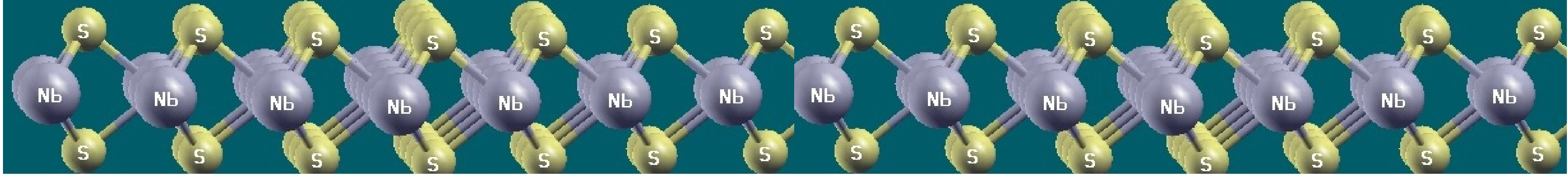


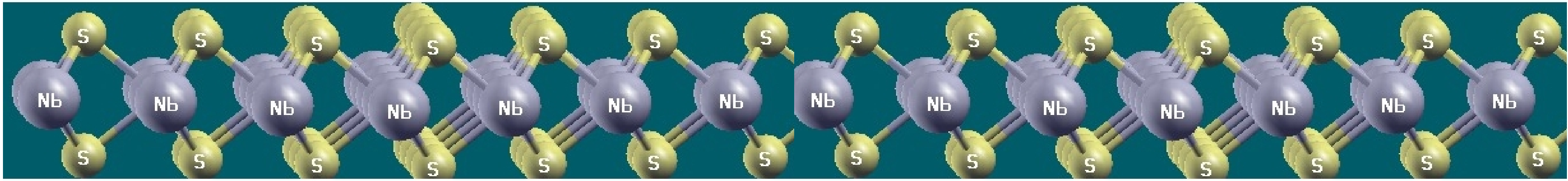
# Spin density instabilities in the NbS2 monolayer

**V. Vildosola**

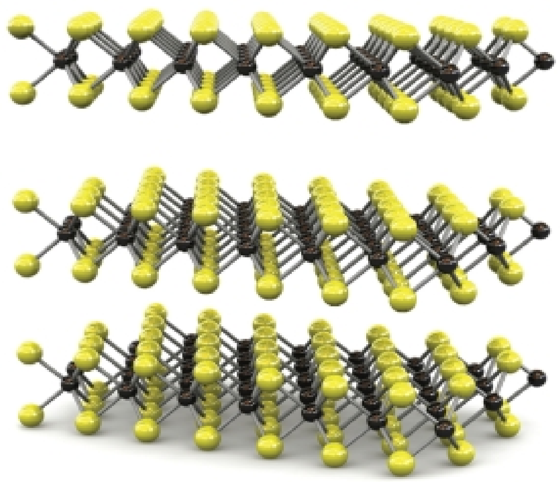
**F. Güller and A.M. Llois**

Departamento de Física de la Materia Condensada
CAC-CNEA, CONICET
ARGENTINA

Workshop on Next Generation Quantum Materials - UNESP

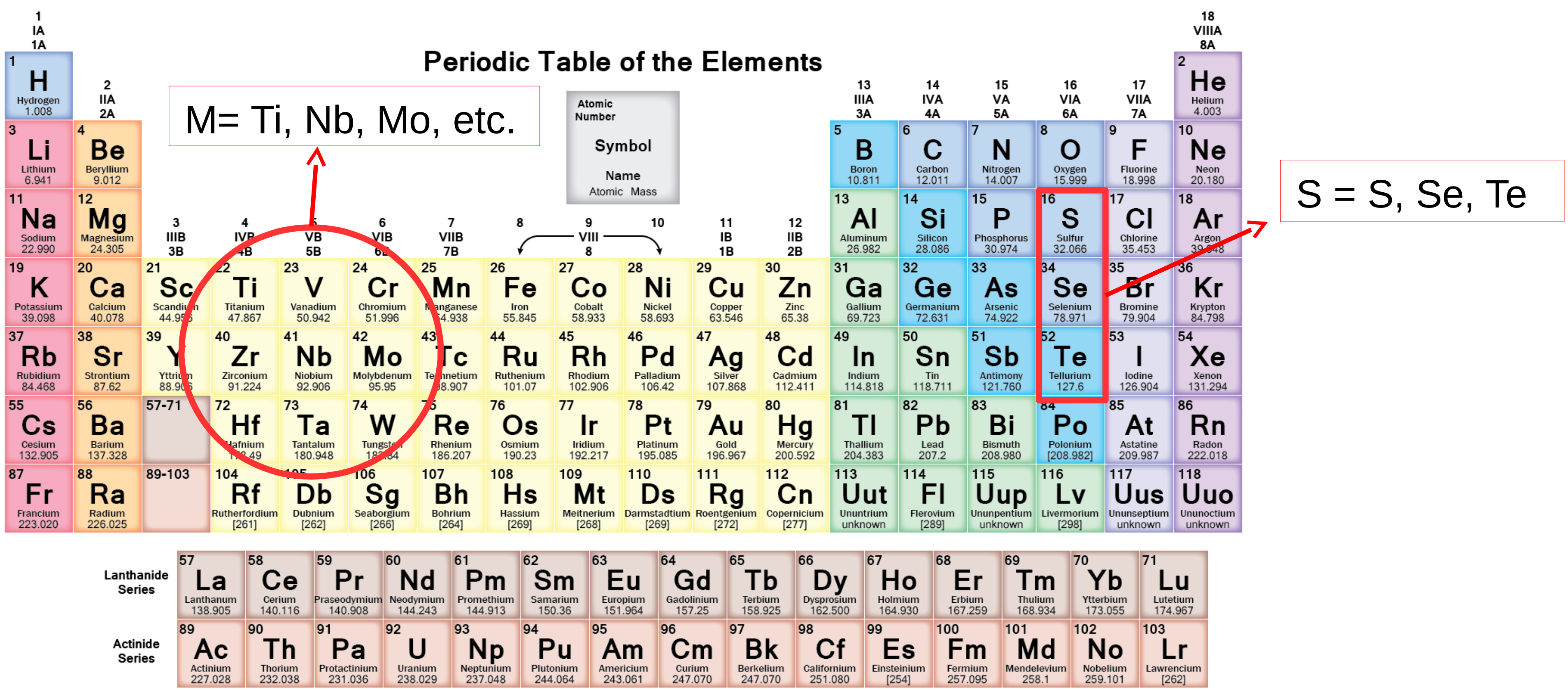


# Transition metal dichalcogenides $MX_2$

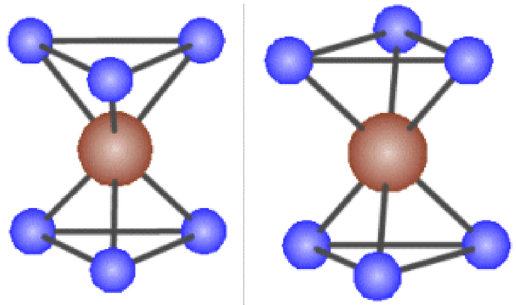


- M planes sandwiched by two chalcogen planes.
- Strong covalent intralayer bonding
- Weak van der Waals coupling between layers.
- Wide variety of properties: CDW, superconductivity, metals,

band insuators, Mott insulators ...

