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Magnetism & Ion Diffusion in Q1D Materials:
A Study by Muons, Neutrons and X-rays

2025-01-10

Prof. Martin Månsson

Sustainable Materials Research & Technologies (SMaRT)
Department of Applied Physics
KTH Royal Institute of Technology

The Energy Problem

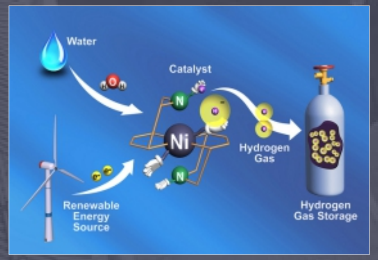
Energy Harvest

- Wind turbines

- Hydro-power

- Solar cells

- Geothermal



- Electrolysis

Energy Storage

- Batteries

- Hydrogen

Energy “Usage”

- Transport

- Heat/Cool

(Metal, paper, chemical, ...)

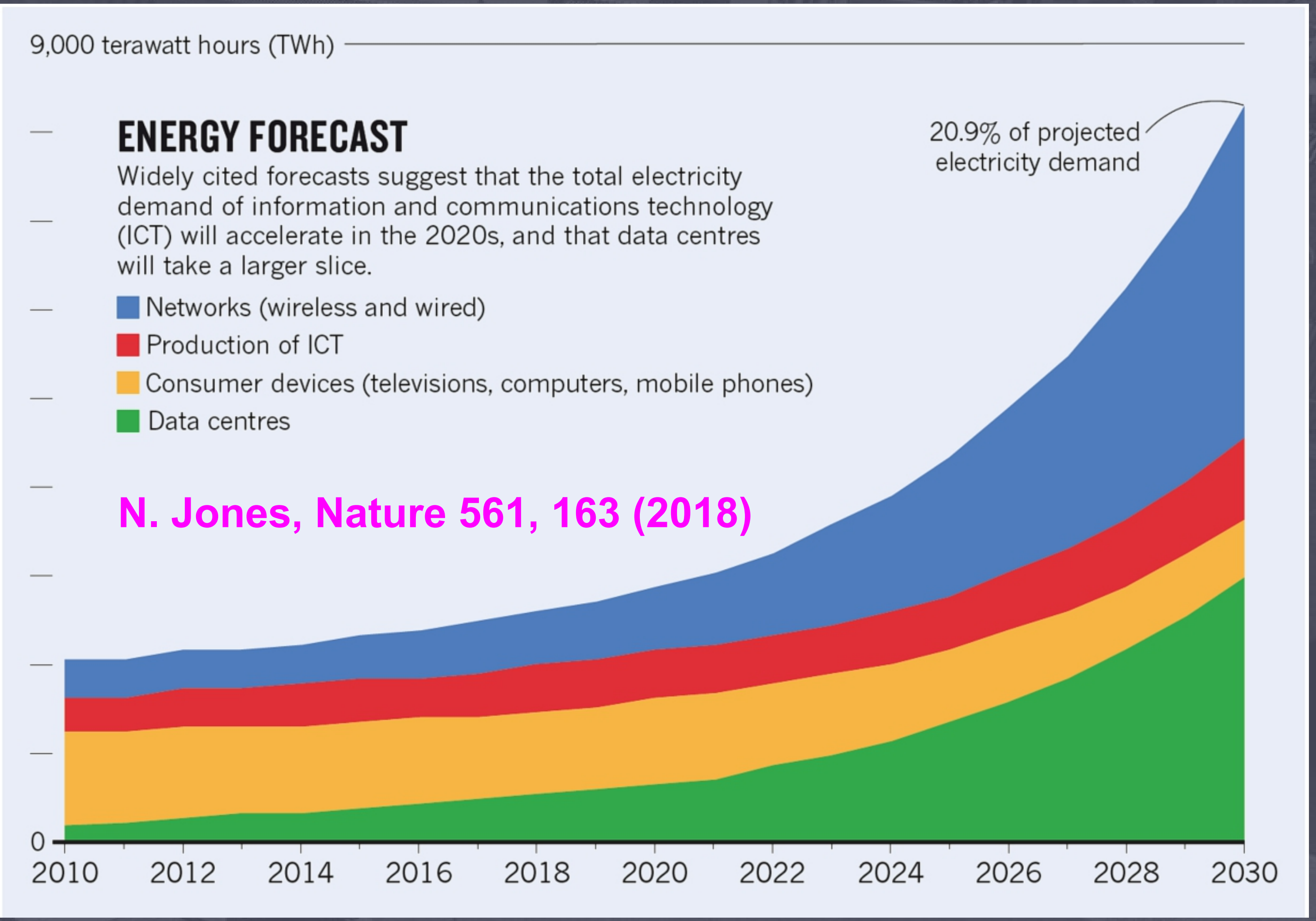
- Industry

- Construction

Professor Martin Månsson - KTH Royal Institute of Technology - condmat@kth.se

Information & Communications Technology (ICT)

- ICT is estimated to constitute 21% (= 9000 TWh/year) of the global electricity demand by 2030.
- Large server halls and networks are the areas that will increase the most (AI not included!)
- Replacing current RAM with existing MRAM can save almost 90% of the energy consumption.
- How significant is this?



Information & Communications Technology (ICT)

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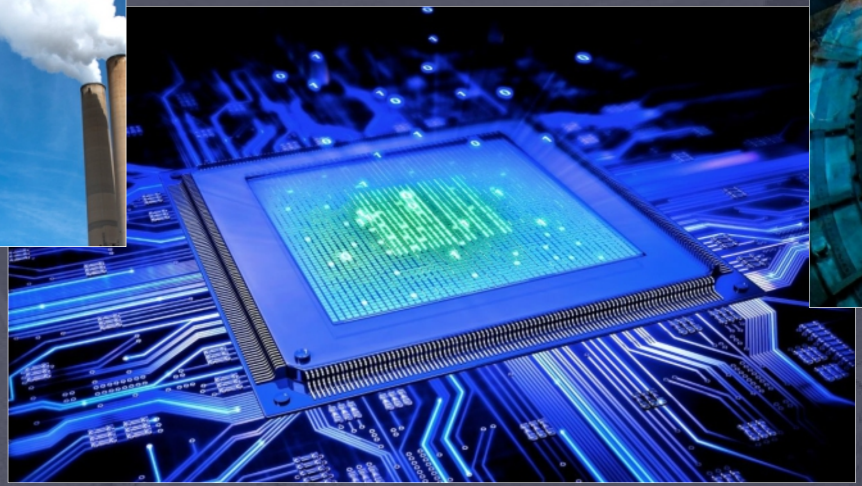
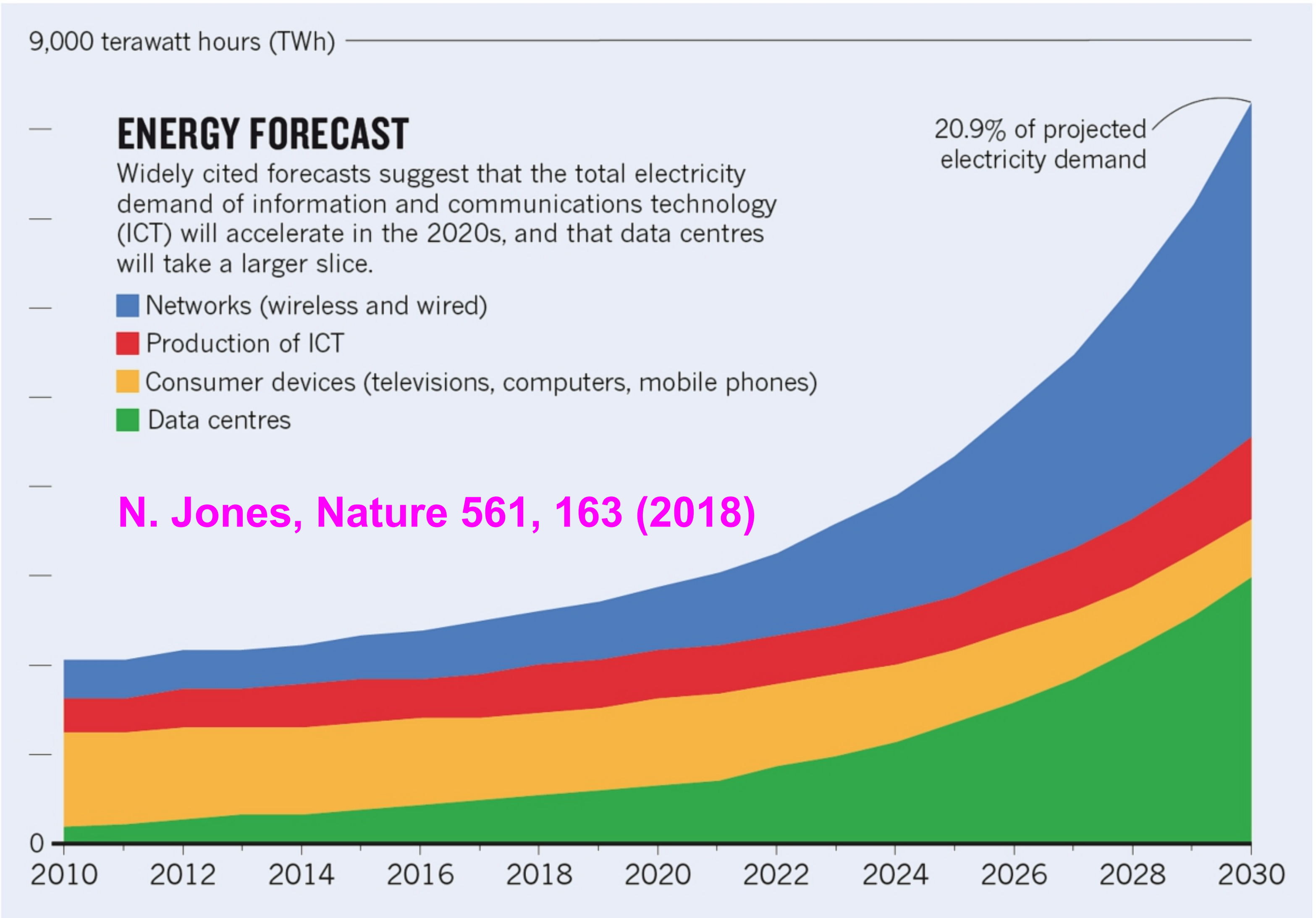
- Large server halls and networks are the areas that will increase the most (AI not included!)
- Replacing current RAM with existing MRAM can save almost 90% of the energy consumption.
- How significant is this?
- If we replace all electronics with spintronics we can save 90% of the 9000 TWh = 8000 TWh/year





N. Jones, Nature 561, 163 (2018)

- This actually equals ALL coal power plants OR 3 times ALL nuclear power in the world !!!

The Energy Problem

Energy Harvest

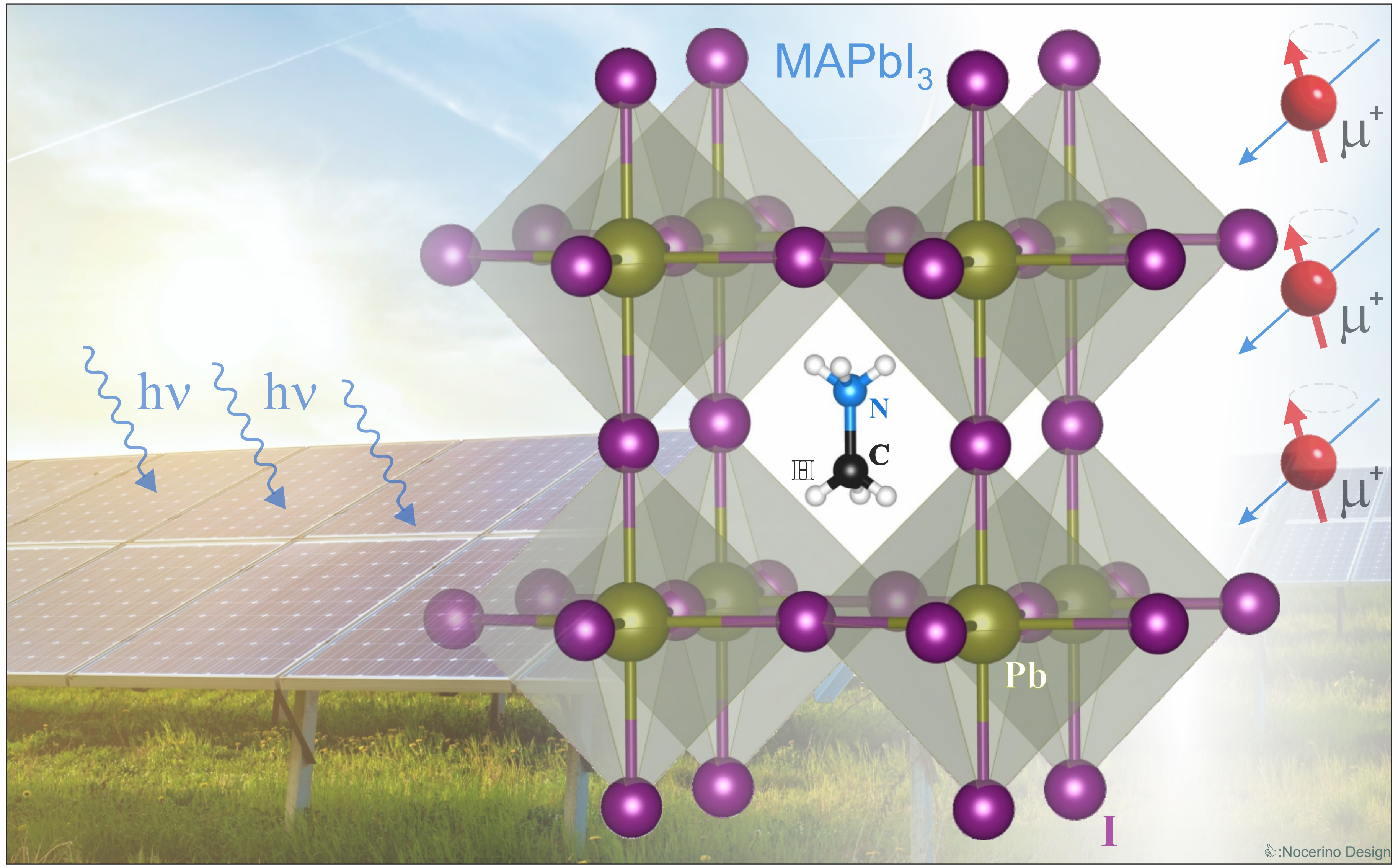
Energy Storage

Energy “Usage”

