

Spin density instabilities in the NbS₂ monolayer

V. Vildosola

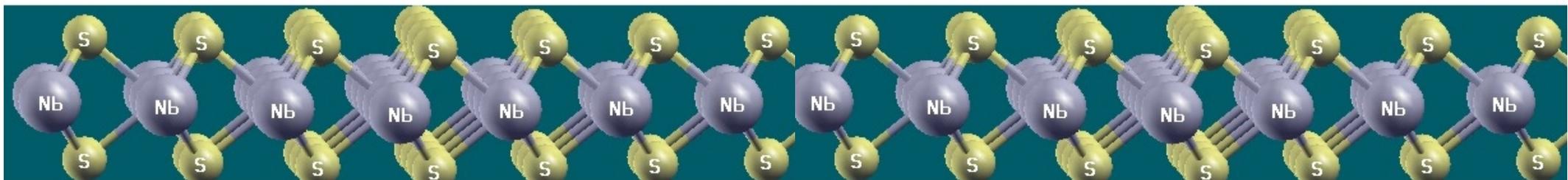
F. Güller and A.M. Llois



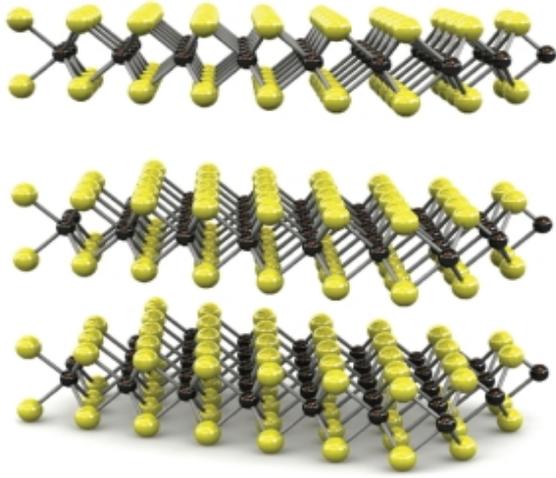
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ARGENTINA



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 insulators, Mott insulators ...

Periodic Table of the Elements

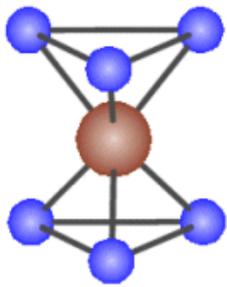
M = Ti, Nb, Mo, etc.

S = S, Se, Te

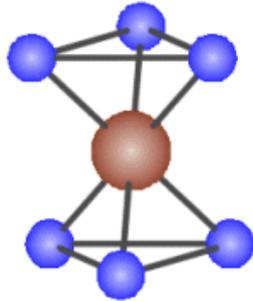
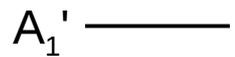
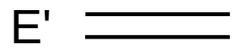
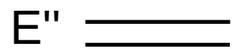
1 IA 1A		2 IIA 2A												3 IIIA 3A	4 IVA 4A	5 VA 5A	6 VIA 6A	7 VIIA 7A	8 VIIIA 8A
1 H Hydrogen 1.008		2 He Helium 4.003																	
3 Li Lithium 6.941	4 Be Beryllium 9.012											5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.180		
11 Na Sodium 22.990	12 Mg Magnesium 24.305	13 Al Aluminum 26.982	14 Si Silicon 28.086	15 P Phosphorus 30.974	16 S Sulfur 32.066	17 Cl Chlorine 35.453	18 Ar Argon 39.948												
19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.867	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.845	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.631	33 As Arsenic 74.922	34 Se Selenium 78.971	35 Br Bromine 79.904	36 Kr Krypton 84.798		
37 Rb Rubidium 84.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.95	43 Tc Technetium 98.907	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.906	46 Pd Palladium 106.42	47 Ag Silver 107.868	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.711	51 Sb Antimony 121.760	52 Te Tellurium 127.6	53 I Iodine 126.904	54 Xe Xenon 131.294		
55 Cs Cesium 132.905	56 Ba Barium 137.328	57-71 Lanthanide Series	72 Hf Hafnium 178.49	73 Ta Tantalum 180.948	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.217	78 Pt Platinum 195.085	79 Au Gold 196.967	80 Hg Mercury 200.592	81 Tl Thallium 204.383	82 Pb Lead 207.2	83 Bi Bismuth 208.980	84 Po Polonium [208.982]	85 At Astatine 209.987	86 Rn Radon 222.018		
87 Fr Francium 223.020	88 Ra Radium 226.025	89-103 Actinide Series	104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [269]	109 Mt Meitnerium [268]	110 Ds Darmstadtium [269]	111 Rg Roentgenium [272]	112 Cn Copernicium [277]	113 Uut Ununtrium unknown	114 Fl Flerovium [289]	115 Uup Ununpentium unknown	116 Lv Livermorium [298]	117 Uus Ununseptium unknown	118 Uuo Ununoctium unknown		

Lanthanide Series		57 La Lanthanum 138.905	58 Ce Cerium 140.116	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.243	61 Pm Promethium 144.913	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.500	67 Ho Holmium 164.930	68 Er Erbium 167.259	69 Tm Thulium 168.934	70 Yb Ytterbium 173.055	71 Lu Lutetium 174.967
Actinide Series		89 Ac Actinium 227.028	90 Th Thorium 232.038	91 Pa Protactinium 231.036	92 U Uranium 238.029	93 Np Neptunium 237.048	94 Pu Plutonium 244.064	95 Am Americium 243.061	96 Cm Curium 247.070	97 Bk Berkelium 247.070	98 Cf Californium 251.080	99 Es Einsteinium [254]	100 Fm Fermium 257.095	101 Md Mendelevium 258.1	102 No Nobelium 259.101	103 Lr Lawrencium [262]

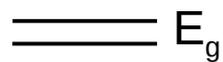
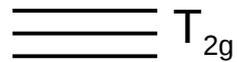
Different behaviour: packing and d band filling



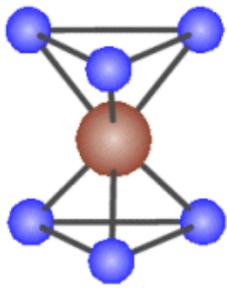
Trigonal
Prismatic
(2H)