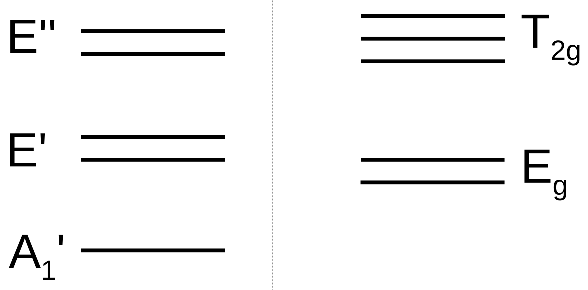


# Different behaviour: packing and *d* band filling



Trigonal Prismatic (2H)

Octahedral (1T)



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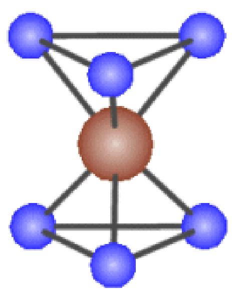

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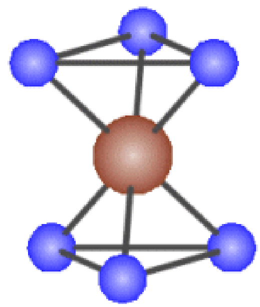
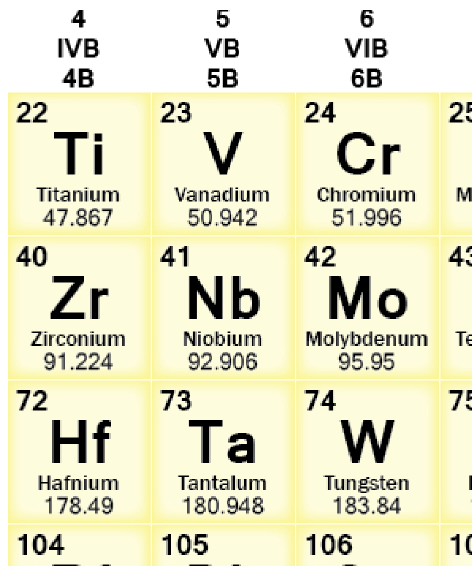


Octahedral (1T)



| 4 IVB 4B | 5 VB 5B | 6 VIB 6B |
|---|---|---|
| 22 Ti Titanium 47.867 | 23 V Vanadium 50.942 | 24 Cr Chromium 51.996 |
| 40 Zr Zirconium 91.224 | 41 Nb Niobium 92.906 | 42 Mo Molybdenum 95.95 |
| 72 Hf Hafnium 178.49 | 73 Ta Tantalum 180.948 | 74 W Tungsten 183.84 |
| 104 | 105 | 106 |

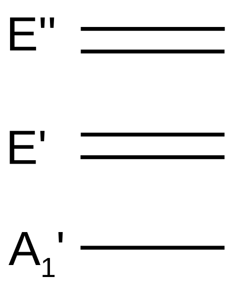
*Same packing...*

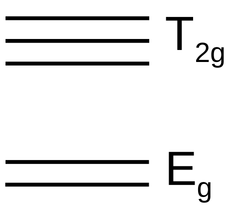
2H-NbS2 metal

2H-MoS2 band insulator

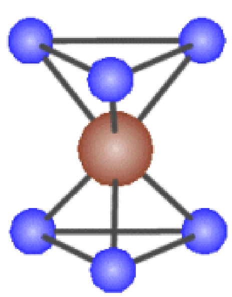
Nb:[Kr] $4d^4 5s^1$ $Nb^{+4}$: $4d^1$

Mo:[Kr] $4d^5 5s^1$ $Mo^{+4}$: $4d^2$

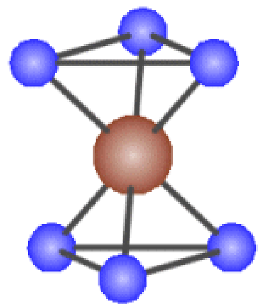


# Different behaviour: packing and *d* band filling



Trigonal Prismatic (2H)



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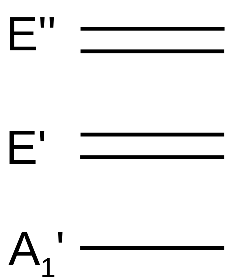
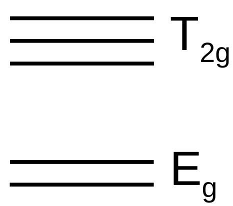
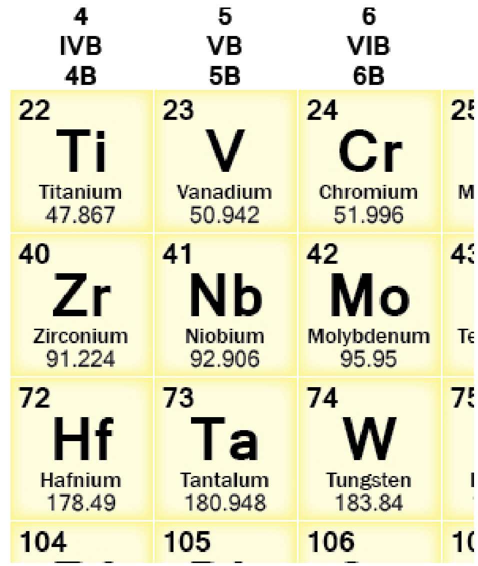



*Same packing...*

2H-NbS2 metal

2H-MoS2 band insulator

Nb:[Kr] $4d^4 5s^1$ $Nb^{+4}$: $4d^1$

Mo:[Kr] $4d^5 5s^1$ $Mo^{+4}$: $4d^2$

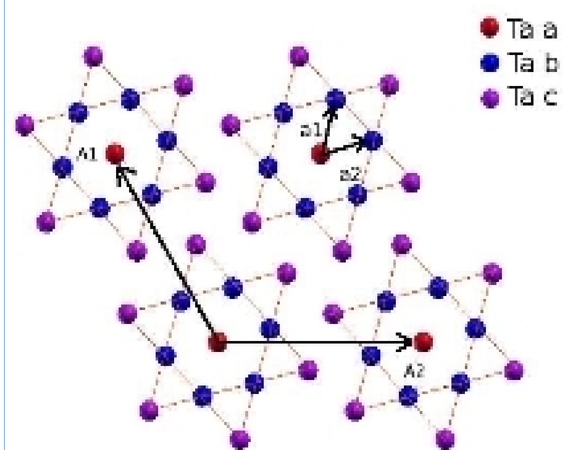
*Same filling...*

**Resistivity**

| | |
|---|---|
| $1T\text{-}TaS_2$ | semiconductor- like<br>Mott transition |
| $2H\text{-}TaS_2$ | metallic- like |