The Energy Problem

Energy Harvest

Photovoltaic Materials



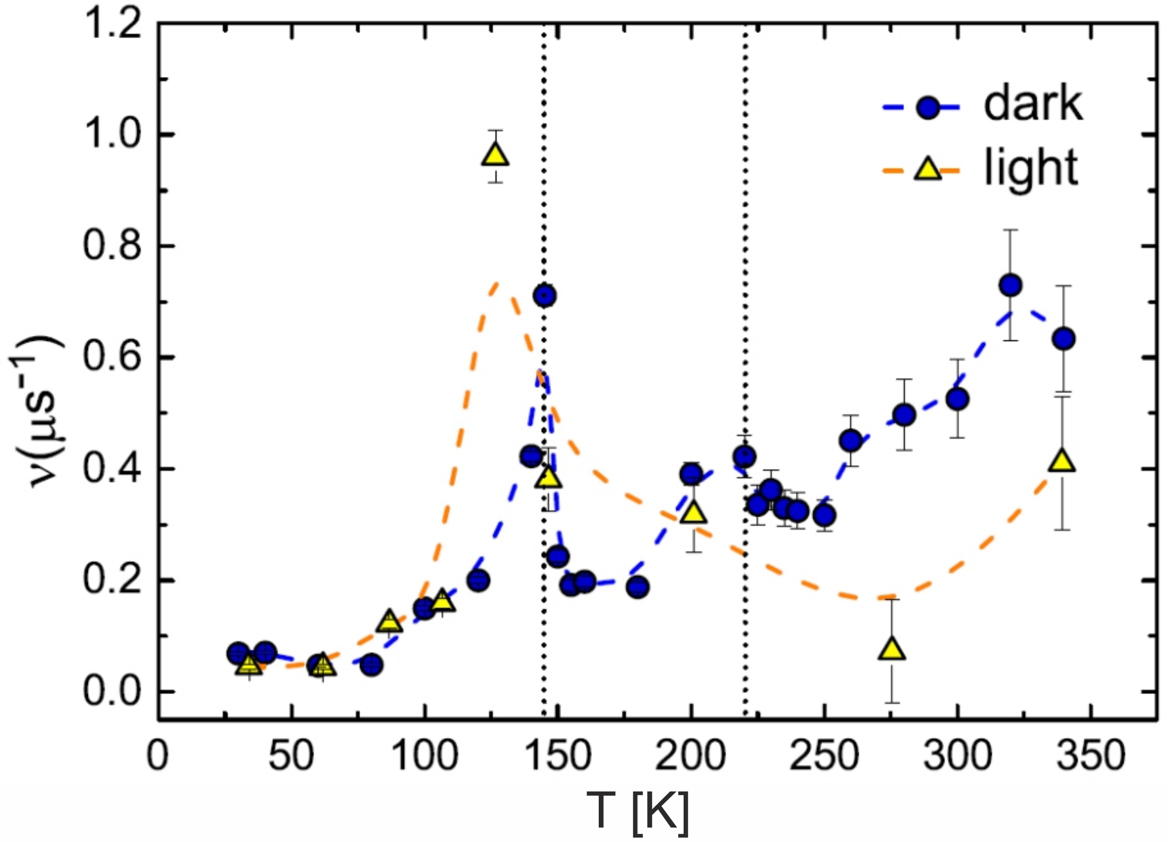
Mixed Halide Perovskites

The Energy Problem

Energy Harvest

μ^+SR "Light on/off" (ISIS/EMU)