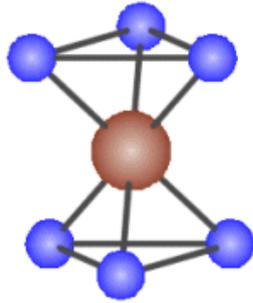
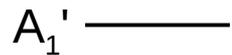
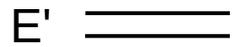
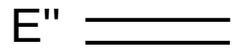
Octahedral
(1T)



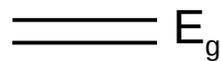
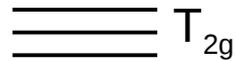
Different behaviour: packing and d band filling



Trigonal
Prismatic
(2H)



Octahedral
(1T)



4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B
22 Ti Titanium 47.867	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938
40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.95	43 Tc Technetium 98.906
72 Hf Hafnium 178.49	73 Ta Tantalum 180.948	74 W Tungsten 183.84	75 Re Rhenium 186.207
104	105	106	107

Same packing...

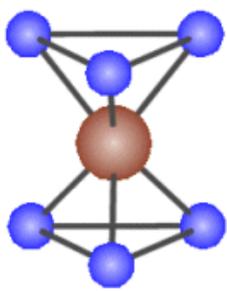
2H-NbS₂ metal

2H-MoS₂ band insulator

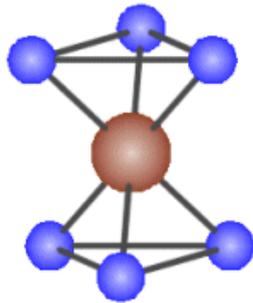
Nb:[Kr] 4d⁴5s¹ Nb⁺⁴: 4d¹

Mo:[Kr] 4d⁵5s¹ Mo⁺⁴: 4d²

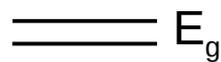
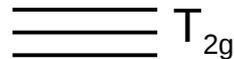
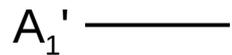
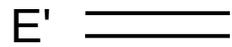
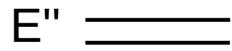
Different behaviour: packing and d band filling



Trigonal Prismatic (2H)



Octahedral (1T)



4 IVB 4B	5 VB 5B	6 VIB 6B	
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72 Hf Hafnium 178.49	73 Ta Tantalum 180.948	74 W Tungsten 183.84	75
104	105	106	107

Same packing...

2H-NbS₂ metal

2H-MoS₂ band insulator

Nb:[Kr] 4d⁴5s¹ Nb⁺⁴: 4d¹

Mo:[Kr] 4d⁵5s¹ Mo⁺⁴: 4d²

Same filling...

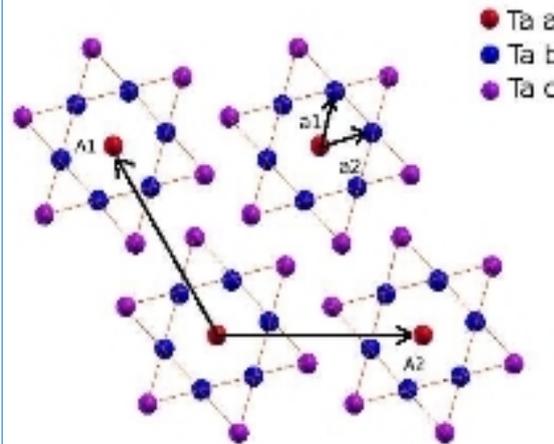
Resistivity

1T-TaS₂ semiconductor- like
Mott transition

2H-TaS₂ metallic- like

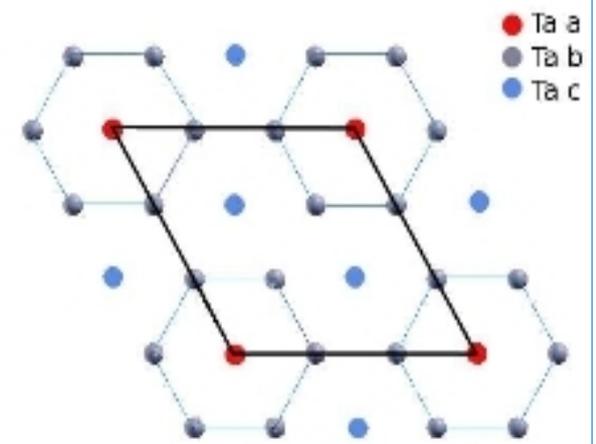
Same filling...

Periodic distortion



1T-TaSe2

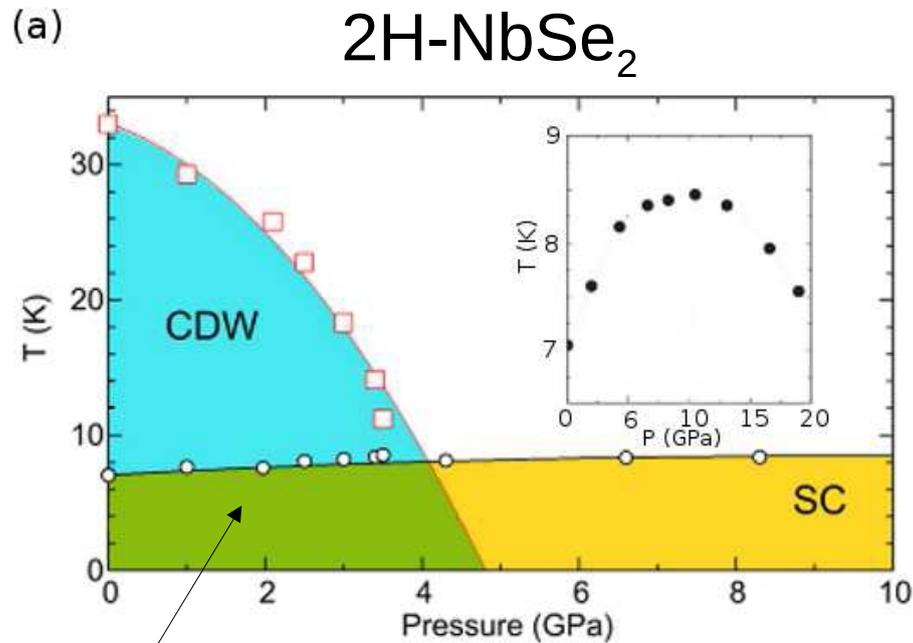
$\sqrt{(13)} \times \sqrt{(13)} \times 1$