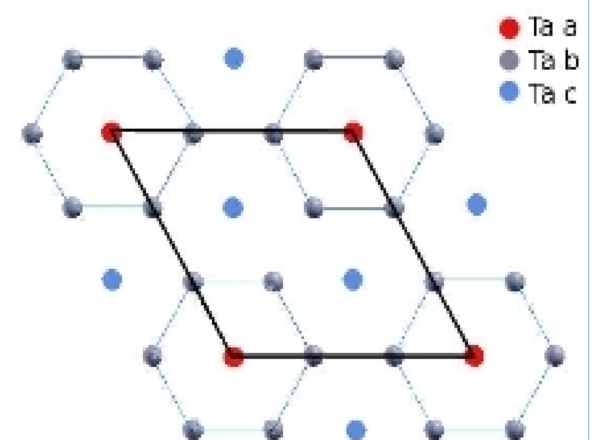
*Same filling...*

**Periodic distortion**




**1T-TaSe2**

√(13)x√(13)x1

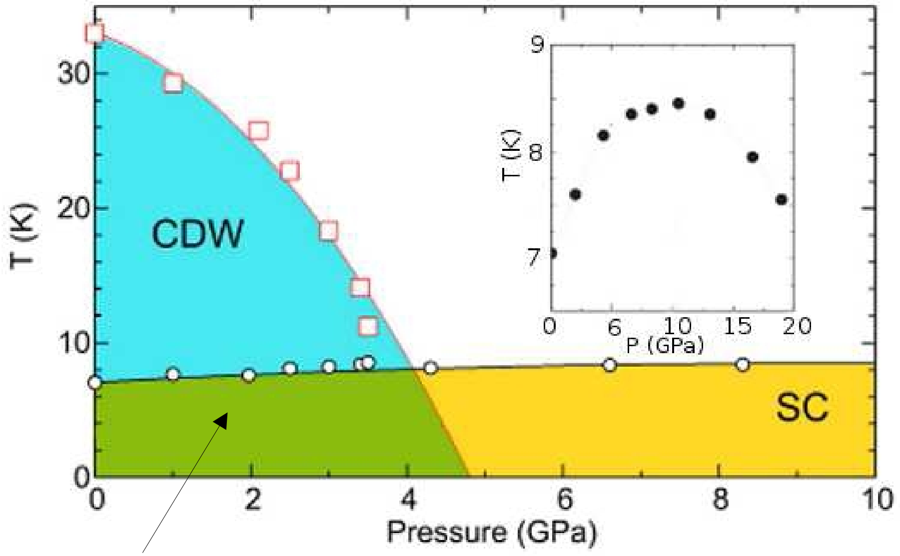



**2H-TaSe2**

3x3x1

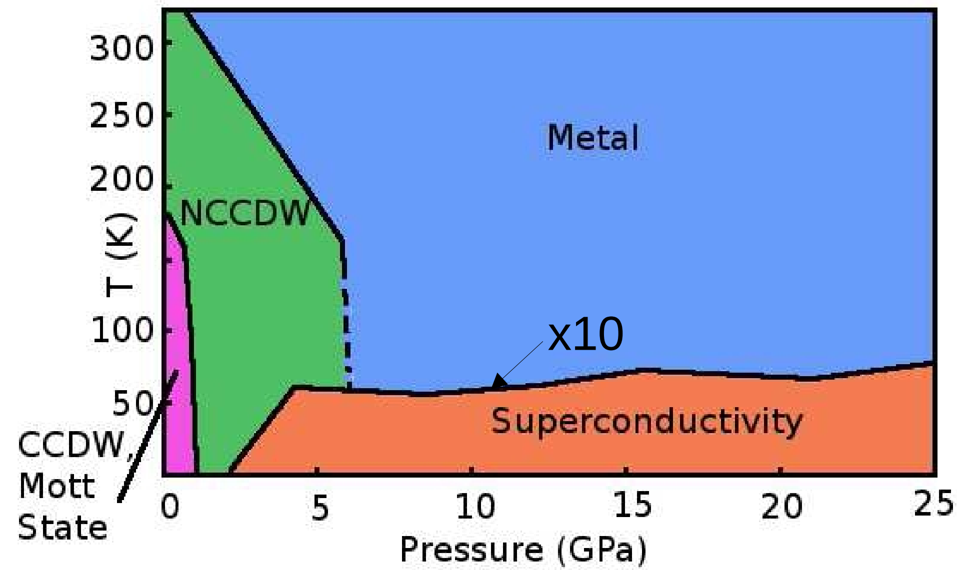
# Similar Phase diagram

(a) 2H-$NbSe_2$




Coexisting and competing phases

(b) 1T-$TaS_2$

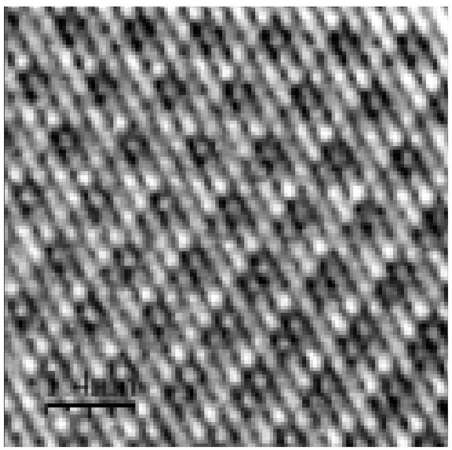



- Electron-phonon coupling (within McMillan formula) can account for the order of Tc
- The CDW and the SC gaps are highly anisotropic
- The CDW gap existed in the normal state ($T > T_{CDW}$) (as the Pseudogap phase of cuprates)
- No long range magnetic order was ever observed
- **CONVENTIONAL** or UNCONVENTIONAL superconductivity ?

# 2H-$NbS_2$ : exceptional case

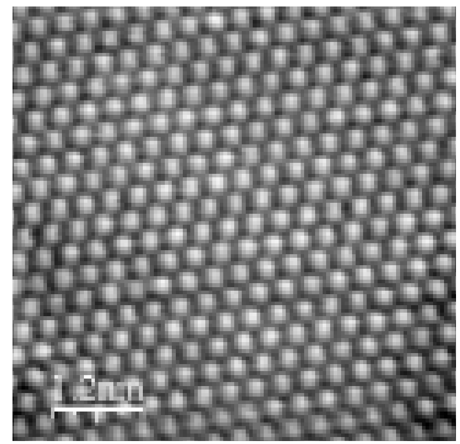
- All the TMDC that are superconductors also exhibit CDW phases **except 2H- $NbS_2$**
- **2H-$NbS_2$** is superconductor below $T_c$= 6 K and does not show CDW.