MAPbX$_3$ (X = Br, Cl) - Single Crystals



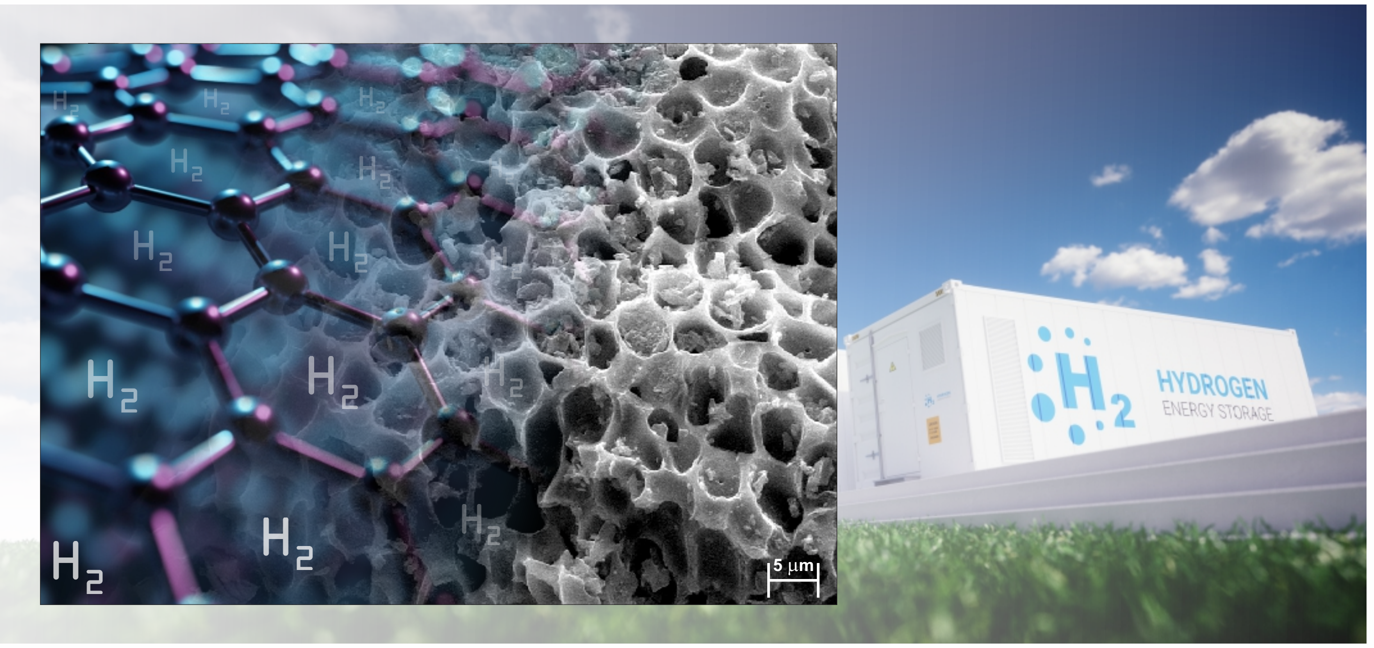
Change in Ion-dynamics

As. Prof. Yasmine Sassa

The Energy Problem

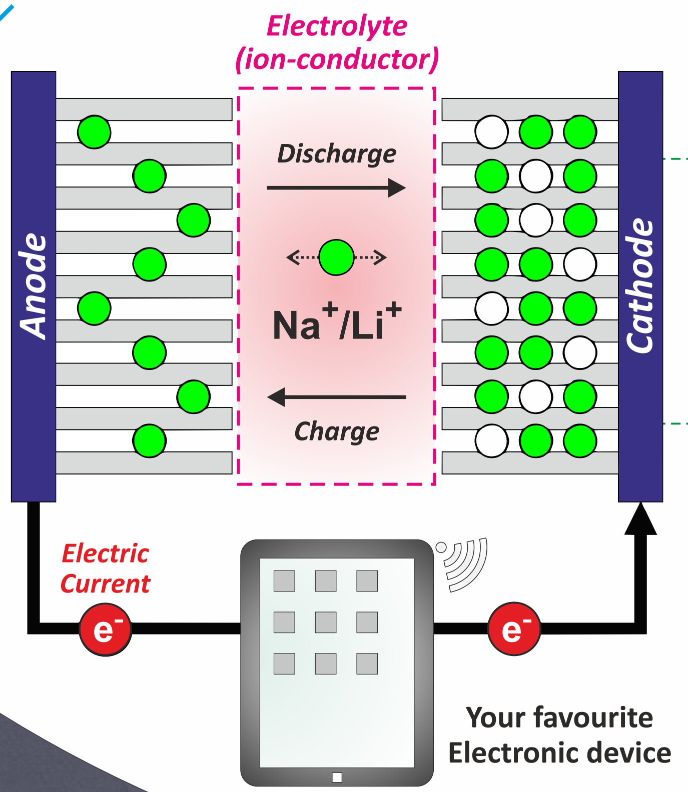
Energy Storage

H-storage

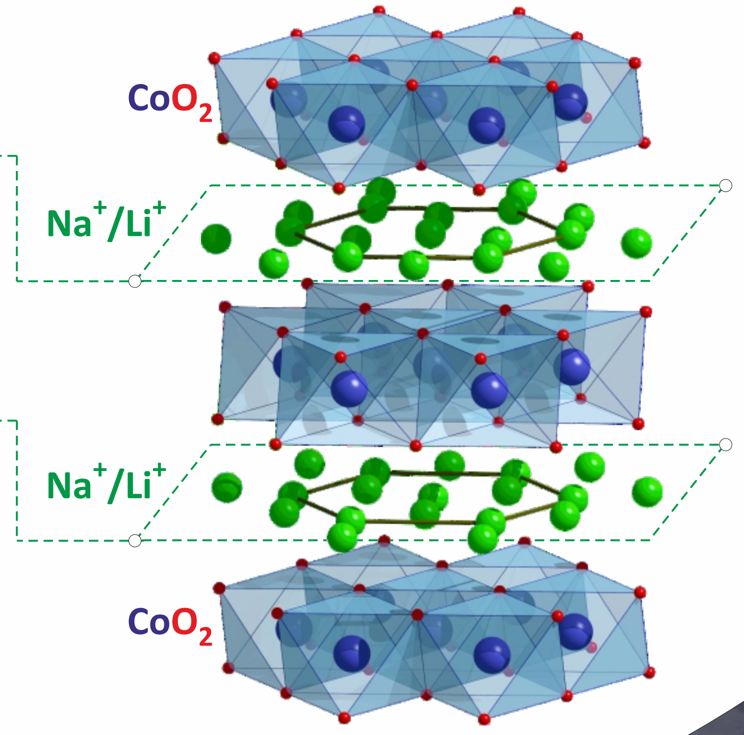


Battery Materials

Battery Device



Battery Electrode/Electrolyte Material



Dr. Jun Sugiyama

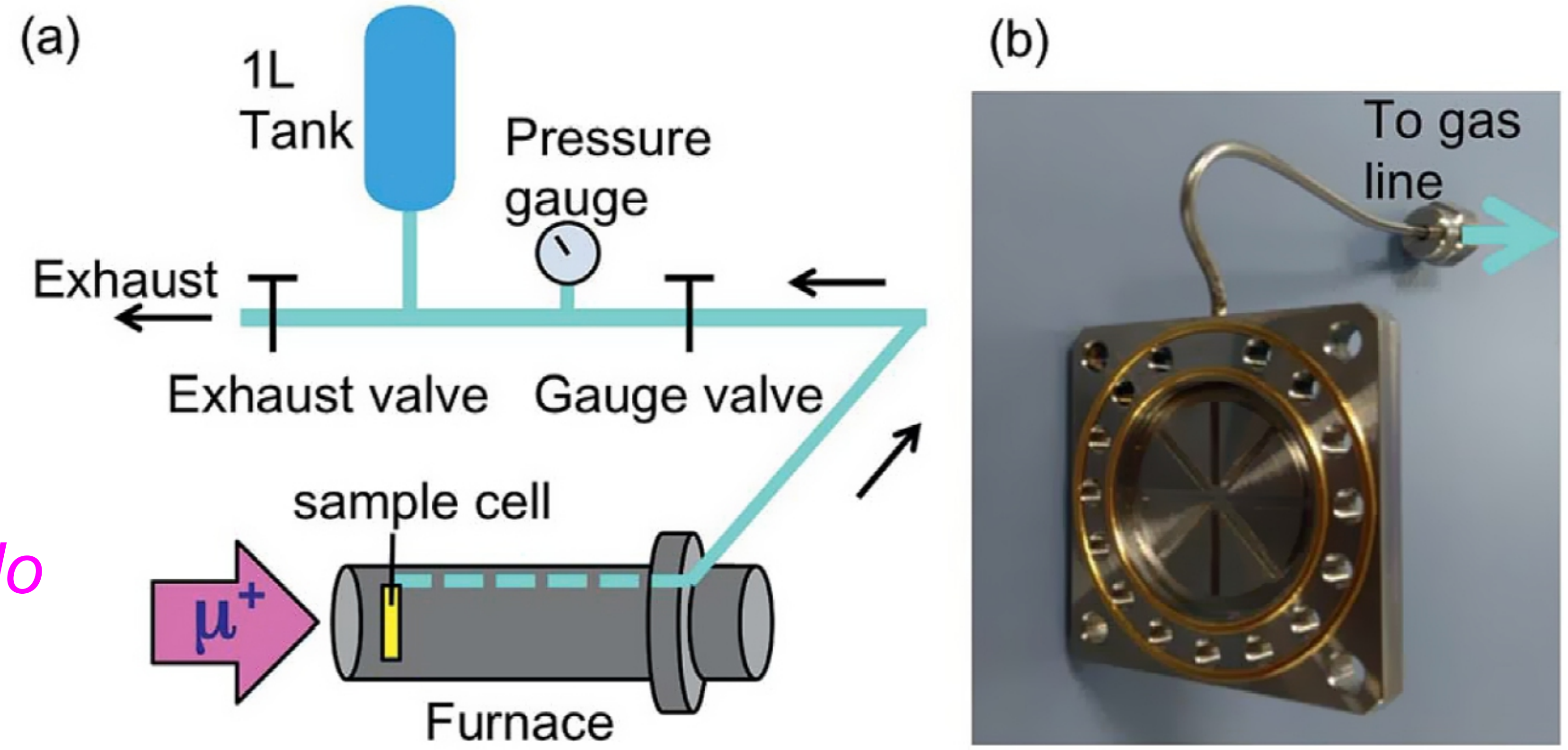
The Energy Problem

Energy Storage

H-storage

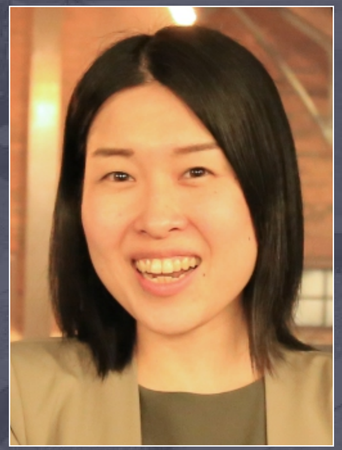
μ^+SR

in-operando



Sustainable Energy & Fuels, 3, 956 (2019)
Physical Review B 81, 092103 (2010)

As. Prof. Izumi Umegaki



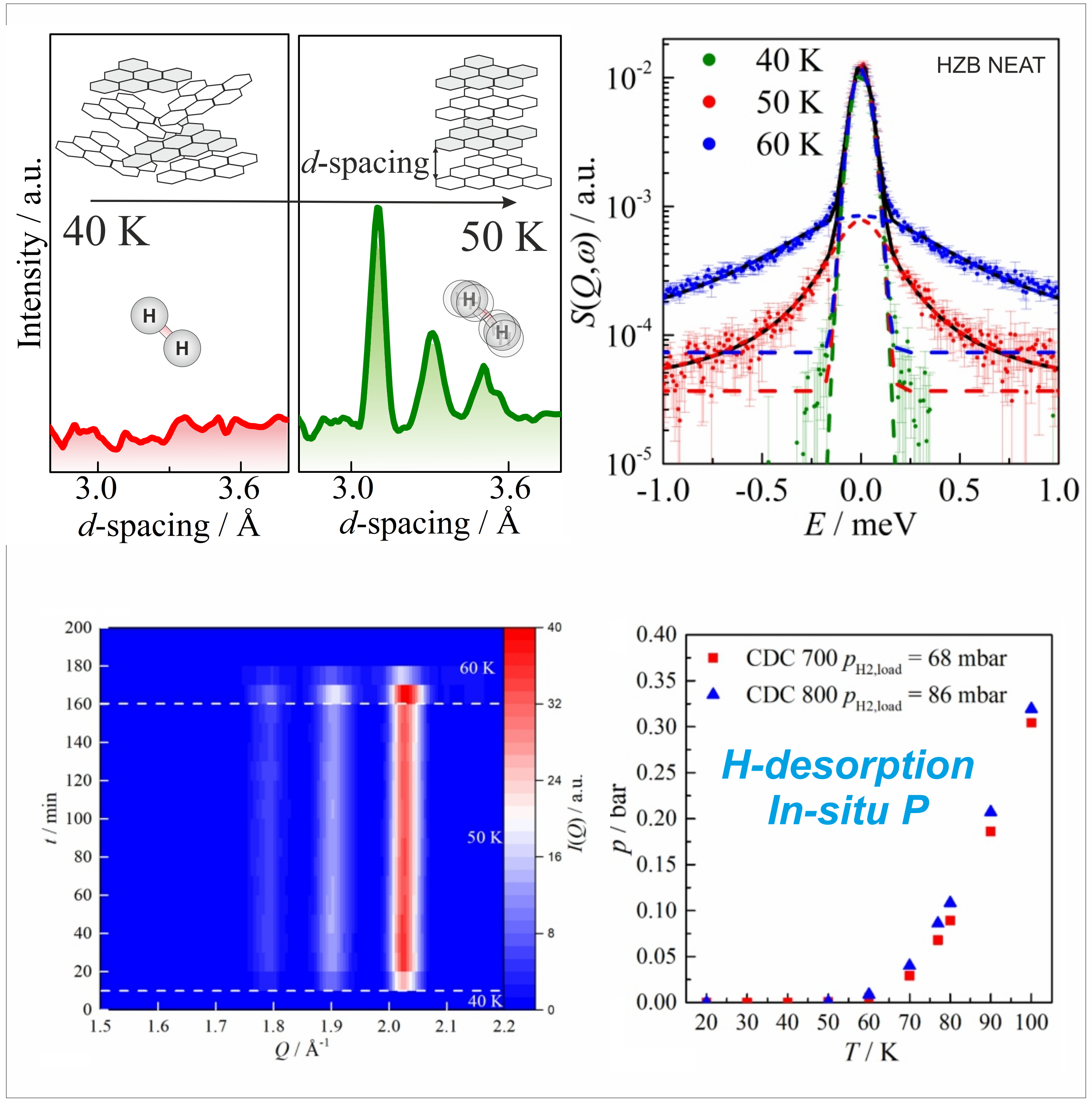
The Energy Problem

Energy Storage

H-storage

Elastic Neutron Scattering (Diffraction)
"Carbon Structure"

Quasi-Elastic Neutron Scattering (QENS)
"Hydrogen Dynamics"



NPD
QENS

in-operando

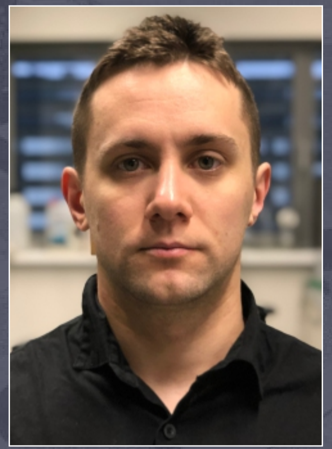
Carbon, 174, 190 (2021)

Int. J. Hydrogen Energy 47, 34195, (2022)

Carbon 197, 359 (2022)

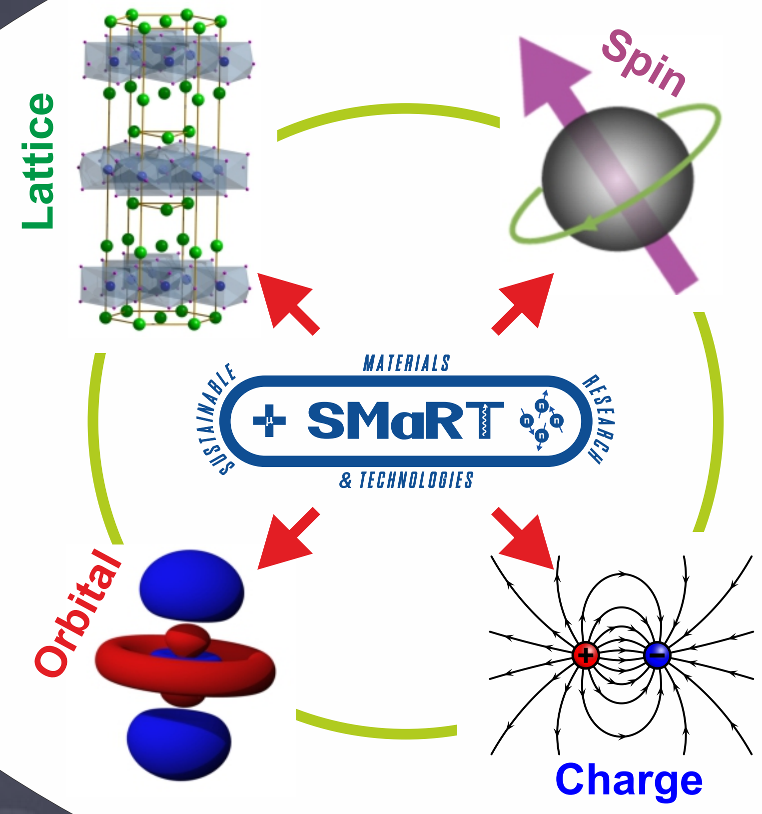
Carbon 219, 118799 (2024)

