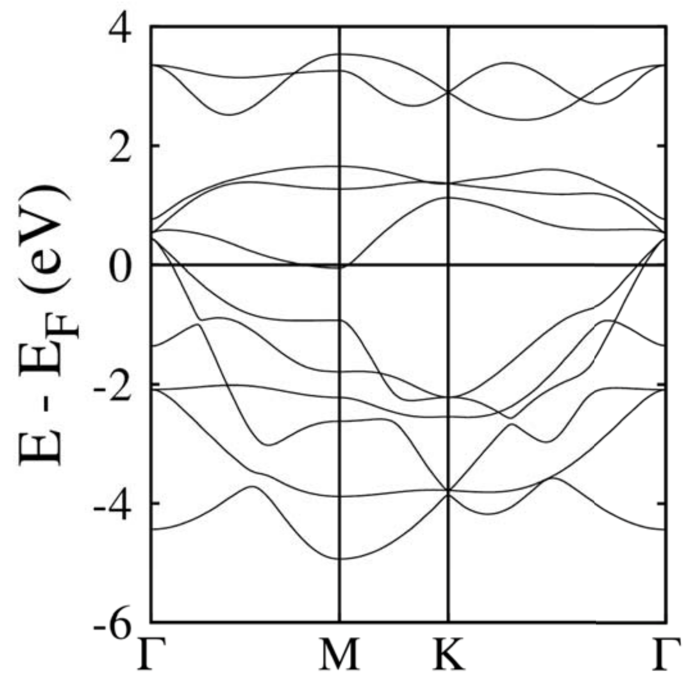
Why is the M phonon unstable?



1Q - M phonon
→ 2x1 pattern



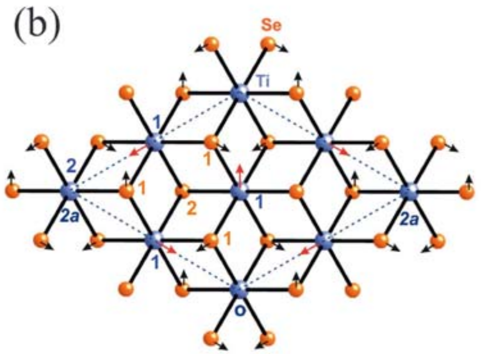




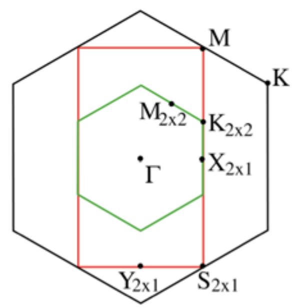
ΔE^{1Q}= 3meV

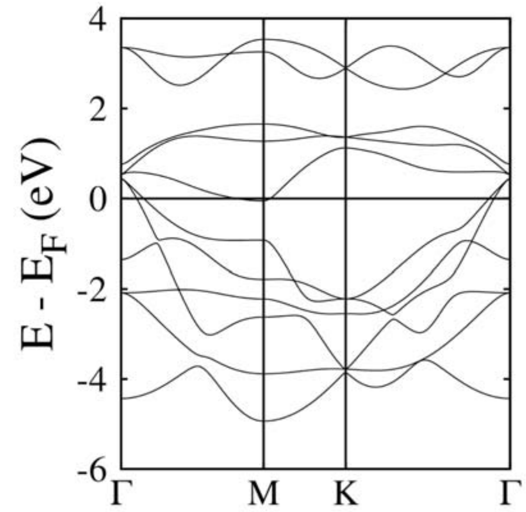
Guster, Canadell, Pruneda and Ordejón, 2D Mater. DOI: https://doi.org/10.1088/2053-1583/aab568