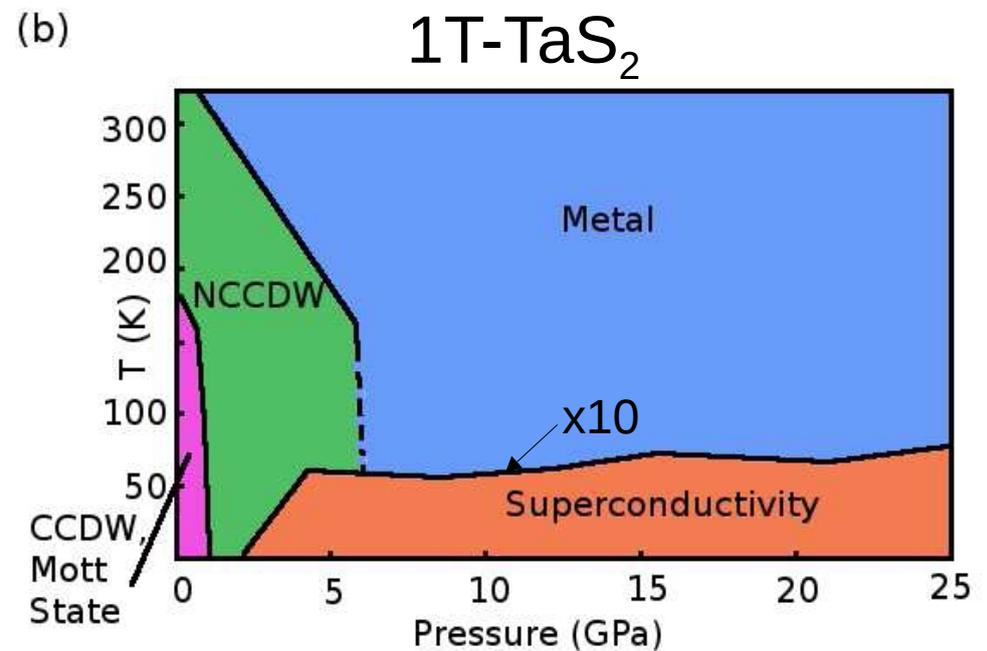
2H-TaSe2

3x3x1

Similar Phase diagram



Coexisting and competing phases

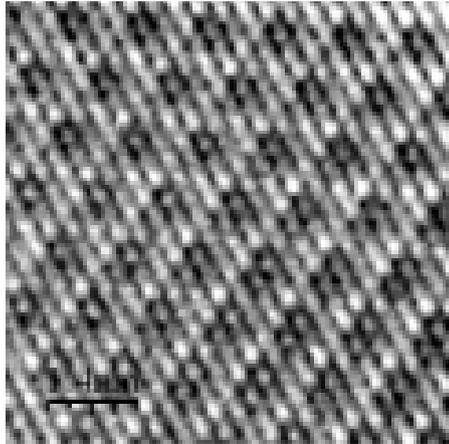


- Electron-phonon coupling (within McMillan formula) can account for the order of T_c
- The CDW and the SC gaps are highly anisotropic
- The CDW gap existed in the normal state ($T > T_{CDW}$) (as the Pseudogap phase of cuprates)
- No long range magnetic order was ever observed
- **CONVENTIONAL** or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

2H-NbS₂ : exceptional case

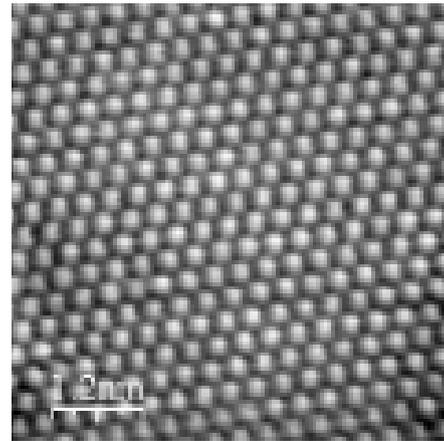
- All the TMDC that are superconductors also exhibit CDW phases **except 2H-NbS₂**
- **2H-NbS₂** is superconductor below $T_c = 6$ K and does not show CDW.

2H-NbSe₂



superperiodicity = CDW

2H-NbS₂



atomic lattice
No CDW

T=100 mK

I. Guillamon PRL 2008

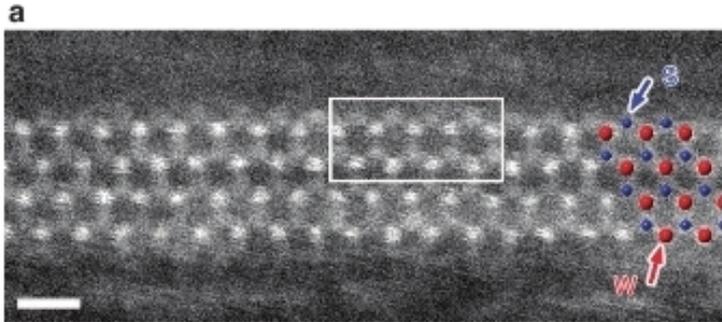
It has been suggested that the CDW in **NbS₂** is suppressed by anharmonic effects.

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

The real interplay between CDW and superconductivity is still under debate

Low dimensional 2H-NbS₂

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



➤ Monolayer **WS₂** nanoribbon encapsulated in carbon NT
Zheng Liu et al, Nature Comm. (2011)

➤ Also **MoS₂** ribbons

Wang et al, JACS 132, 13840–13847 (2010)

Only zigzag edges were observed

➔ Very recently **NbSe₂** monolayer with $T_{\text{CDW}} = 145\text{K}$!