As. Prof. Rasmus Palm

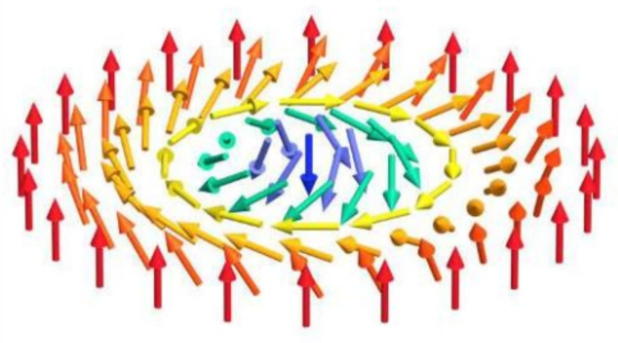


The Energy Problem

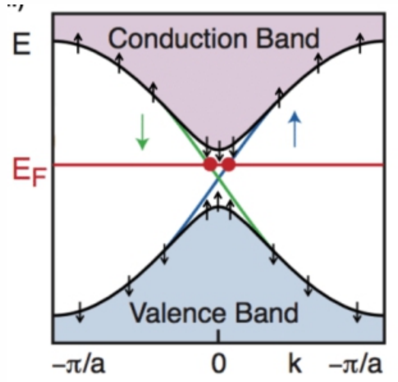
Quantum Materials

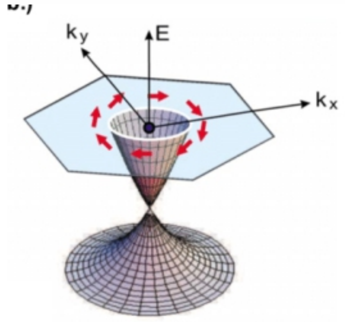


Skyrmions

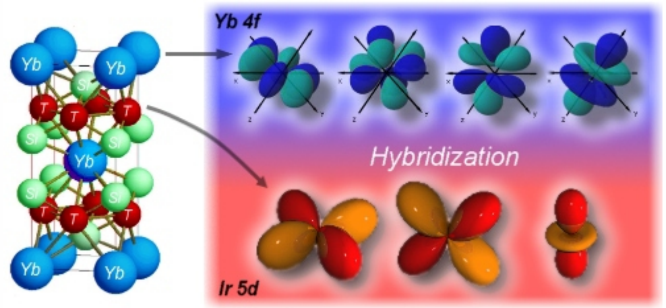


Topological Insulators / Weyl Semimetals

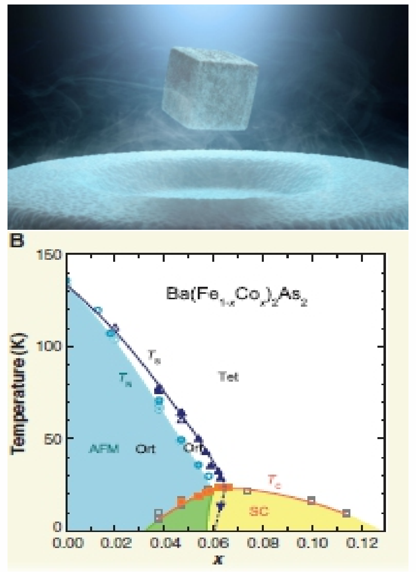




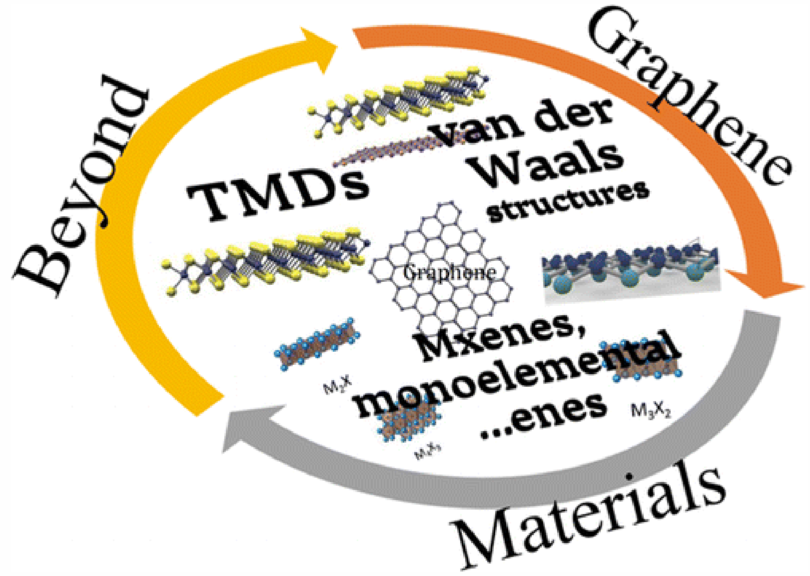
Heavy Fermions



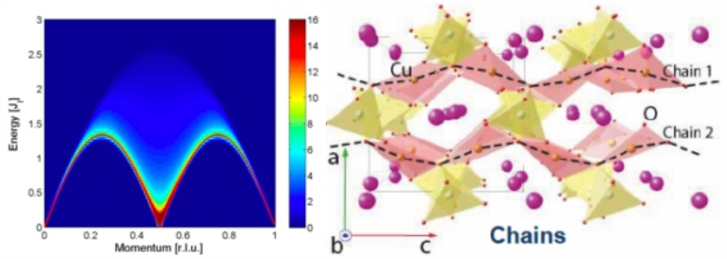
High-T Superconductors



2D (vdW) Materials

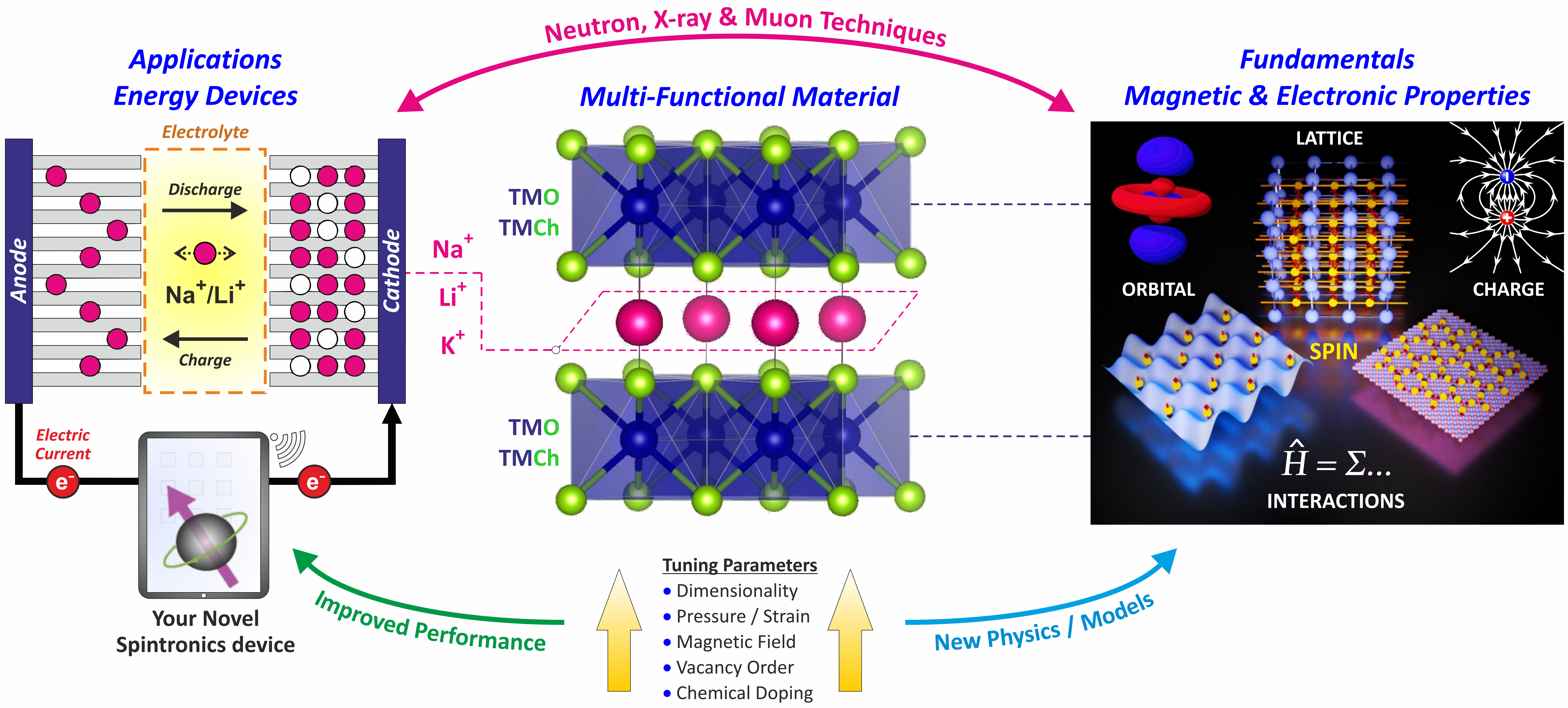


Quantum Magnets / Spin Liquids



Energy “Usage”