2H-$NbSe_2$



superperiodicity = CDW

2H-$NbS_2$



atomic lattice
No CDW

T=100 mK

*I. Guillamon PRL 2008*

It has been suggested that the CDW in **$NbS_2$** is suppressed by <u>anharmonic effects.</u>

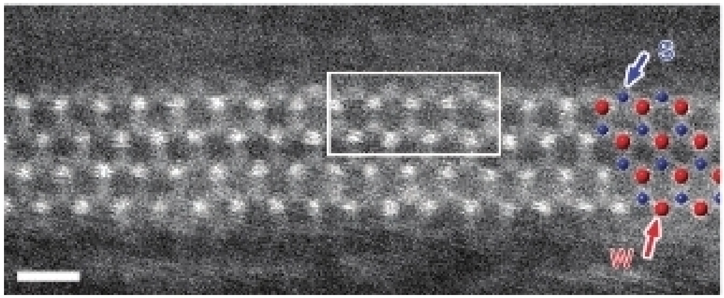
*Leroux, et al, Phys. Rev. B 86, 155125 (2012)*

**The real interplay between CDW and superconductivity is still under debate**

# Low dimensional 2H-$NbS_2$

Exfoliation techniques used to obtain graphene have been adjusted to TMDC to get few layers, monolayers and even nanoribbons or flakes.

a




Only zigzag edges were observed

- Monolayer **$WS_2$** nanoribbon encapsulated in carbon NT
  *Zheng Liu et al, Nature Comm. (2011)*
- Also **$MoS_2$** ribbons
  *Wang et al, JACS 132, 13840–13847 (2010)*

Very recently **$NbSe_2$** monoloyer with $T_{CDW}$ = 145K !

*Xi et al, Nature Matt. 143, 1 (2015)*

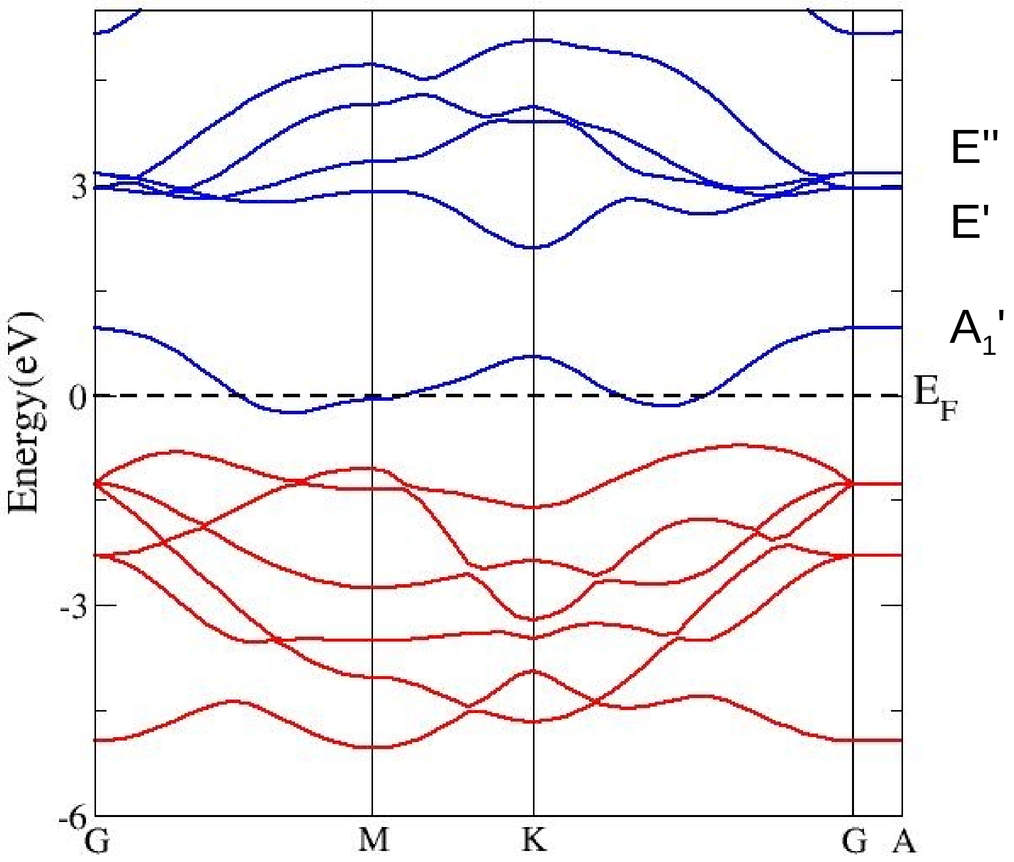
**What about magnetism??**

In this work, we study the magnetic properties of the NbS2 monolayer by means of DFT calculations

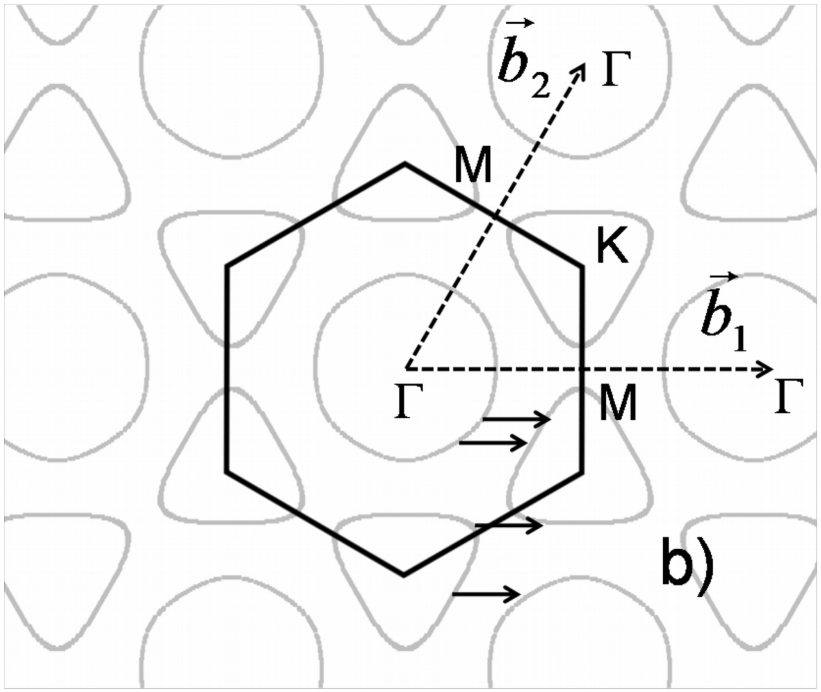
# Electronic structure of the $NbS_2$ monolayer

- $A_1$' band half filled
- The electronic structure is very similar to undistorted $NbSe_2$

$NbS_2$ monolayer




Fermi surface




The monolayer is more prone to nesting effects than the bulk.
Quasi-1D portion of FS can be anticipated.