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

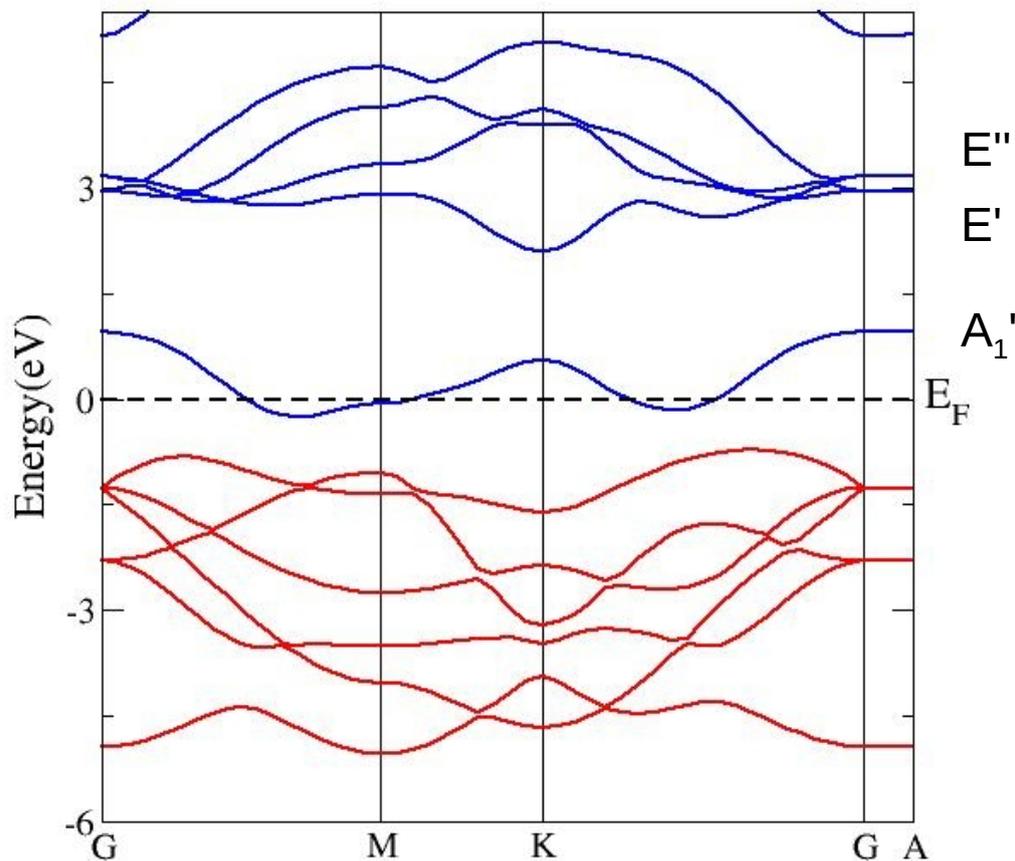
What about magnetism??

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

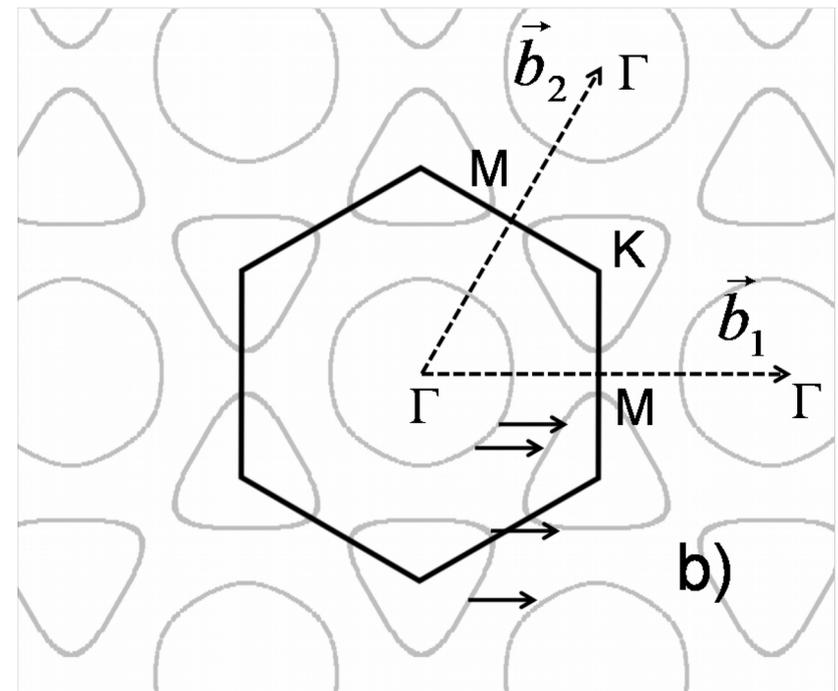
Electronic structure of the NbS₂ monolayer

- A₁' band half filled
- The electronic structure is very similar to undistorted NbSe₂

NbS₂ monolayer



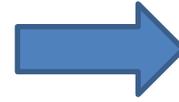
Fermi surface



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

Magnetic properties NbS₂ monolayer

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

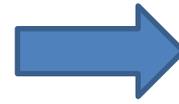


High
susceptibility

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

Magnetic properties NbS₂ monolayer

1x1 cell: paramagnetic, boring.
But: ferromagnetic state very close in energy ($< 1\text{MeV}/\text{Nb}$)



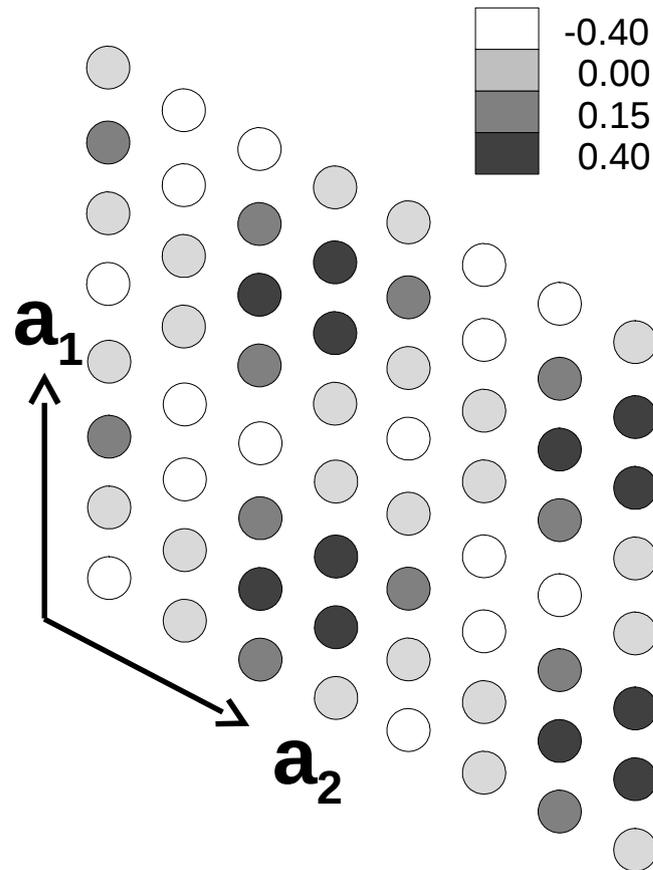
High susceptibility

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



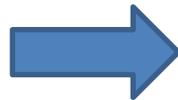
Pristine NbS₂:

- Several solutions very close in energy:
ground state ?



Magnetic properties NbS₂ monolayer

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High susceptibility

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

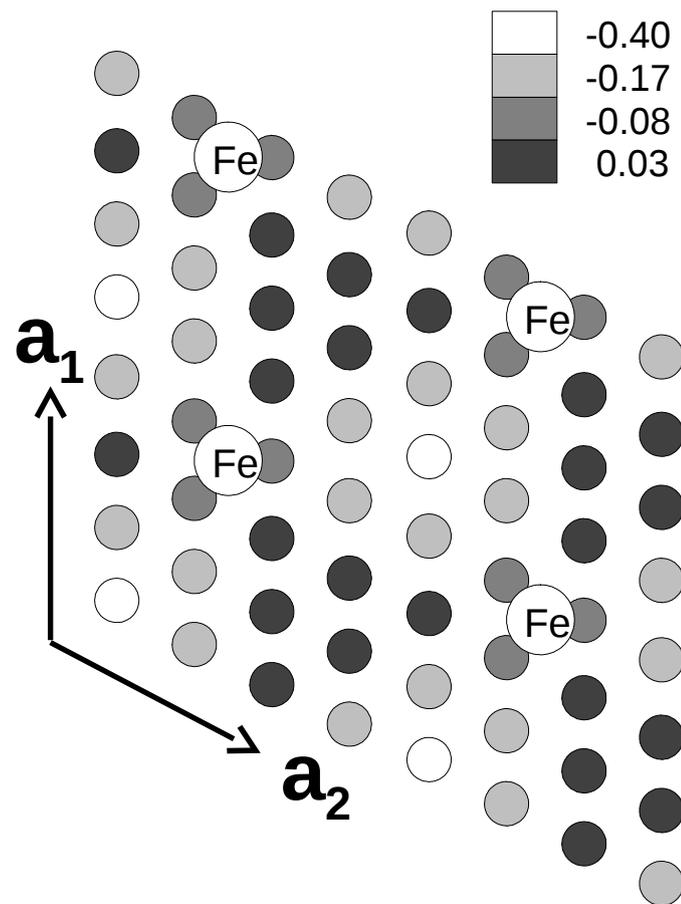
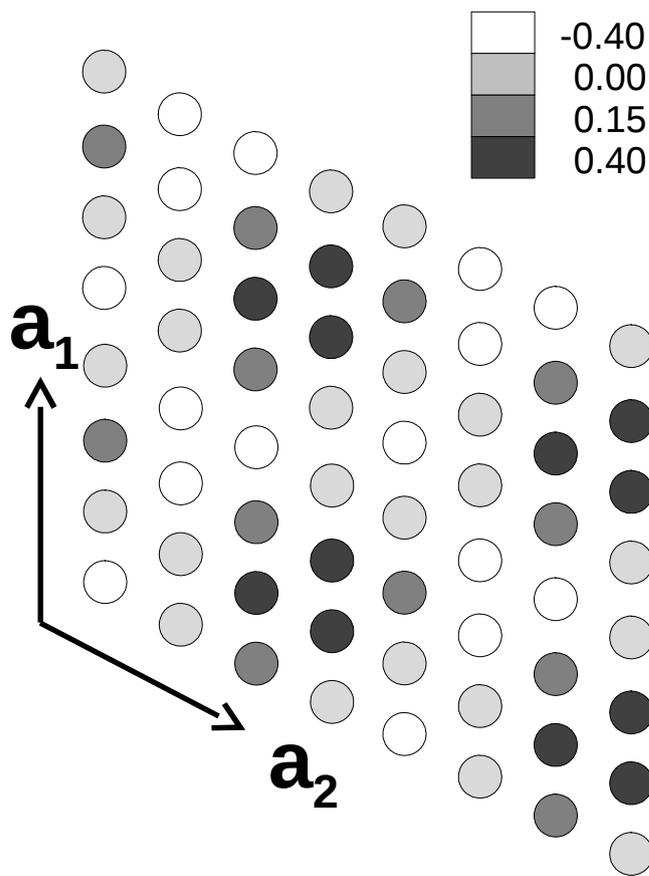