Multifunctional Materials



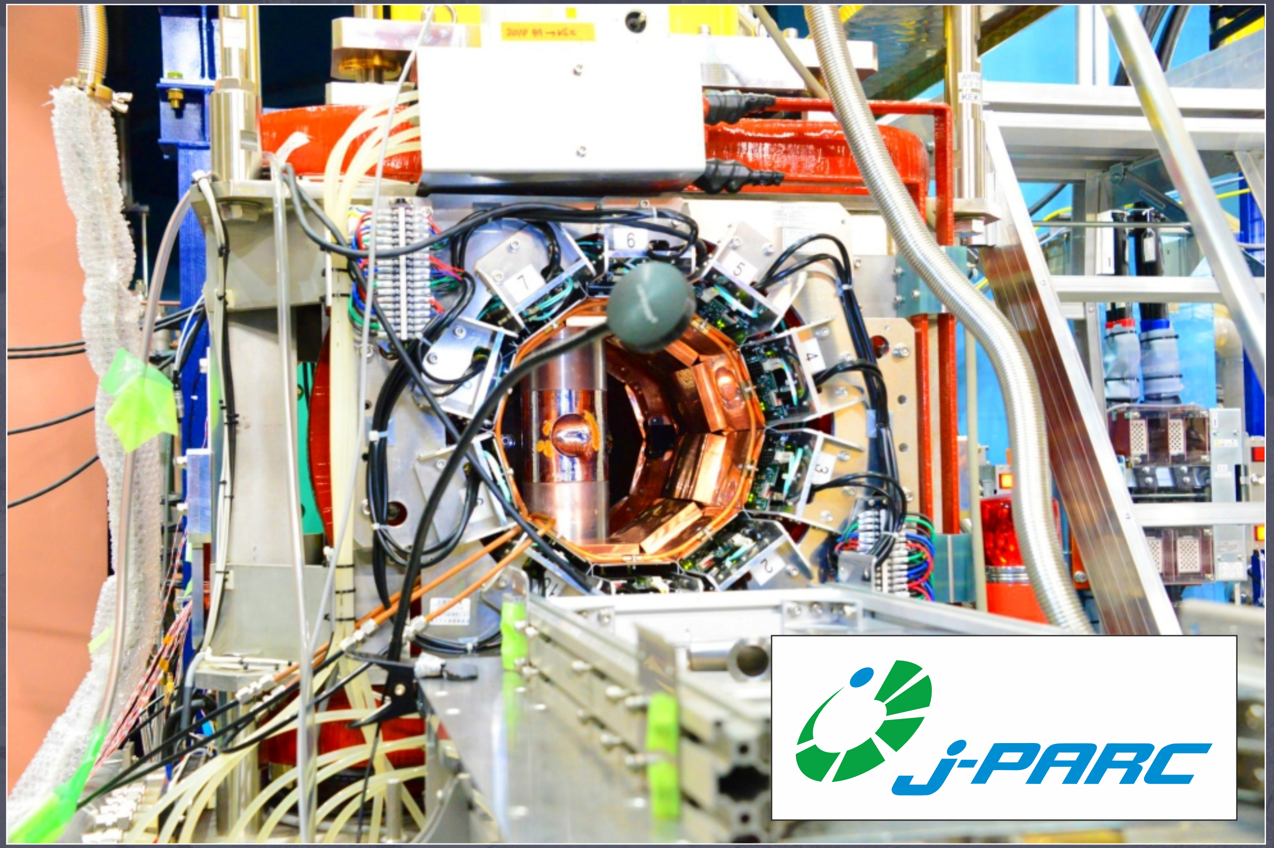
Large-scale Infrastructures

Synchrotron X-ray Sources

High-energy X-rays / FEL

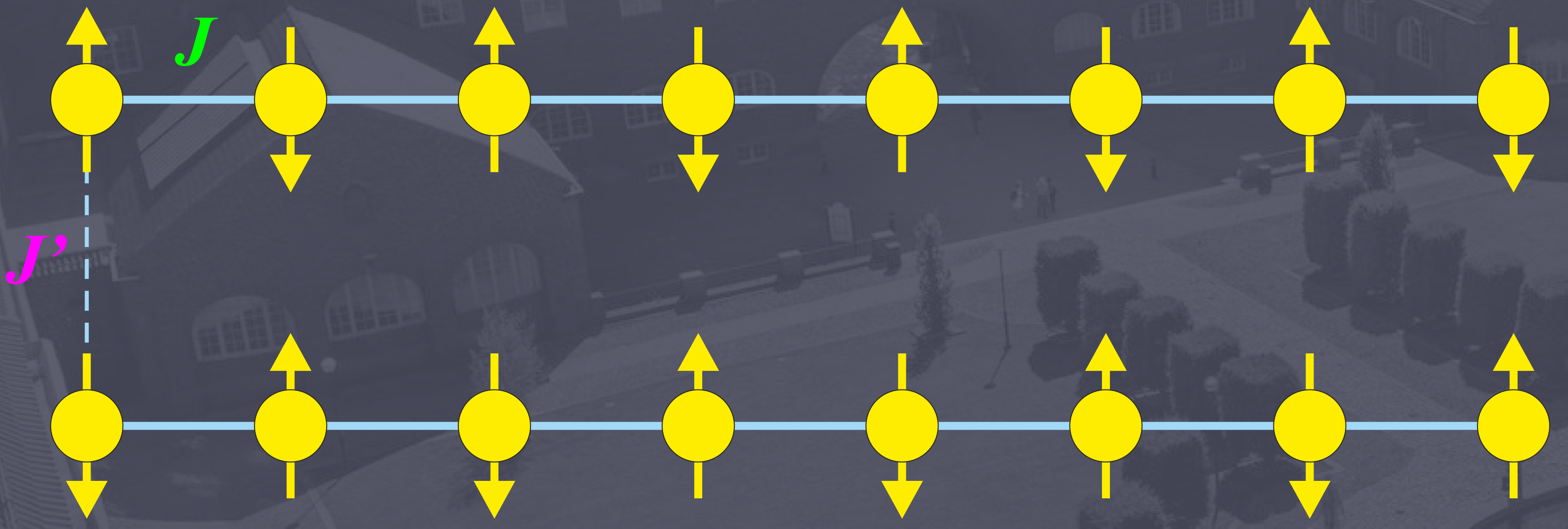
Neutron Sources

Muon Sources



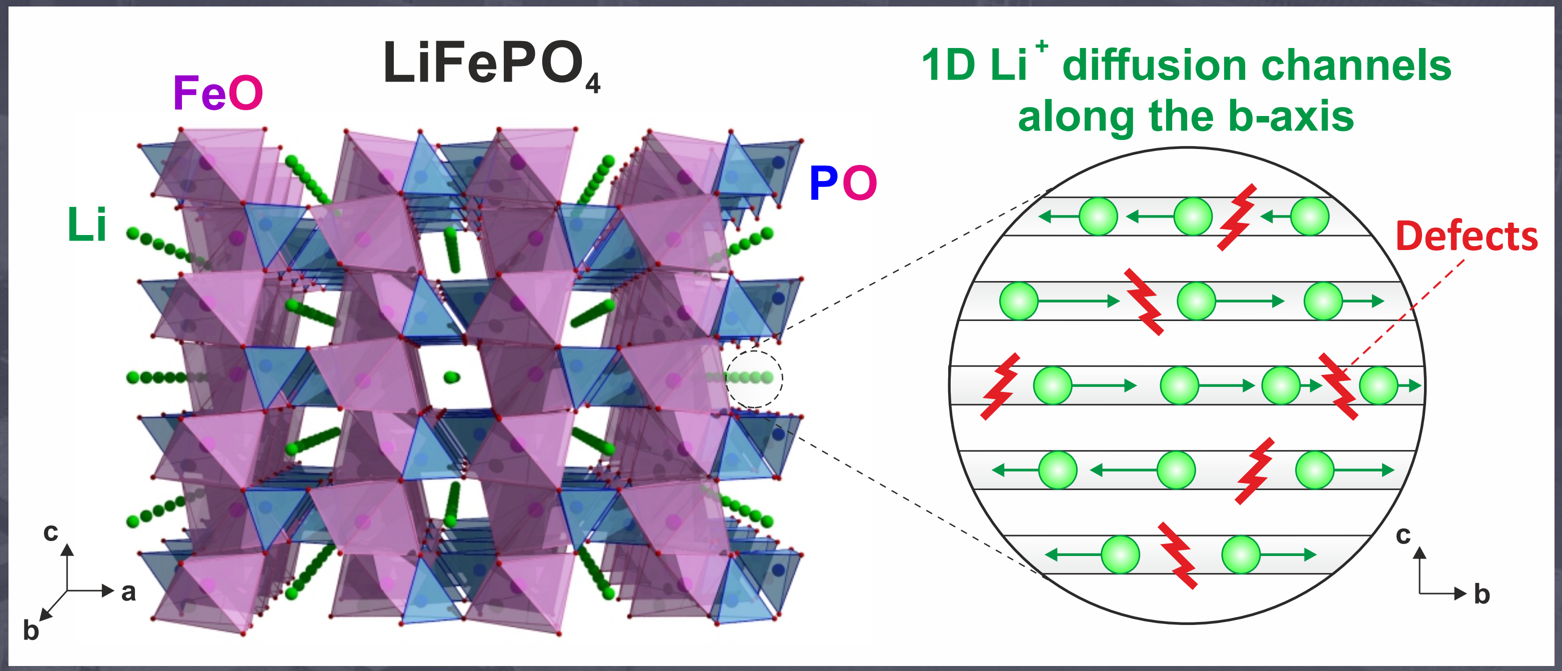
Low-D (Quasi-1D) Materials

- Ideal 1D antiferromagnet (AF) show no long-range order for T > 0 K (quantum spin fluctuations).
- However, when considering not only the strong intra-chain interactions (*J*) but also the much weaker inter-chain interactions (*J'*), long-range AF order can appear.



- The family of quasi-1D AF compounds therefore display a wide range of intriguing phenomena due to the delicate competition and/or frustration between *J* and *J'*.

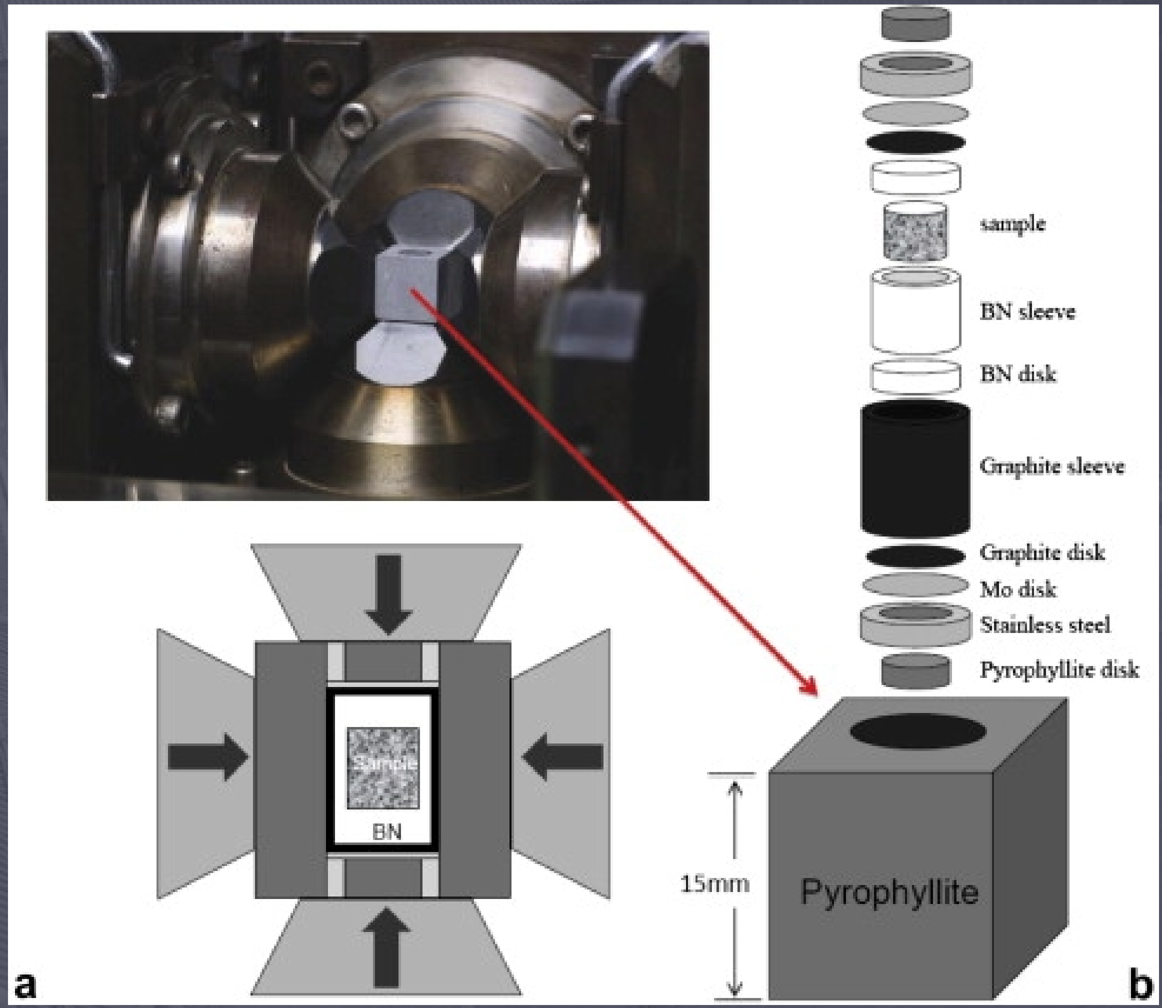
- The Phospho-olivine compound $LiFePO_4$ is a 'famous' battery cathode material (extensively studied)
- LFPO Display preferential Li-ion dynamics along the 1D diffusion channels parallel to the b-axis, which makes the Li-ion dynamics sensitive to defects in the diffusion channels.