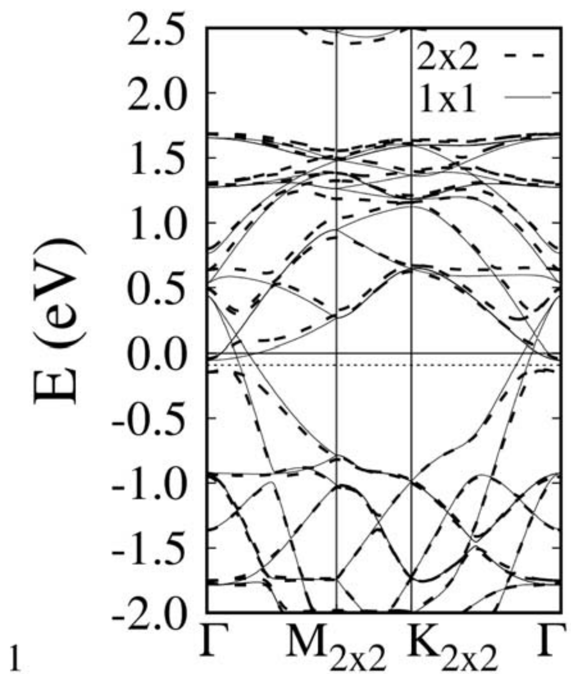
Why 3Q combination?



3Q – phonon
→ 2x2 pattern

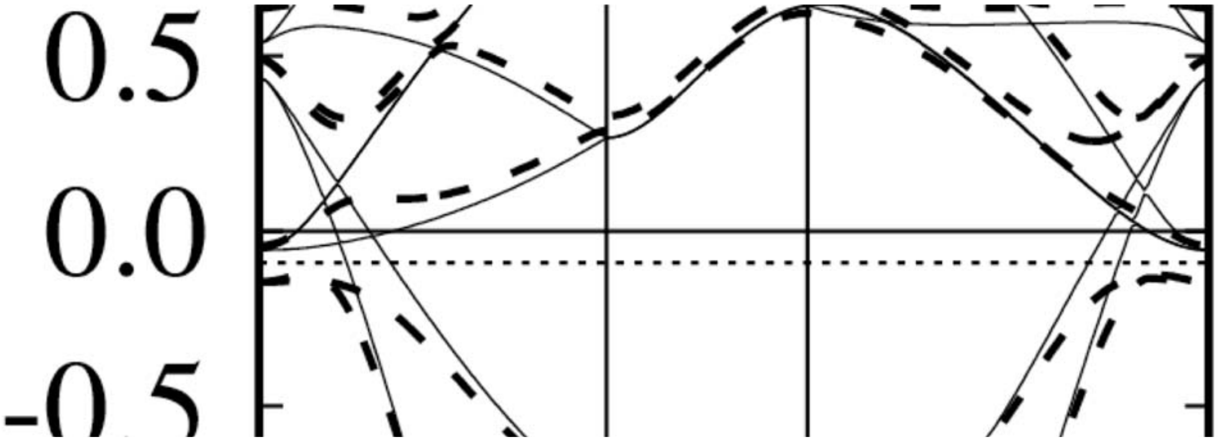


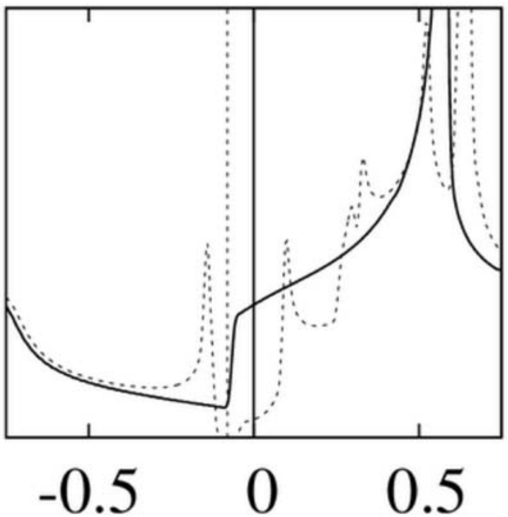




Guster, Canadell, Pruneda and Ordejón, 2D Mater. DOI: https://doi.org/10.1088/2053-1583/aab568

Why 3Q combination?