Stabilized by impurities, adsorption, vacancies



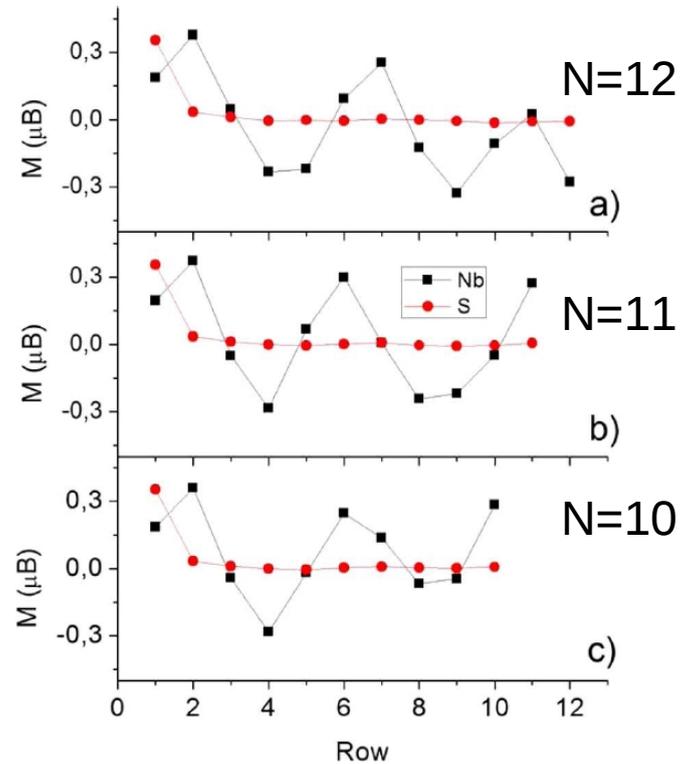
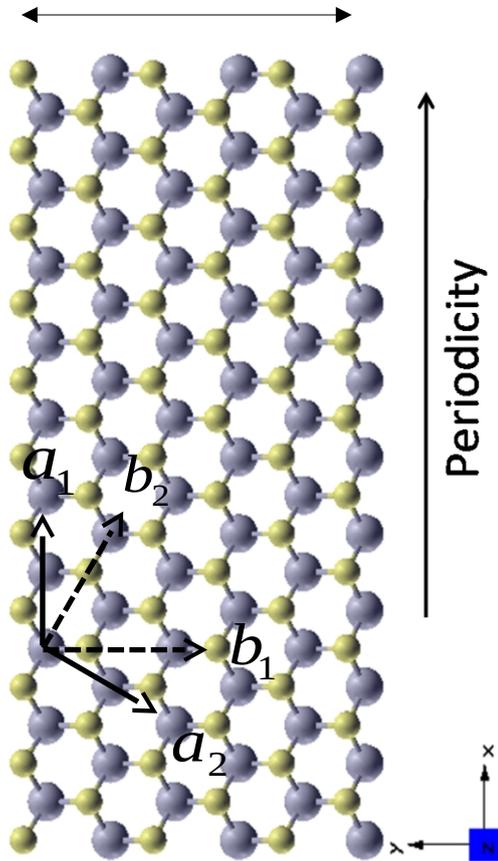
Pristine NbS₂:

- Many solutions very close in energy:
ground state ?



Magnetic properties of NbS₂ zig-zag ribbons

Width (rows)



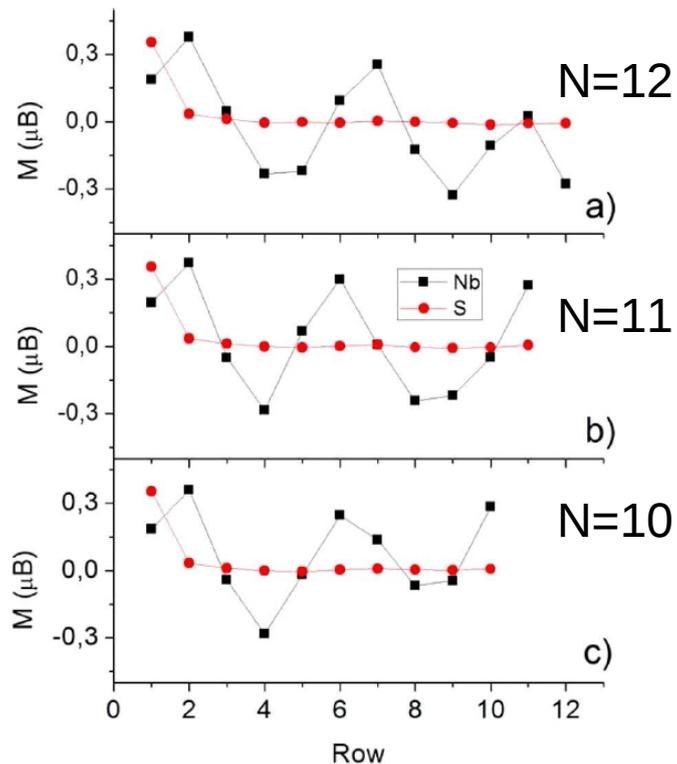
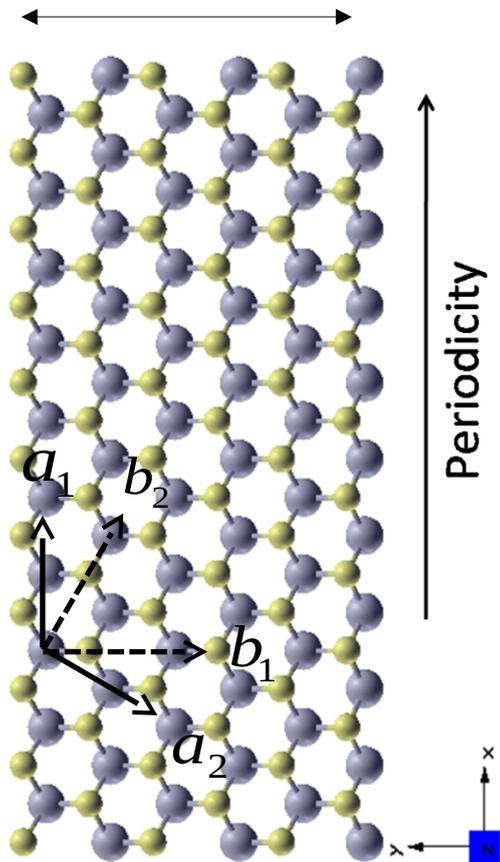
Magnetic moment per atom
as a function of row number

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

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

Magnetic properties of NbS₂ zig-zag ribbons

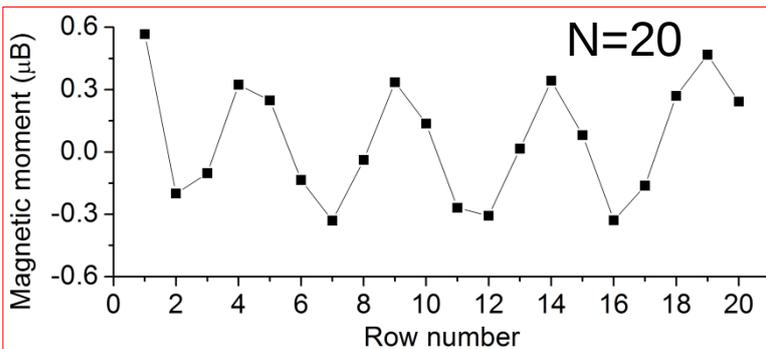
Width (rows)