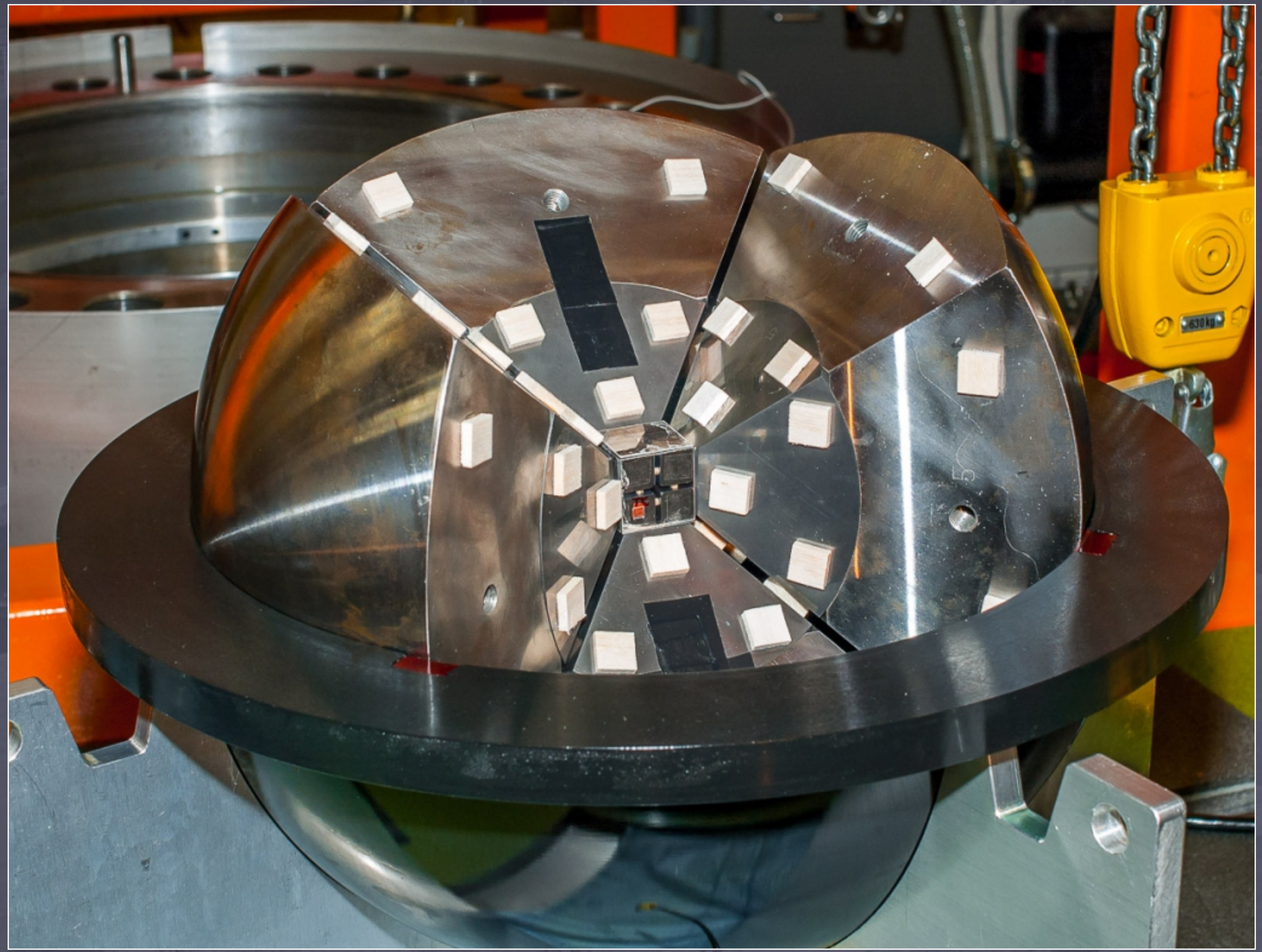


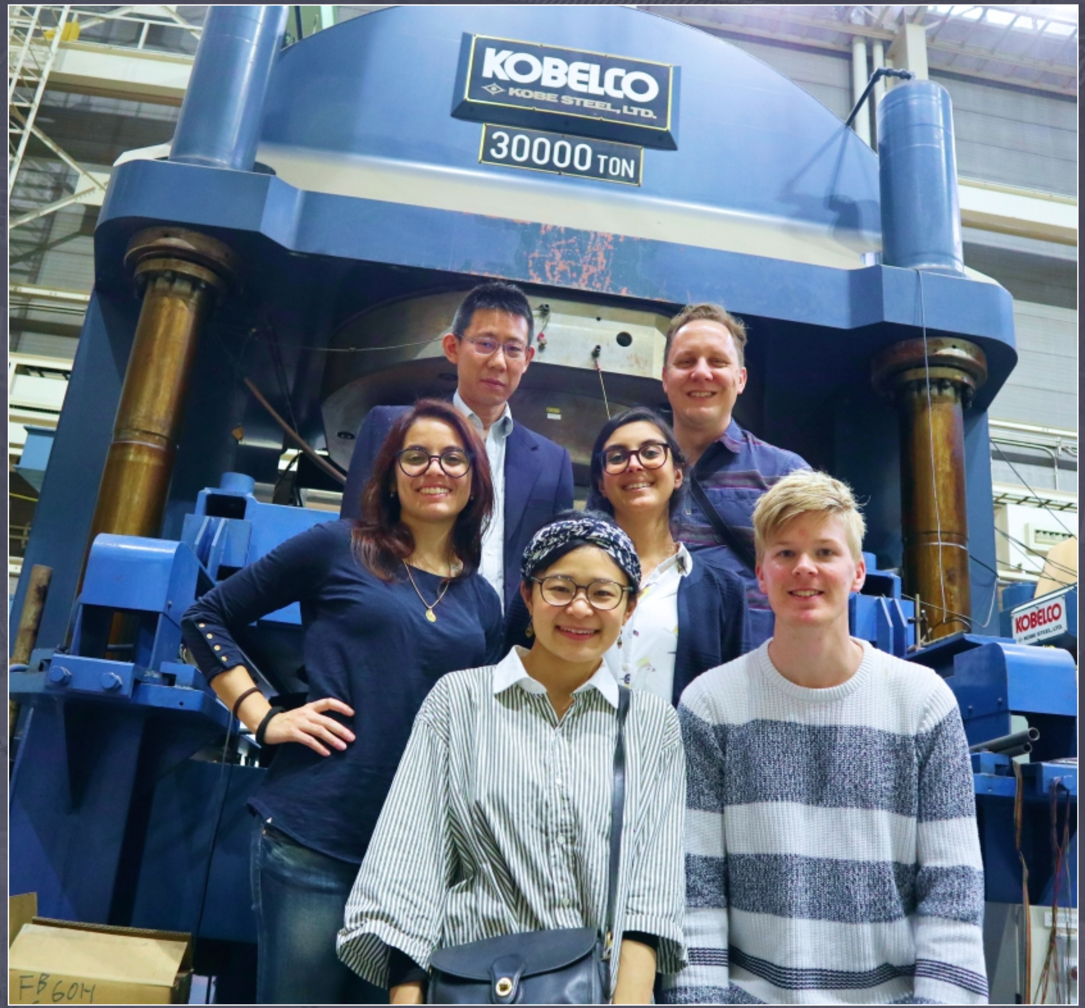
J. Phys.: Conf. Ser. 2462, 012049 (2023)
Phys. Rev. Res. 2, 033161 (2020)
ACS Appl. Mat. & Interf. 12, 14, 16243 (2020)
Sustainable Energy & Fuels 3, 508 (2019)
Phys. Rev. B 85, 054111 (2012)
Phys. Proc. 30, 190 (2012)
Phys. Proc. 30, 160 (2012)
Phys. Rev. B 84, 054430 (2011)

High-Pressure Materials Synthesis

- High-pressure synthesis allow us to stabilize structures/compounds not accessible by “normal” materials synthesis methods (c.f. diamonds).
- A small volume of starting materials are encapsulated into a very complex container that is placed inside a set of anvils consisting of 8 sintered diamond cubes inside a “split-sphere”.







- Using a 30'000 ton press and a furnace, the synthesis can be performed up to 50 GPa and 2000 K.
- Sample volume/mass of final material is usually small, m = 100 mg or less !!!

NaM_2O_4O (M = V, Mn, Ti, Cr)

- **Family of compounds synthesize by high-P techniqe, which display Q1D channels/chains along the crystallographic b-axis (can also replace/dope Na by Ca).**

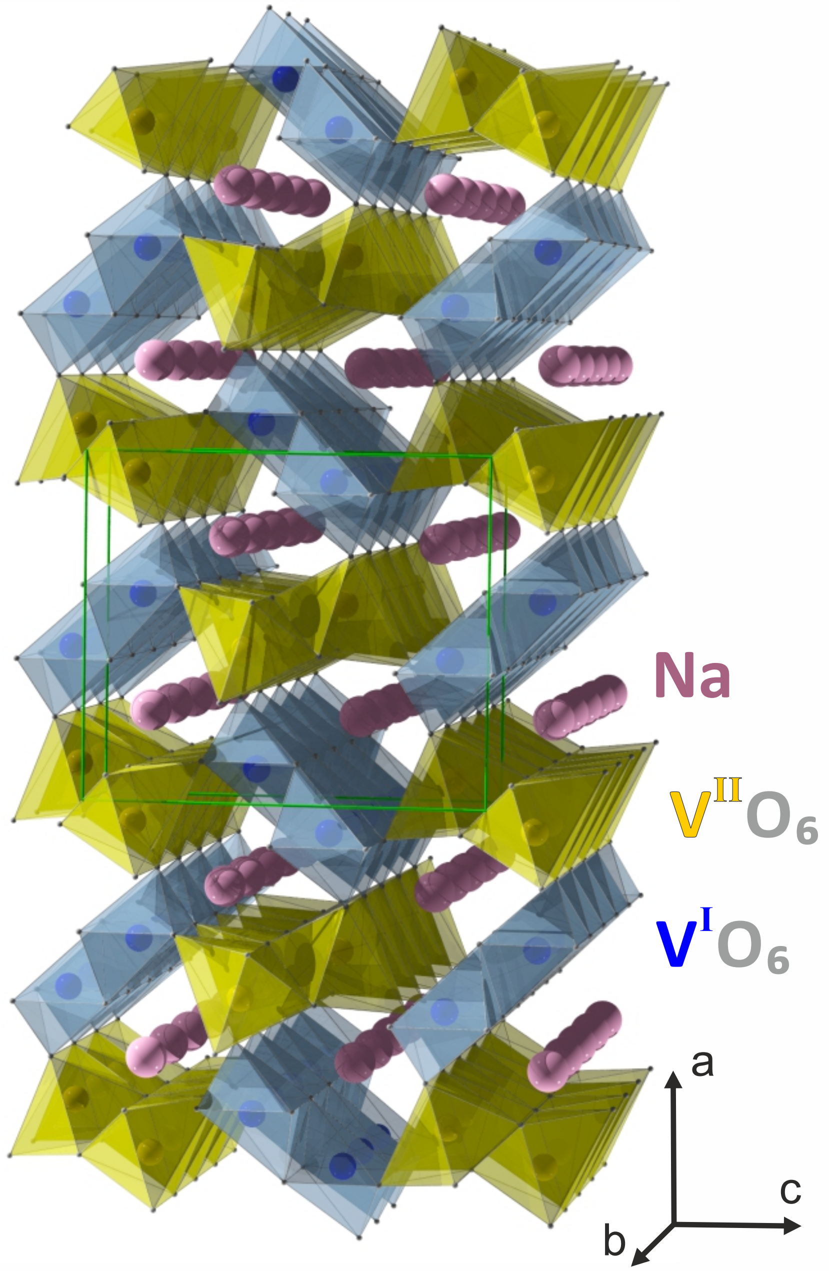
NaV_2O_4

NaV_2O_4

Orthorhombic
Pnma (62)

a = 9.1304 Å
b = 2.8844 Å
c = 10.6284 Å

$\alpha = \beta = \gamma = 90°$
V = 279.91 $Å^3$
Z = 4
M = 188.87 g/mol
ρ_{theor} = 4.482 g/cm^3

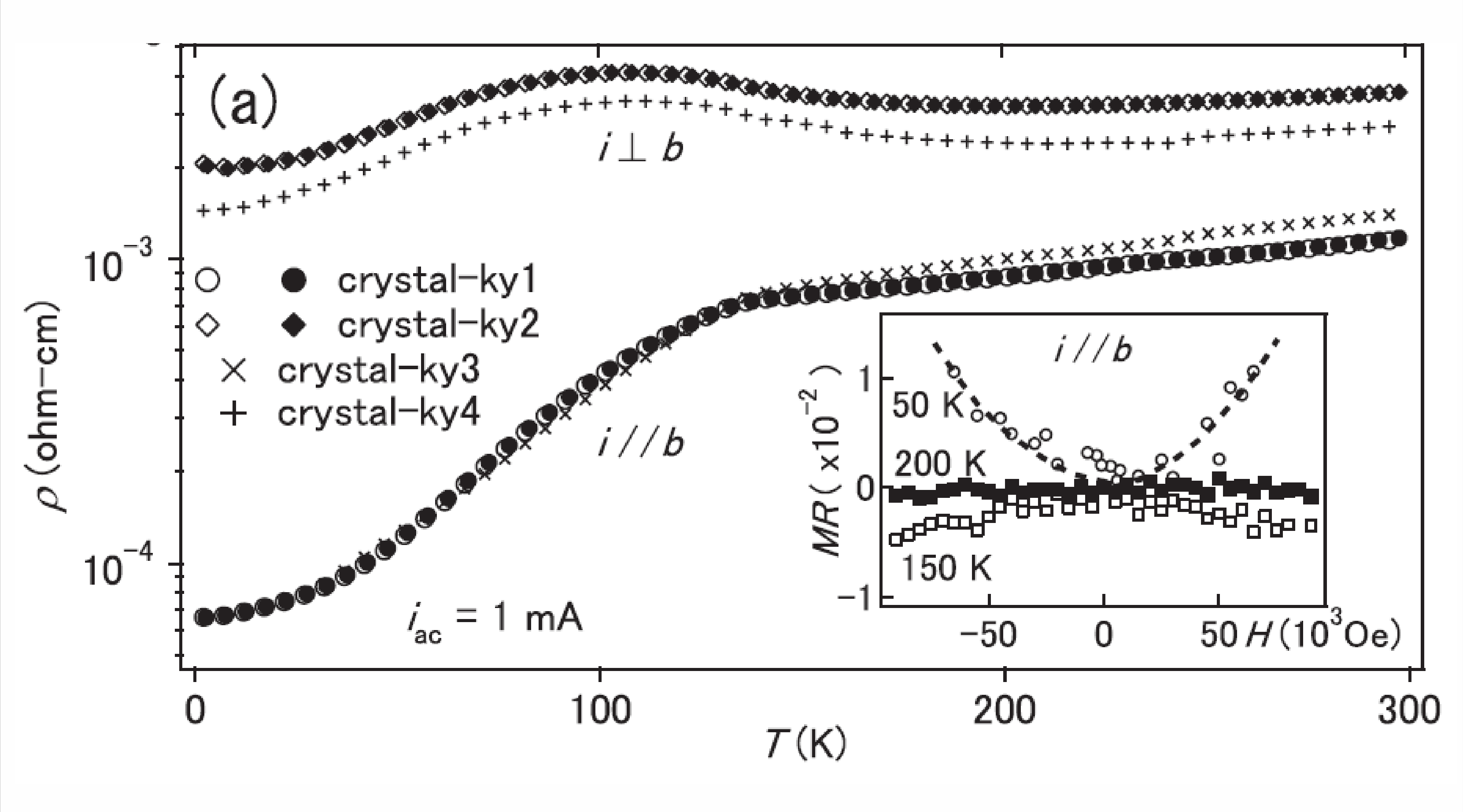


- **Belongs to the $CaFe_2O_4$-type orthorhombic structure having a *Pnma* space group**
- **Display V_2O_4 double (zig-zag) chains formed by edge-sharing VO_6 octahedra aligned along the b-axis**
- **Irregular hexagonal 1D channels are formed in which the Na-ions are located (*potentially diffuses* = Na-ion battery applications?).**
- **There are two slightly different V-sites = could display a mixed valence state: $V^{+3.5}$**