# Magnetic properties $NbS_2$ monolayer

**1x1 cell**: nonmagnetic, boring.
***But:*** ferromagnetic state very close in energy (< 1Mev/Nb)

High suceptibility

**4x4 cell**: nonmagnetic and **wave-like state** (<1 meV/Nb)

# Magnetic properties $NbS_2$ monolayer

**1x1 cell**: paramagnetic, boring.
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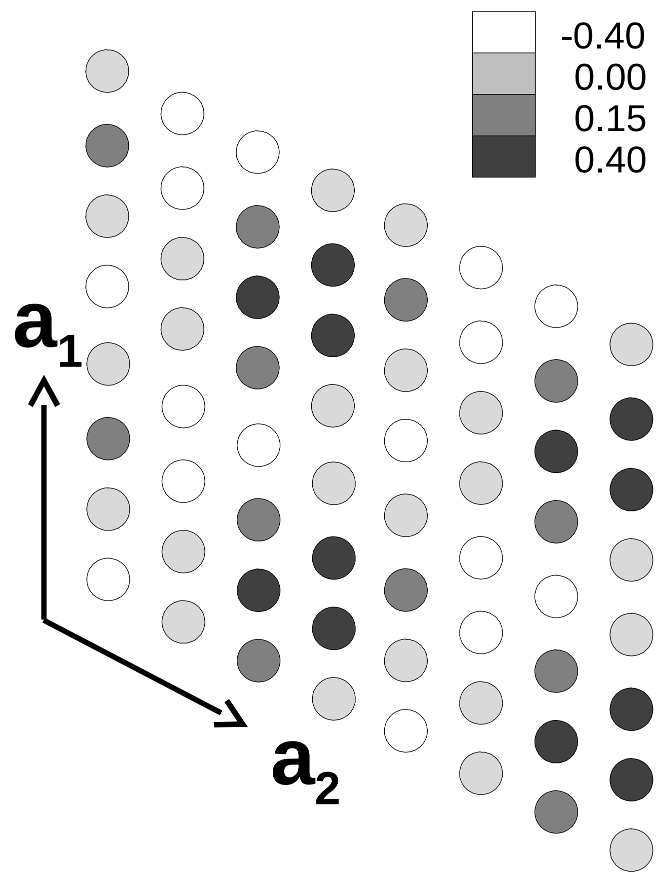
High suceptibility

**4x4 cell**: paramagnetic and **2D wave-like state** (<1 meV/Nb)

**Pristine $NbS_2$:**

- **Several solutions very close in energy:**

**ground state ?**



# Magnetic properties $NbS_2$ monolayer

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***But:*** ferromagnetic state very close in energy (< 1Mev/Nb)

High suceptibility

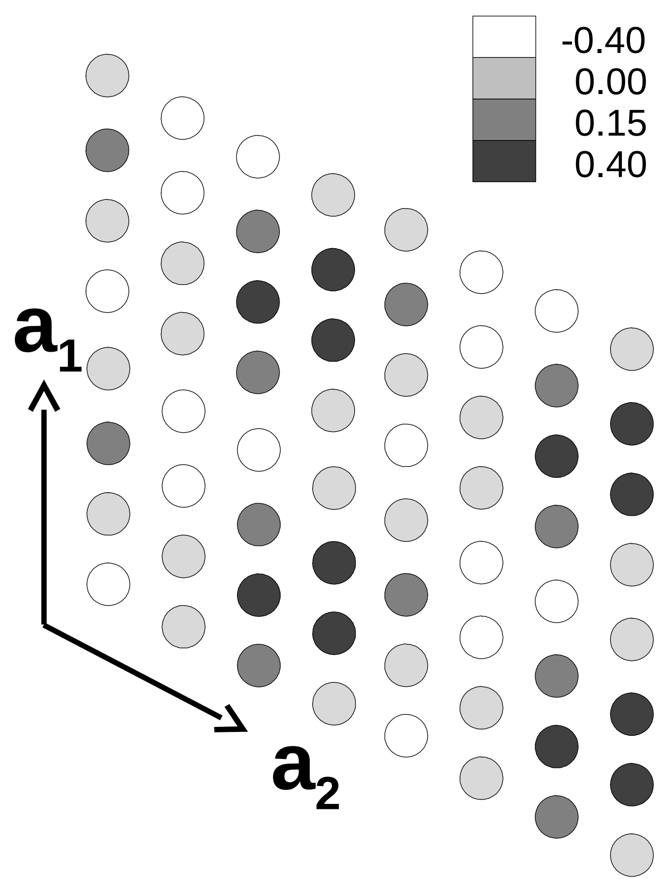
**4x4 cell**: paramagnetic and **2D wave-like state** (<1 meV/Nb)

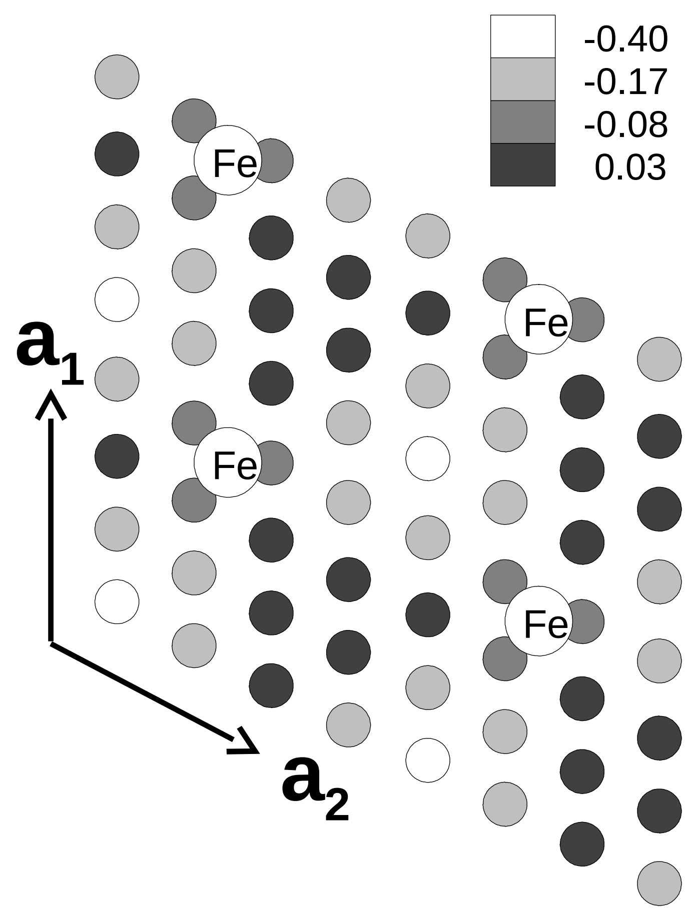
Stabilized by impurities, adsorption, vacancies