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

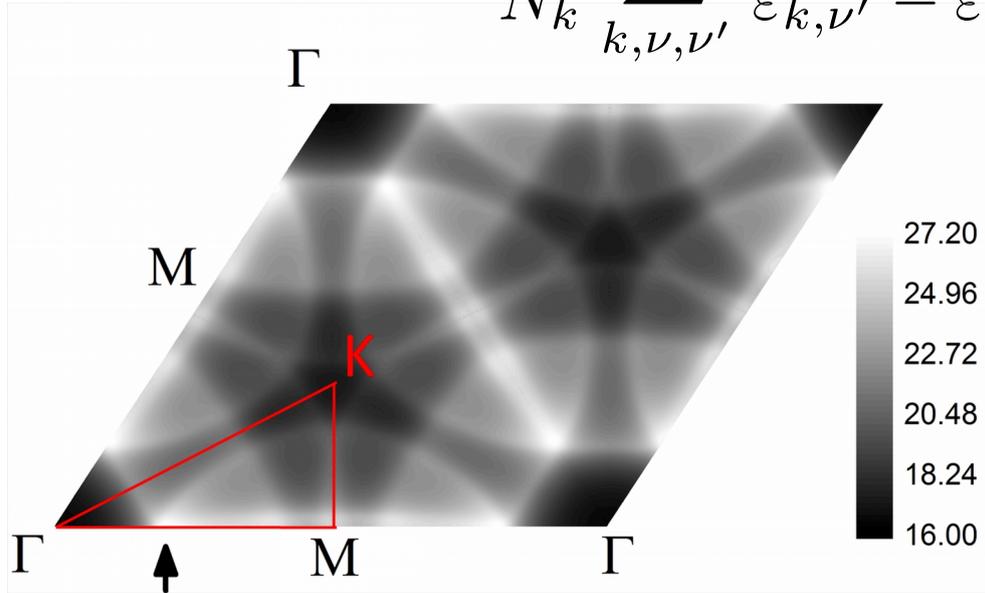
Condition for SDW instability:

$$\bar{V}_q \chi'(q) \geq 1$$

$\bar{V}_q = \langle k + q, k' | V | k, k' + q \rangle$
local approx. of exchange matrix elements

Real part of static bare χ

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



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

Condition for SDW instability:

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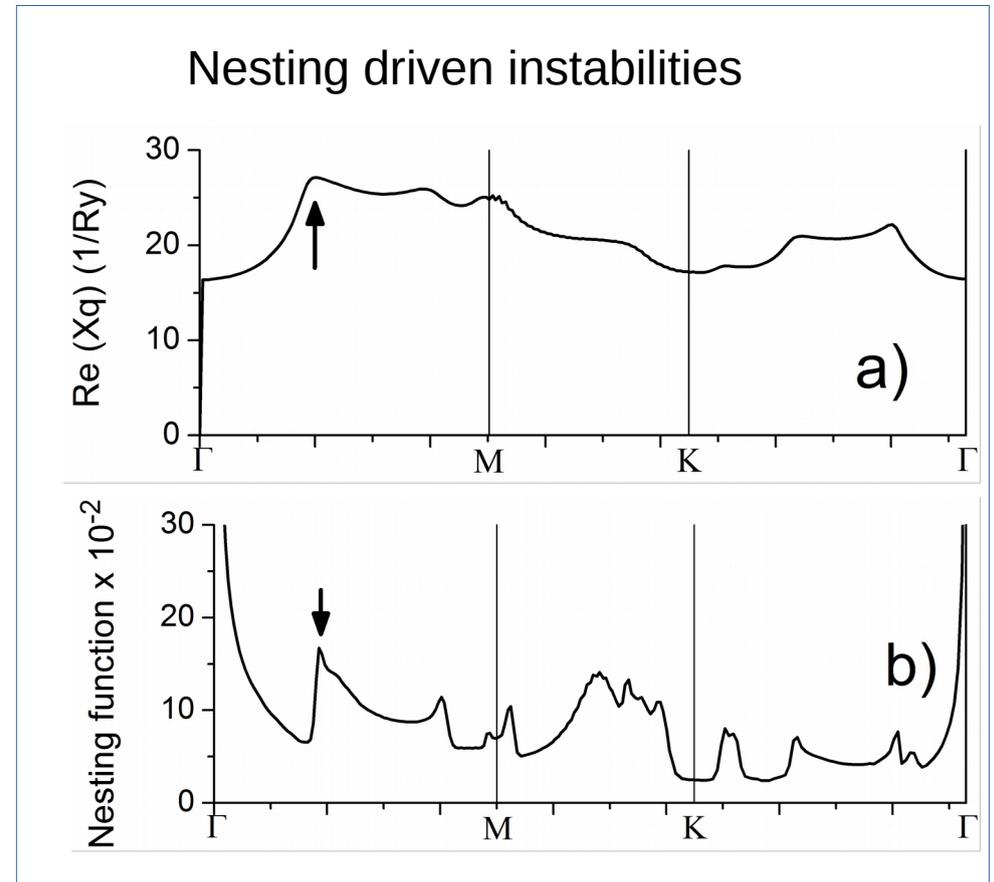
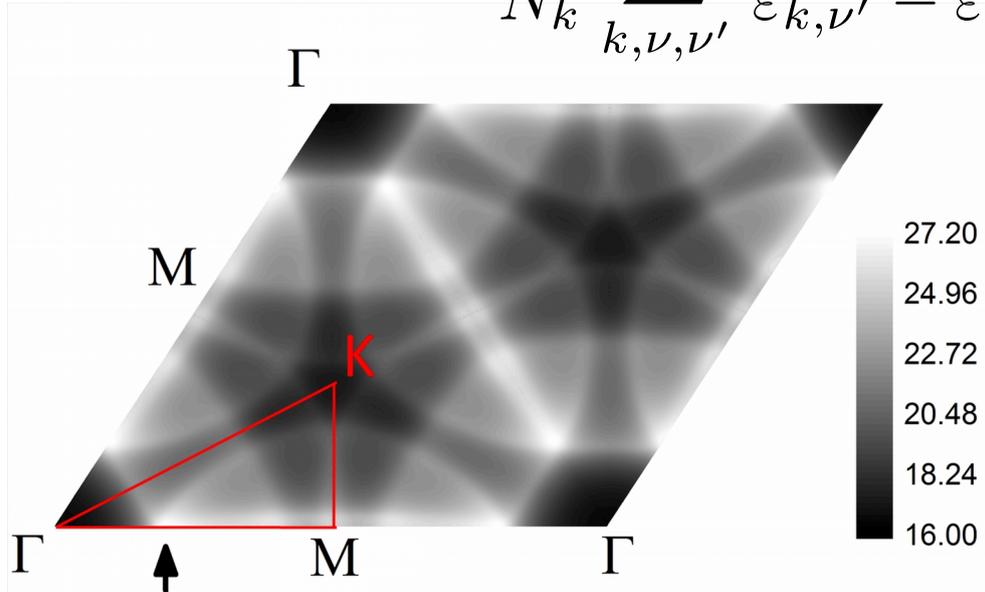
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➤ SDW instability at maxima of $\chi(q)$