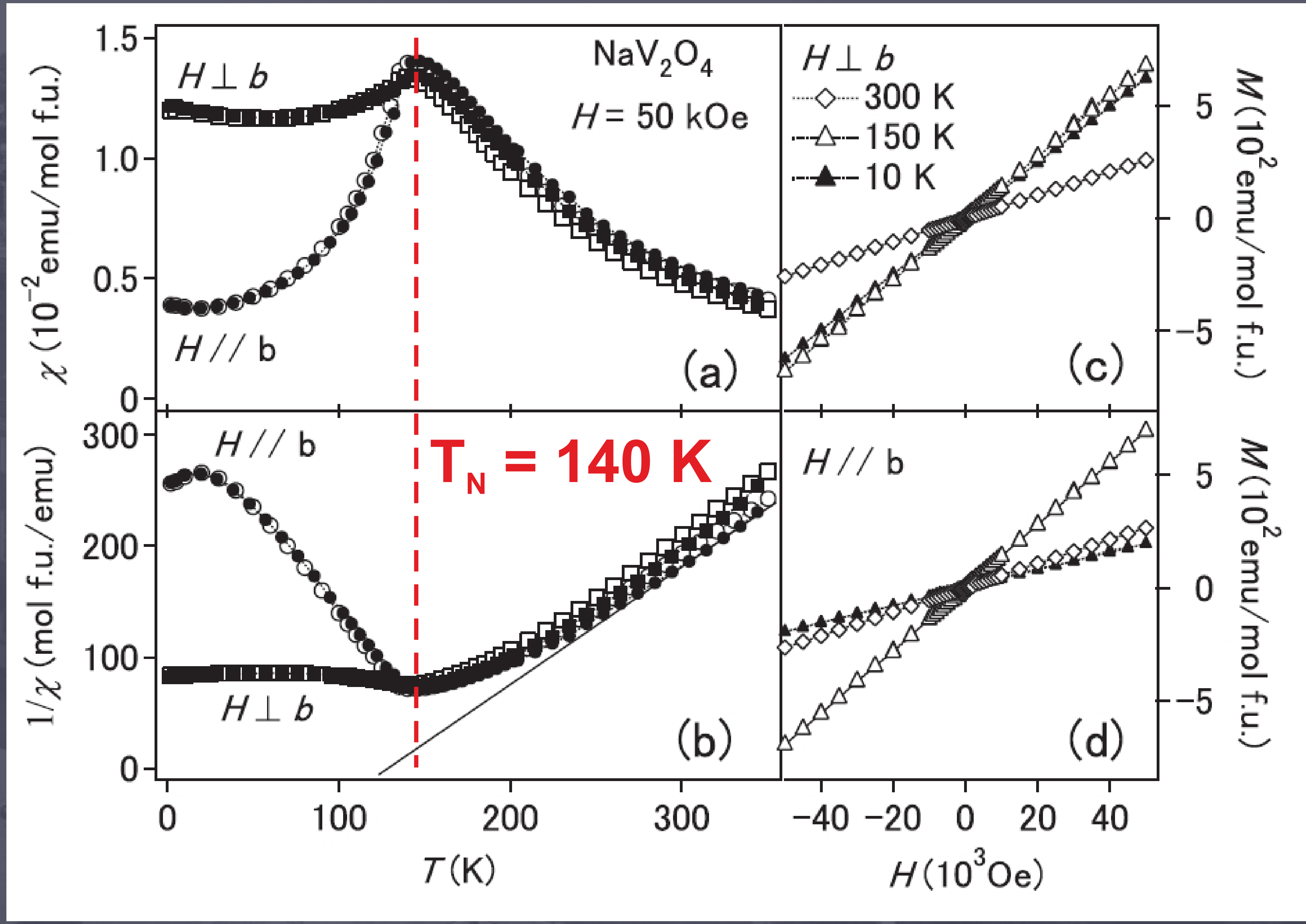
Bulk Characterizations

- Magnetic susceptibility clearly show that NaV_2O_4 enters an antiferromagnetic (AF) ordered state below T_N = 140 K.

- Magnetic anisotropy studies (single crystals) indicates: FM intra-chain ($J > 0$)
  AF inter-chain ($J' < 0$)



Physical Review Letters 99, 196601 (2007)

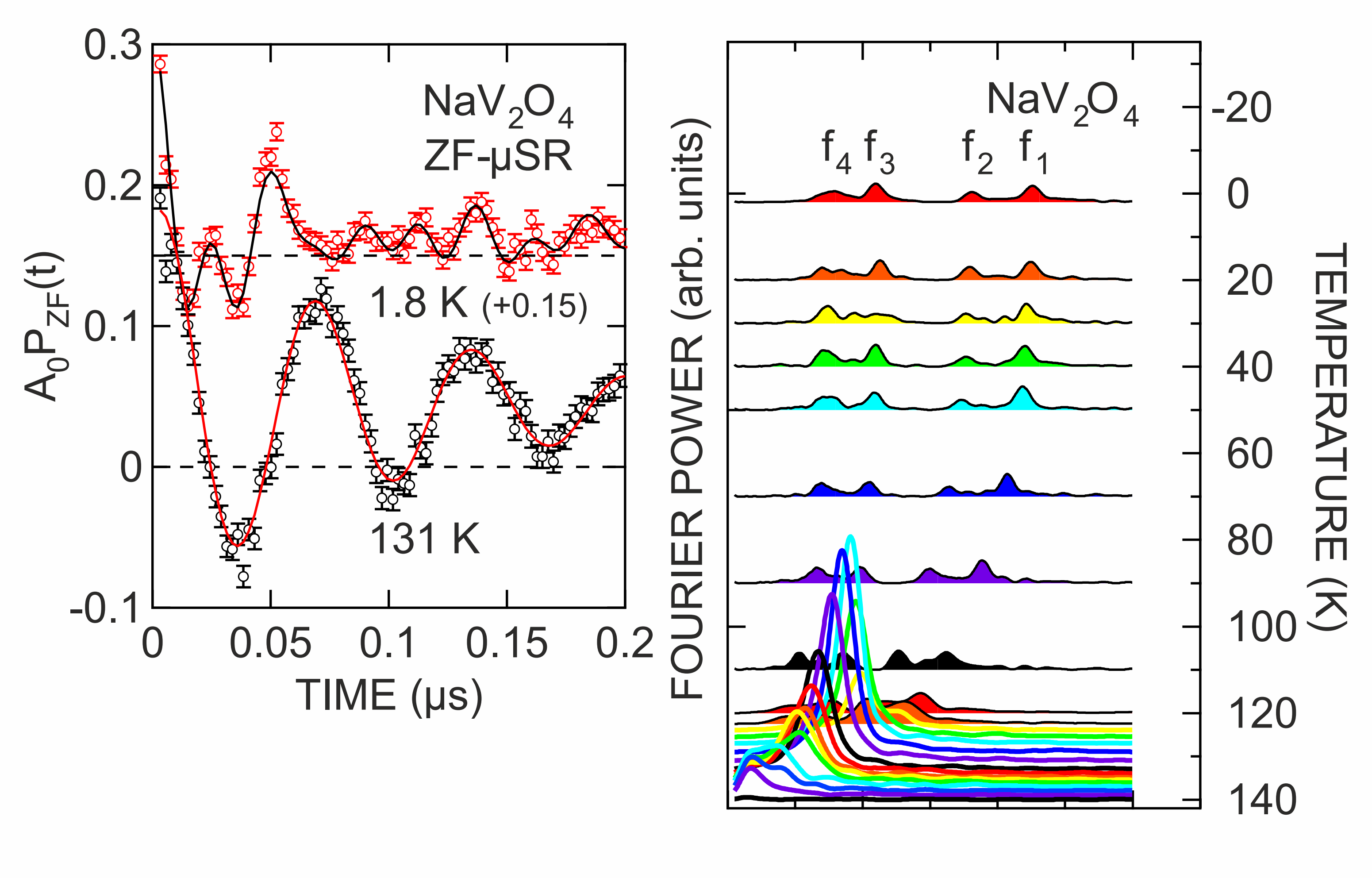


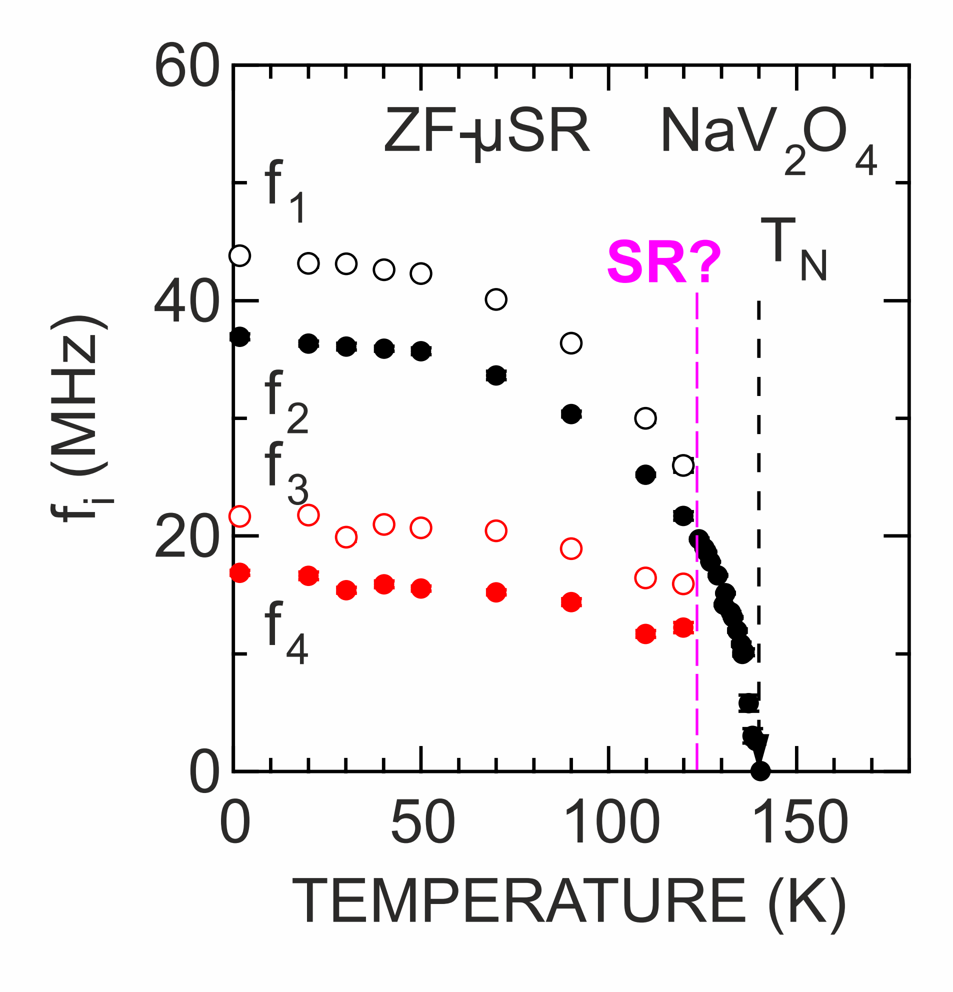
- The mixed valence of V causes this material to display metallic conductivity down to at least T = 40 mK, i.e. NaV_2O_4 is an AF metal !

- The isostructural CaV_2O_4 compound with V^{+3} is a typical AF insulator with T_N = 80 K.

NaV_2O_4: ZF μ^+SR

- Zero-field (ZF) muon measurements are extremely sensitive to small changes in the spin order.
- Our measurements for the parent NaV_2O_4 compound clearly show the appearance of long-range order (muon spin precession = oscillations) below T_N.
- Fourier transform clearly show the presence of multiple frequencies indicating either several muon stopping sites and/or a complex magnetic structure.