## Pristine $NbS_2$:

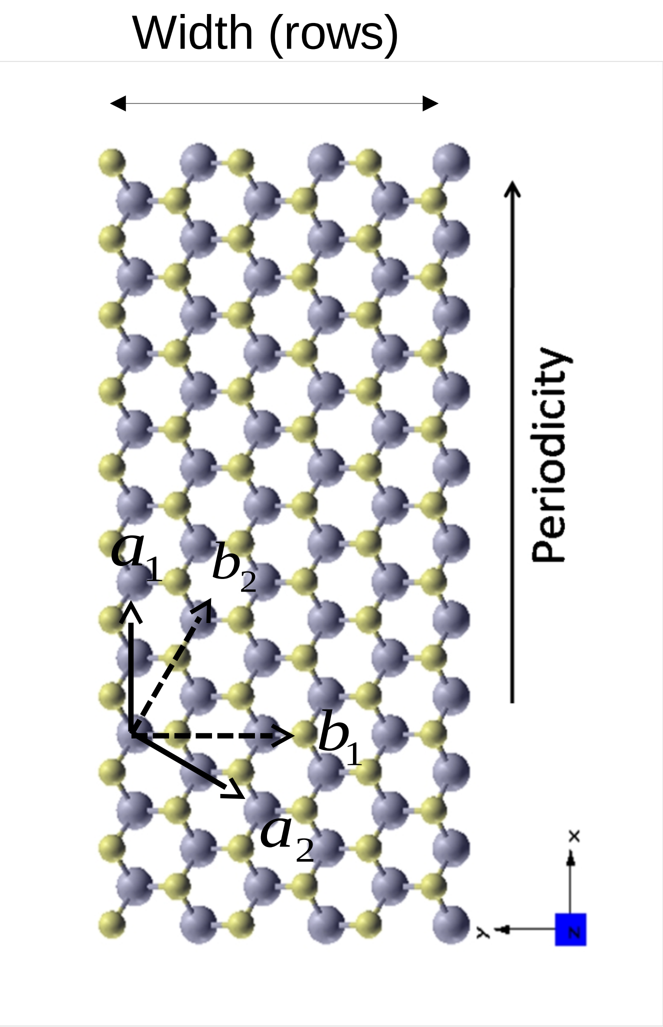
- **Many solutions very close in energy:**

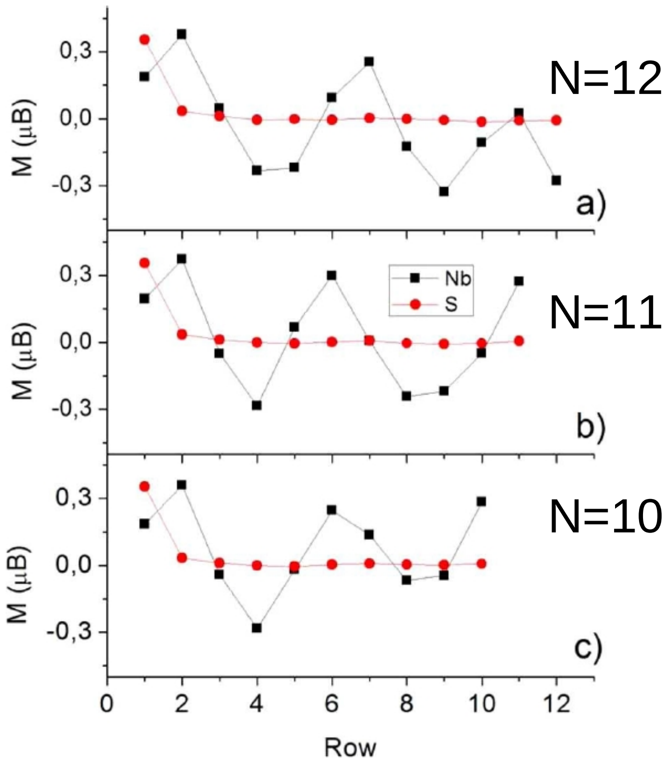
**ground state ?**



# Magnetic properties of $NbS_2$ zig-zag ribbons



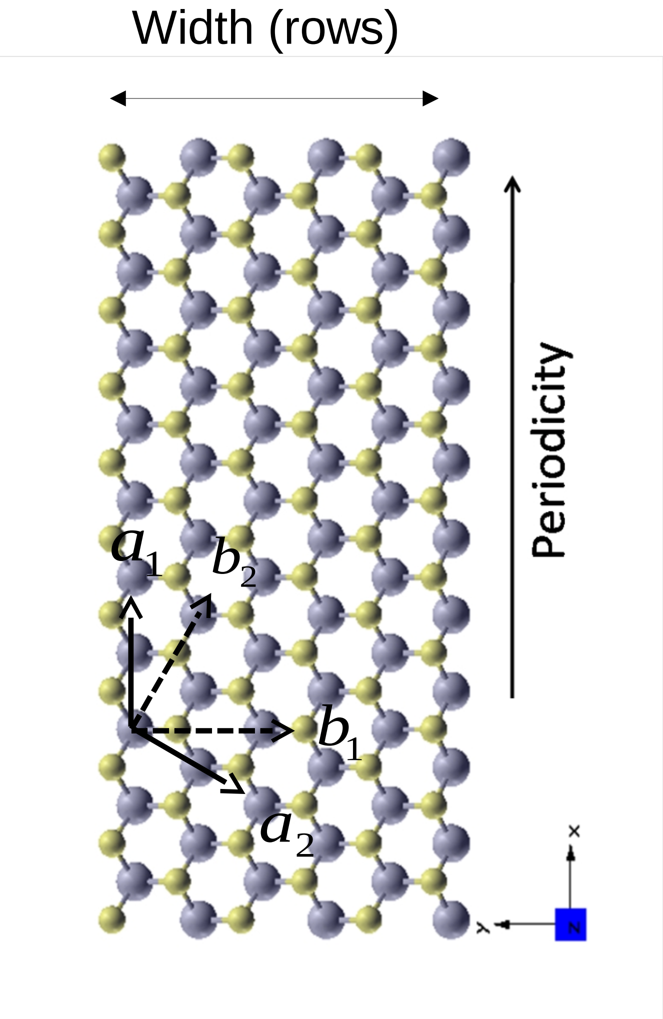



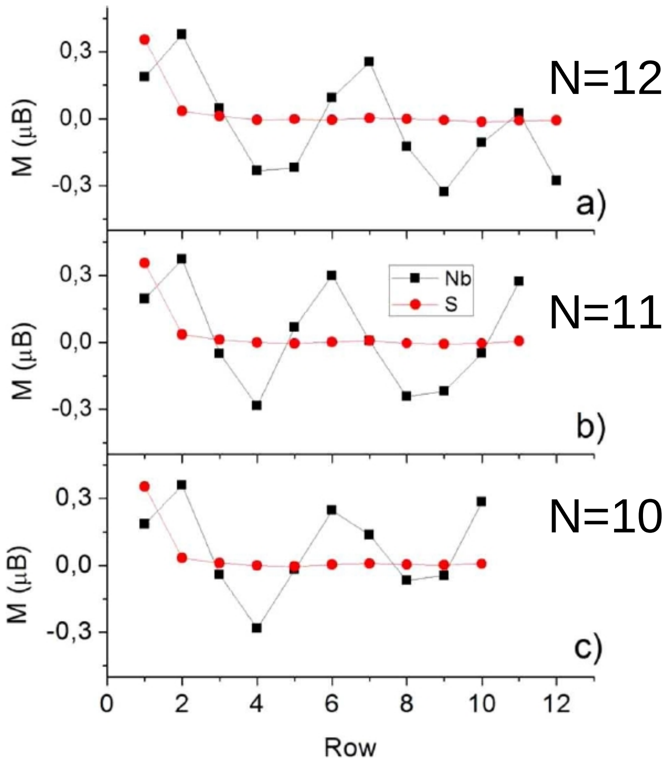

Magnetic moment per atom
as a function of row number

- Ferromagnetic edges (dangling bonds)
- 1D Wave-like magnetic order, edge to edge
- Well defined ground state
- Large finitee size effects

*F. Guller, V. V., and AM Llois, IEEE Transactions on Magnetics **49,** 4538 (2013)*