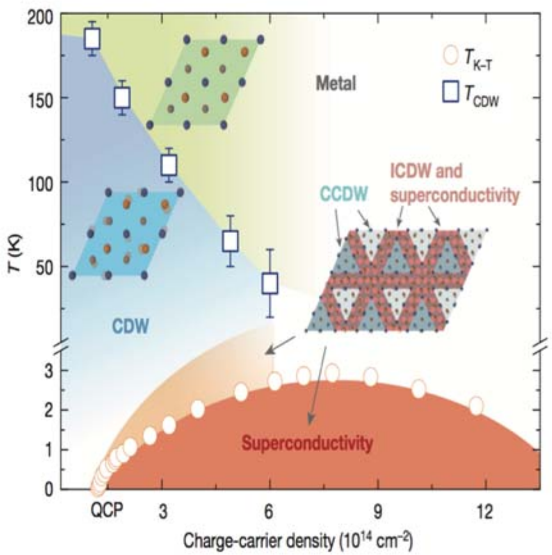


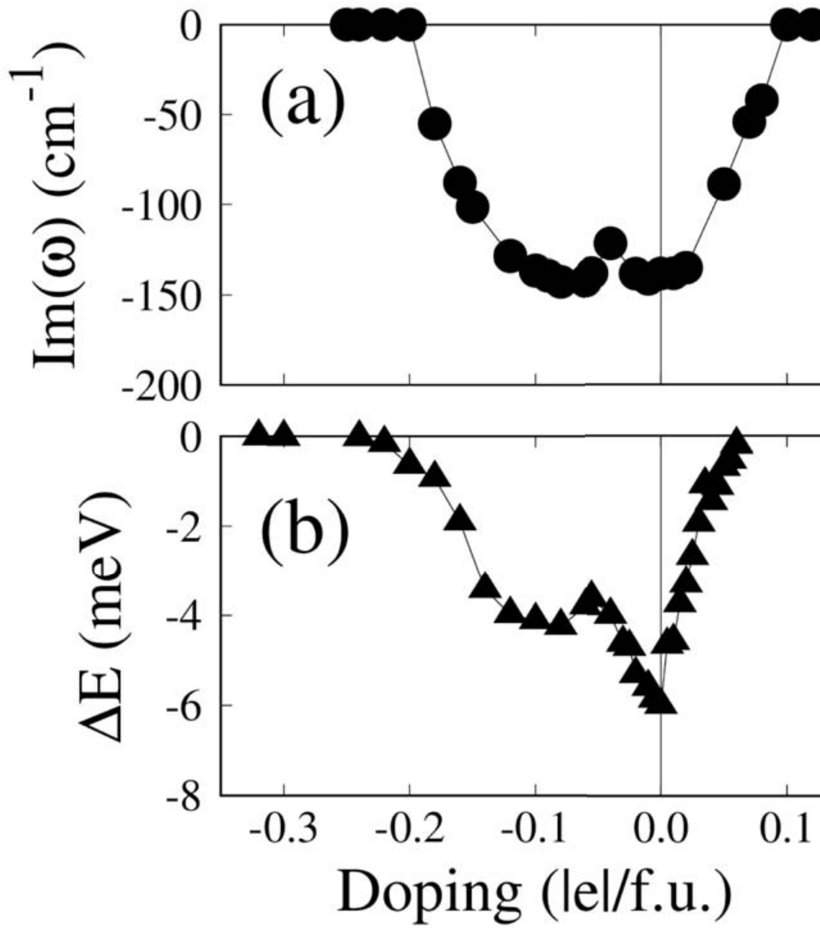
ΔE^{1Q}= 3meV
ΔE^{3Q}= 6meV

Guster, Canadell, Pruneda and Ordejón, 2D Mater. DOI: https://doi.org/10.1088/2053-1583/aab568

Effect of Doping

CDW survives doping for a significant range, but disappears at some doping values