➤ Wavelength/direction given by q .



Nesting function

$$N_f = \sum_k \delta(\epsilon_k - \epsilon_f) \cdot \delta(\epsilon_{k+q} - \epsilon_f) = \lim_{\omega \rightarrow 0} \frac{\text{Im}(Xq)}{\omega}$$

Wavelengths

$$\lambda_q = 13.35 \text{ \AA}$$

$$\text{Least square fit (ribbon)} = 13.88 \text{ \AA}$$

Less than 4%

$$q \sim 0.2 b_1$$

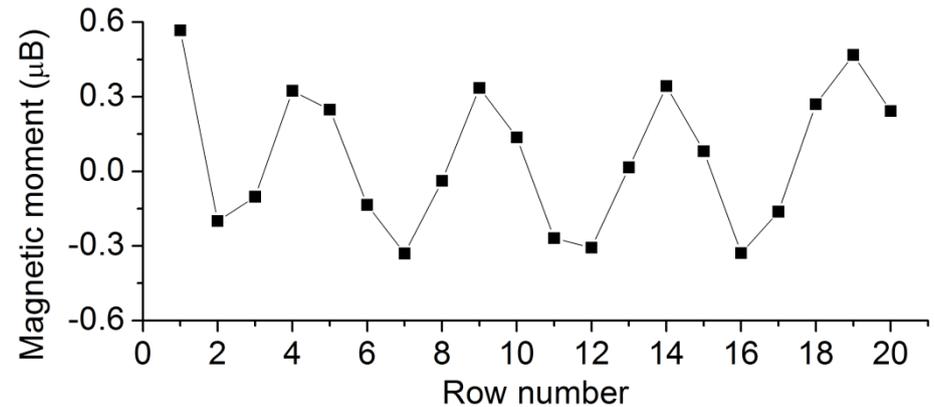
Requisites for SDW formation: strong exchange interactions and nesting

NbS₂ monolayer: high susceptibility, 4d bands

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

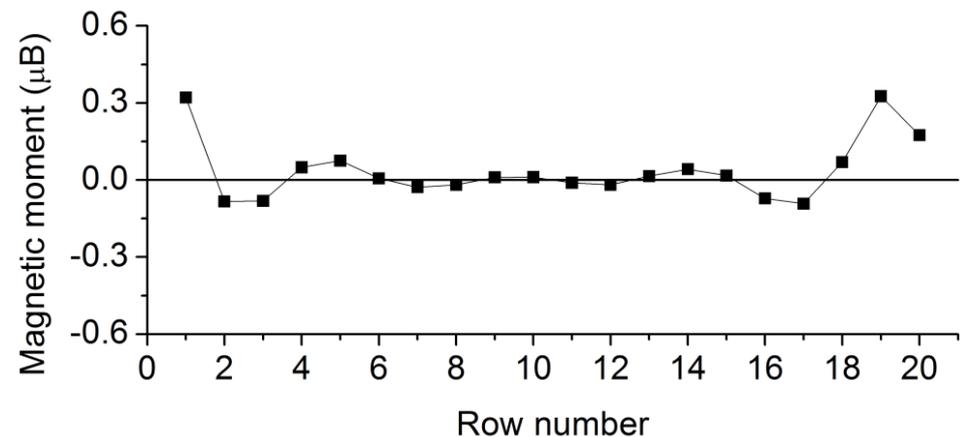
Testing the importance of the Coulomb interactions for a SDW formation

NbS₂ ribbon: magnetic edges trigger a SDW



TaS₂ (undistorted) ribbon:

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



Estimation of the spin fluctuations ξ

Fluctuation dissipation theorem

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

Fluctuation: $\xi = \hat{S} - \langle \hat{S} \rangle$

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

We underestimate $\text{Im}\chi$, 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 $\mu \sim 0.4 \mu_B \rightarrow$ Fluctuations are large !!!
- To be expected in for a system close to a quantum critical transition.

.We predict important spin fluctuations for $\mathbf{q} \sim 0.2 \mathbf{b}_1$

Summary

In this work, we find that the **NbS₂** 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.

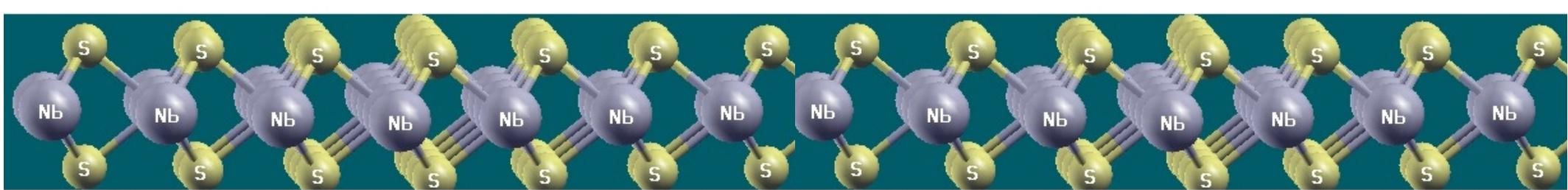
Neutrons?

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-NbS₂ 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-NbS₂?



OBRIGADO!!

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