# Magnetic properties of $NbS_2$ zig-zag ribbons

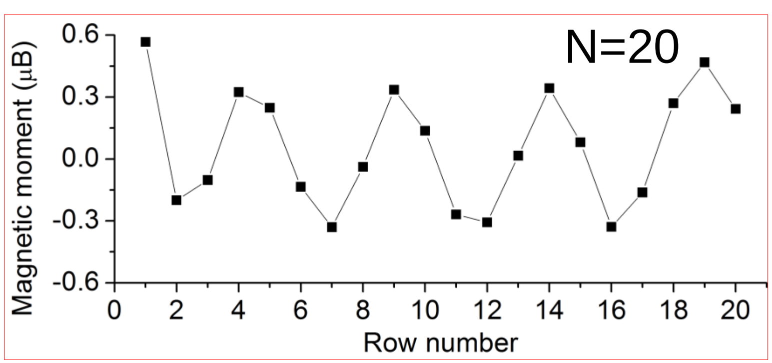



Magnetic moment per atom as a function of row number

- Ferromagnetic edges (dangling bonds)
- 1D Wave-like magnetic order, edge to edge
- Well defined ground state
- Edge effects still large

*F. Guller, V. V., and AM Llois, IEEE Transactions on Magnetics* ***49,*** *4538 (2013)*




**It is a SDW!**

- Well defined wavelength (least squares): 13.88 Å
- Formation energy ~12 meV/Nb

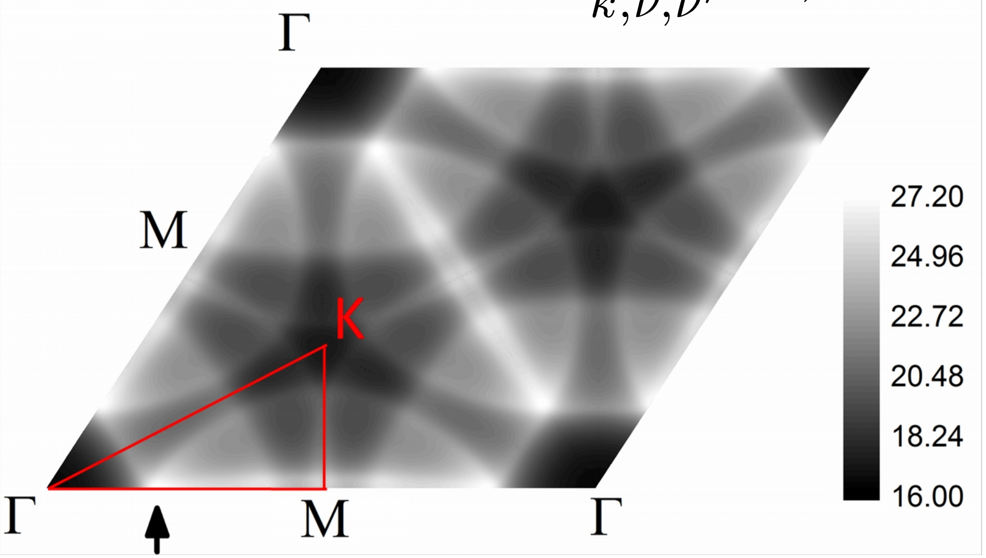
**Condition for SDW instability:** $\bar{V}_q \chi'(q) \geq 1$

$\bar{V}_q =< k+q, k'|V|k, k'+q >$

local approx. of exchange matrix elements

**Real part of static bare $\chi$**

$$\chi'(q) = \frac{1}{N_k} \sum_{k,\nu,\nu'} \frac{f_{k+q,\nu} - f_{k,\nu'}}{\varepsilon_{k,\nu'} - \varepsilon_{k+q,\nu}}$$




- SDW instability at maxima of $\chi(q)$
- Wavelength/direction given by *q*.

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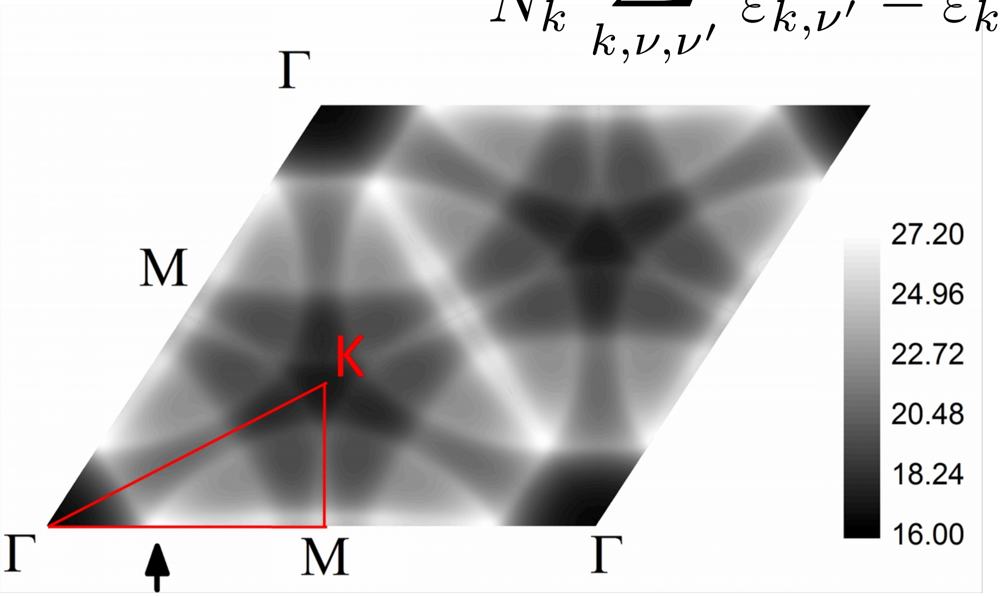
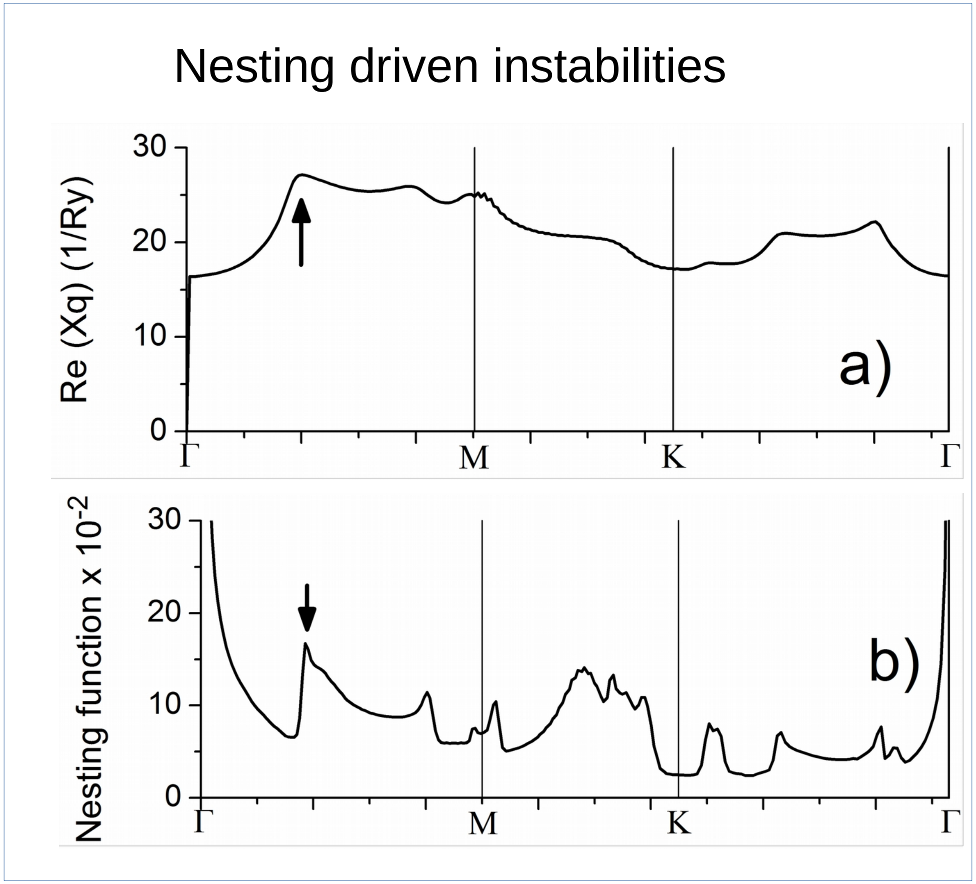