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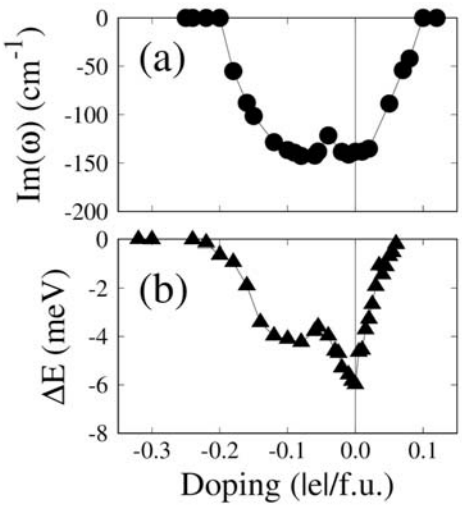
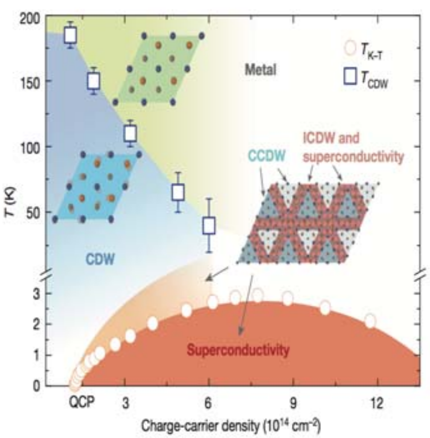
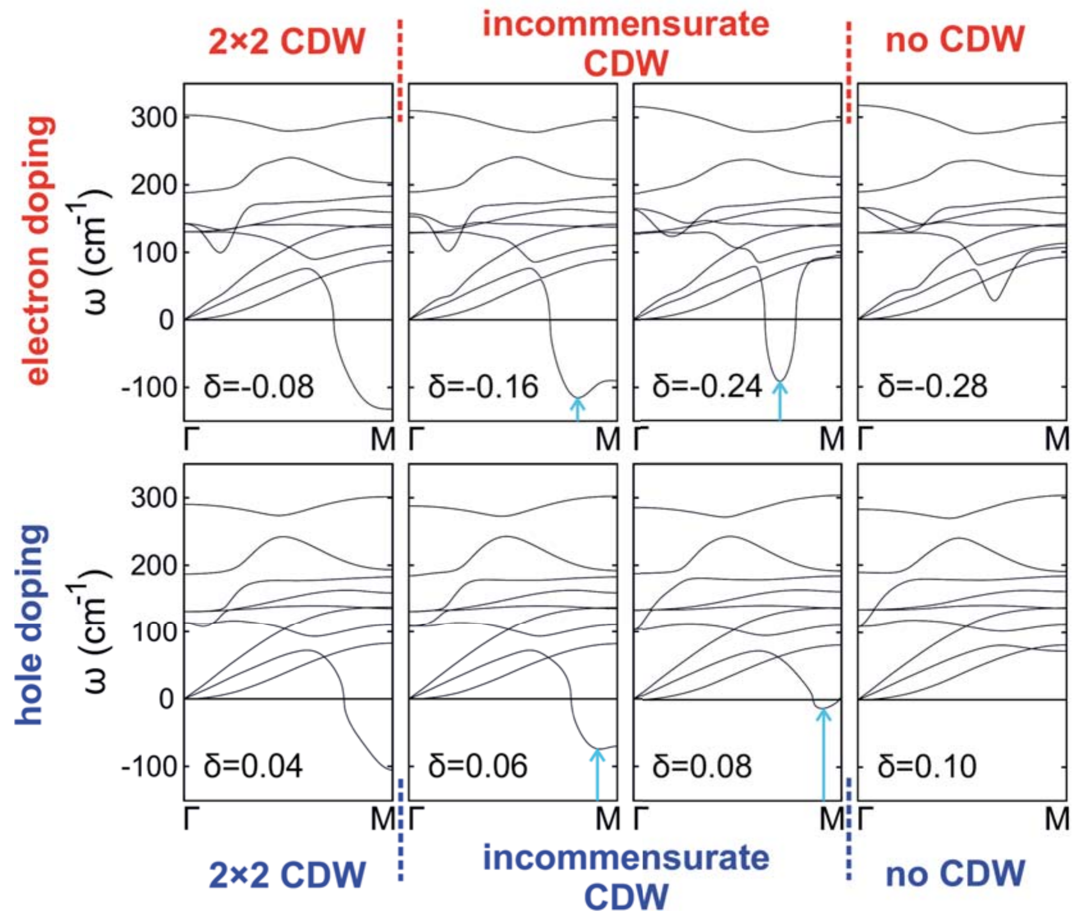
Effect of Doping

For large doping values, instability shifts from M point → incommensurate CDW?