**Nesting function**

$$N_f = \sum_k \delta(\varepsilon_k - \varepsilon_f).\delta(\varepsilon_{k+q} - \varepsilon_f) = \lim_{\omega \to 0} \frac{\mathrm{Im}(Xq)}{\omega}$$

**Wavelengths**

**$\lambda_q$ = 13.35 Å**

**Least square fit (ribbon) = 13.88 Å**

**Less than 4%**

**q** ~ 0.2 **$b_1$**

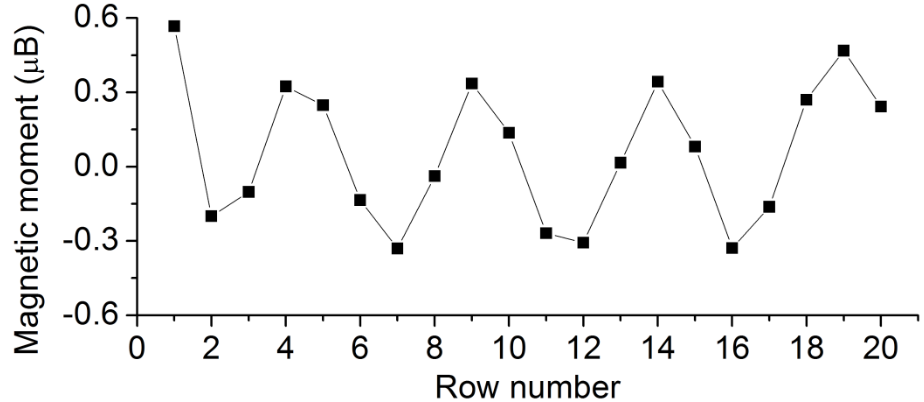
# Requisites for SDW formation: strong exchange interactions and nesting

## $NbS_2$ monolayer: high susceptibility, 4d bands

Our calculations indicate that it is on the verge of a SDW

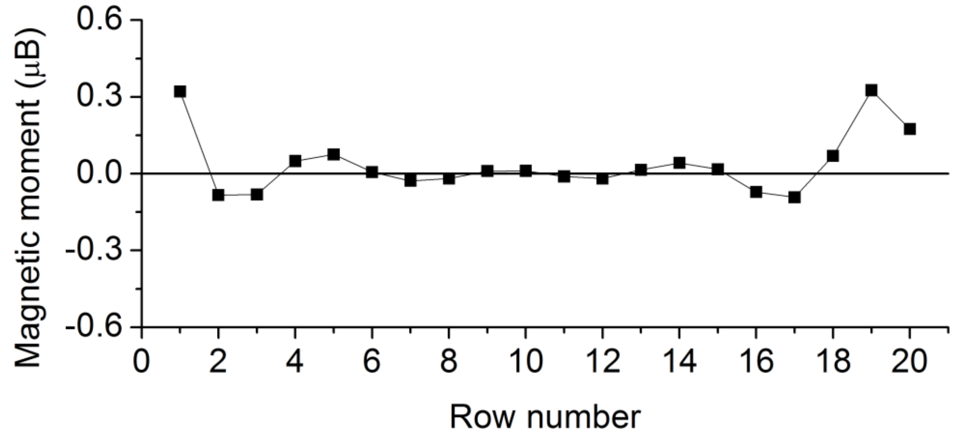
### Testing the importance of the Coulomb interactions for a SDW formation

$NbS_2$ ribbon: magnetic edges trigger a SDW




$TaS_2$ (undistorted) ribbon:

Nesting properties but weaker exchange (5d bands). Wave pattern with small decaying magnetic mom.



# Estimation of the spin fluctuations ξ

**Fluctuation disipation theorem**

$$\xi^2 = \frac{2\hbar}{\Omega} \int d^3q \int \frac{d\omega}{2\pi} \mathrm{Im}(\chi_{q,\omega})$$

Fluctuation: $\xi = \hat{S} - < \hat{S} >$

Disipation: $Im\chi(q,\omega) \rightarrow Im\chi_0(q,\omega) = \sum_{\mathbf{k}} [f(\epsilon_{\mathbf{k}}) - f(\epsilon_{\mathbf{k}+\mathbf{q}})]\delta(\epsilon_{\mathbf{k}+\mathbf{q}} - \epsilon_{\mathbf{k}} - \omega)$

We underestimate Im χ, since an enhancement of the spin-fluctuations is expected when considering the scattering of the electron-hole pairs due to all the electron-electron interactions.

- We estimate $\xi \sim 0.2\ \mu_B$
- SDW amplitude $\mu \sim 0.4\ \mu_B$ → Fluctuations are large !!!
- To be expected in for a system close to a quantum critical transition.

.We predict important spin fluctuations for **q** ~0.2 $\mathbf{b_1}$

## Summary

In this work, we find that the **$NbS_2$** monolayer presents a high magnetic susceptibility, large spin-fluctuations and it is on the verge of a SDW that could be activated by magnetic edges, impurities or doping.

## Experiments

There are no reported experimental works investigating the spin-fluctuations of any TMDC, up to now.
Neutrons?
NMR?
RIXS?

## Open questions

**- In most metallic TMDs, superconductivity coexists or it is next to a CDW.**
**- For a long time, a CDW state was a "requisite" for superconductivity.**
**- 2H-$NbS_2$ is an exception. The fermiology is very similar but there is no CDW and it is superconductor.**
**- Have these magnetic instabilities any role in the superconducting mechanism in 2H-$NbS_2$?**

# OBRIGADO!!

F. Güller, VV, A.M. Llois, PRB 93, 094434 (2016)

Workshop on Next Generation Quantum Materials

Instituto de Fisica Teorica – UNESP- São Paulo - Brasil

ICTP SAIFR