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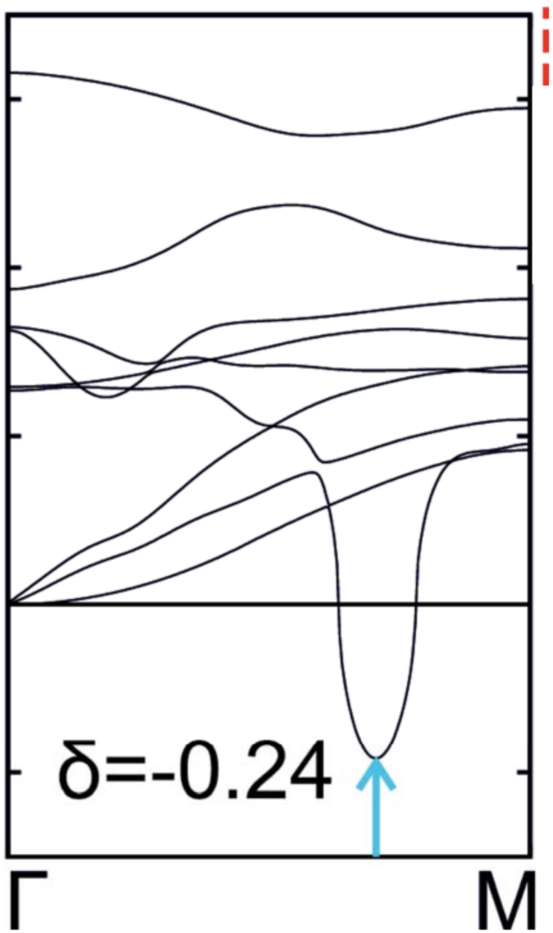
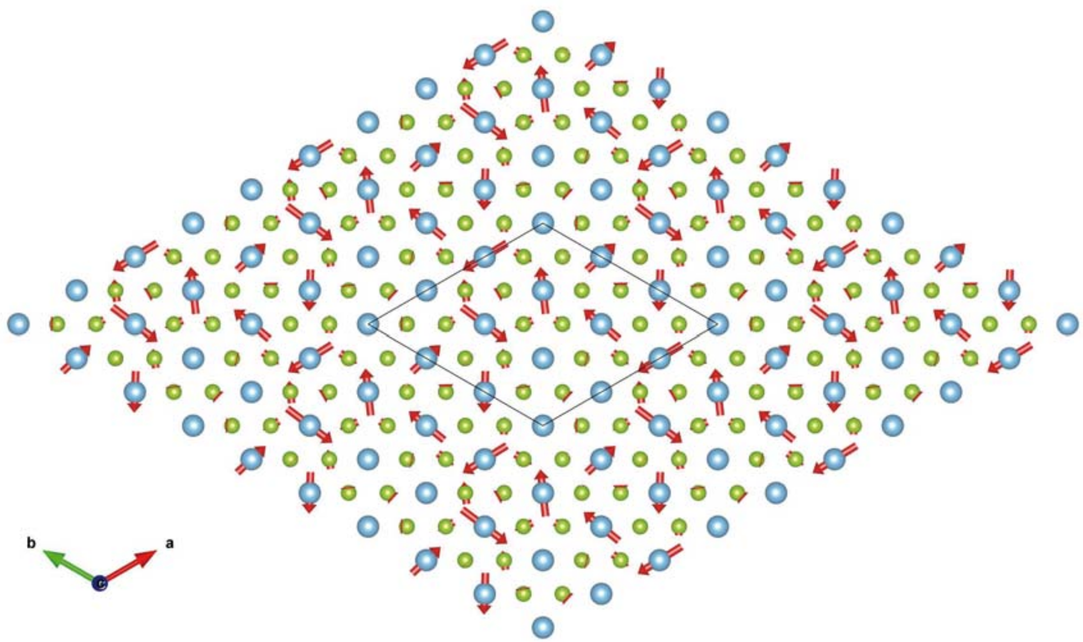
Effect of Doping



Minimum of the unstable mode ~ 2/3 Γ-M

→ ~3x periodicity

→ 3Q leads to ~3x3 CDW



Guster, Canadell, Pruneda and Ordejón, 2D Mater. DOI: https://doi.org/10.1088/2053-1583/aab568

Conclusions

- The richness of the physics of low dimensional solids can now be explored in the new 2D materials – a revival of the field, and many new opportunities to explore new physics

- Theory, and in particular DFT, can provide very valuable insight to understand experiments and validate simple models

- $NbSe_2$
  - CDW still not fully understood (2D: Gap at Ef found in STM)
  - Interplay between Superconductivity and CDW

- $TiSe_2$
  - Mechanism for CDW is now well understood – band gap opening, but not Peierls
  - (2x2) distortion: 3Q CDW – combination of the three M-point phonons
  - Effect of doping: CDW survives for some degree of doping, then it disappears
  - For large doping: Incommensurate CDW, with wavevector shifting with doping

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Miguel Pruneda (ICN2)

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European Regional Development Fund

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