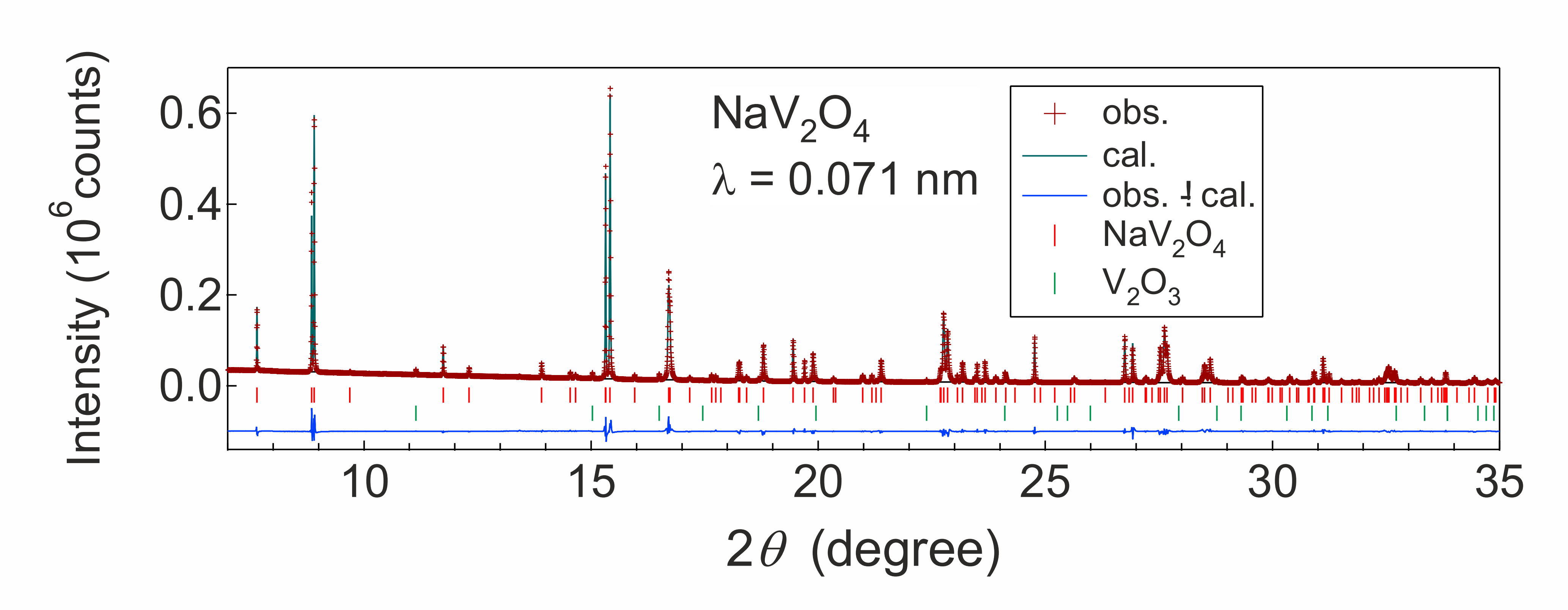
Physical Review B 78, 224406 (2008)

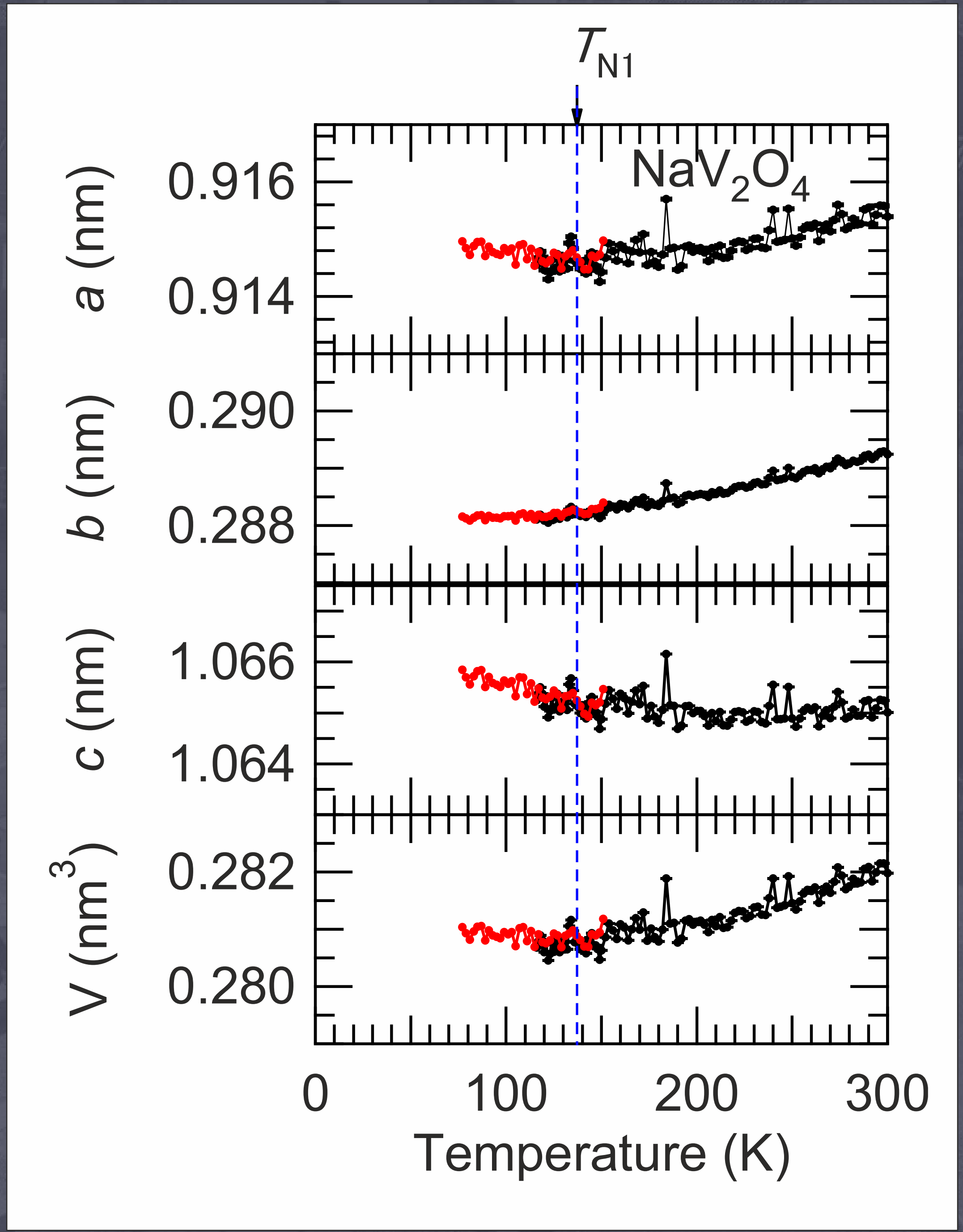
- Indications for spin re-orientations (SR) below T_N (number of frequencies are reduced).
- However, this could also be a subtle structural transition that changes the muon sites !!!
- **Other Techniques Needed**

Synchrotron X-ray Powder Diffraction

- We performed synchrotron measurements at PSI / SLS / MS-beamline in order to search for subtle structural changes around and below T_N.

- We find <u>no clear evidence</u> of such structural transitions and the reduction in muon frequencies is most likely related to changes within a complex spin structure.

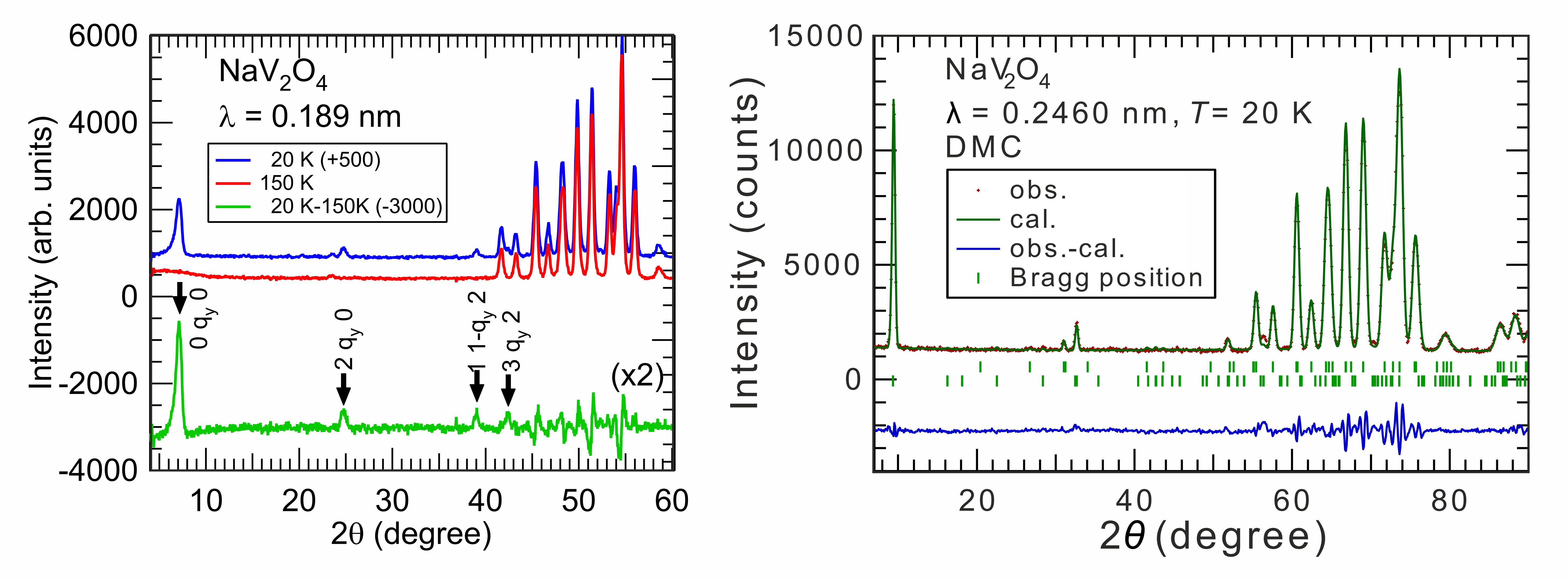




Physical Review B, 81, 100410(R) (2010)

Neutron Powder Diffraction

- We performed neutron powder diffraction at PSI / SINQ / HRPT & DMC (thermal & cold) in order to gain further information on the spin structure and magnetic order parameter.
- A series of AF peaks clearly appears below T_N and we are able to find a good fit to the data where magnetic peaks are indexed by an incommensurate propagation vector **k = [0, 0.191, 0]** i.e. along the b-axis = chain direction !

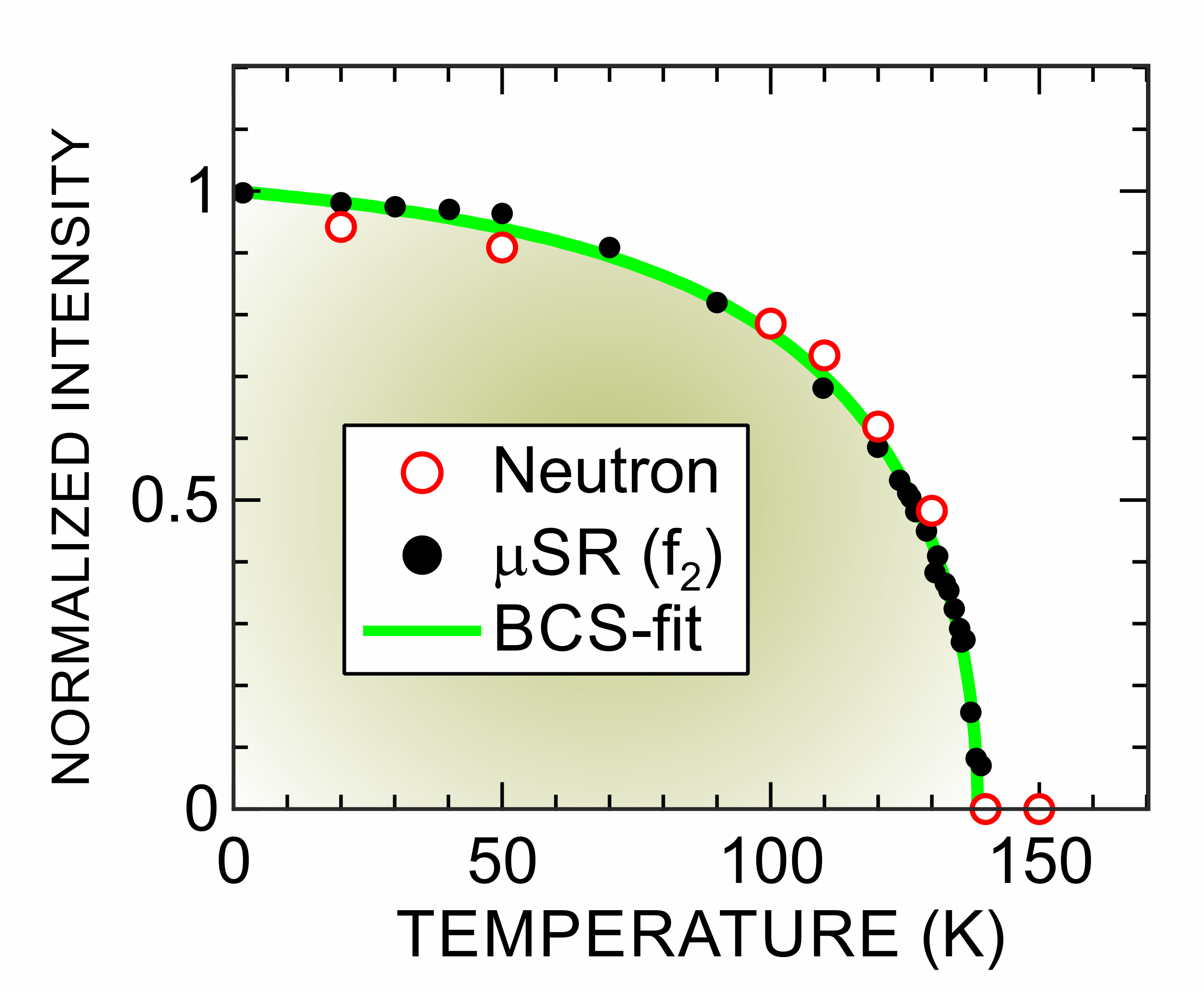


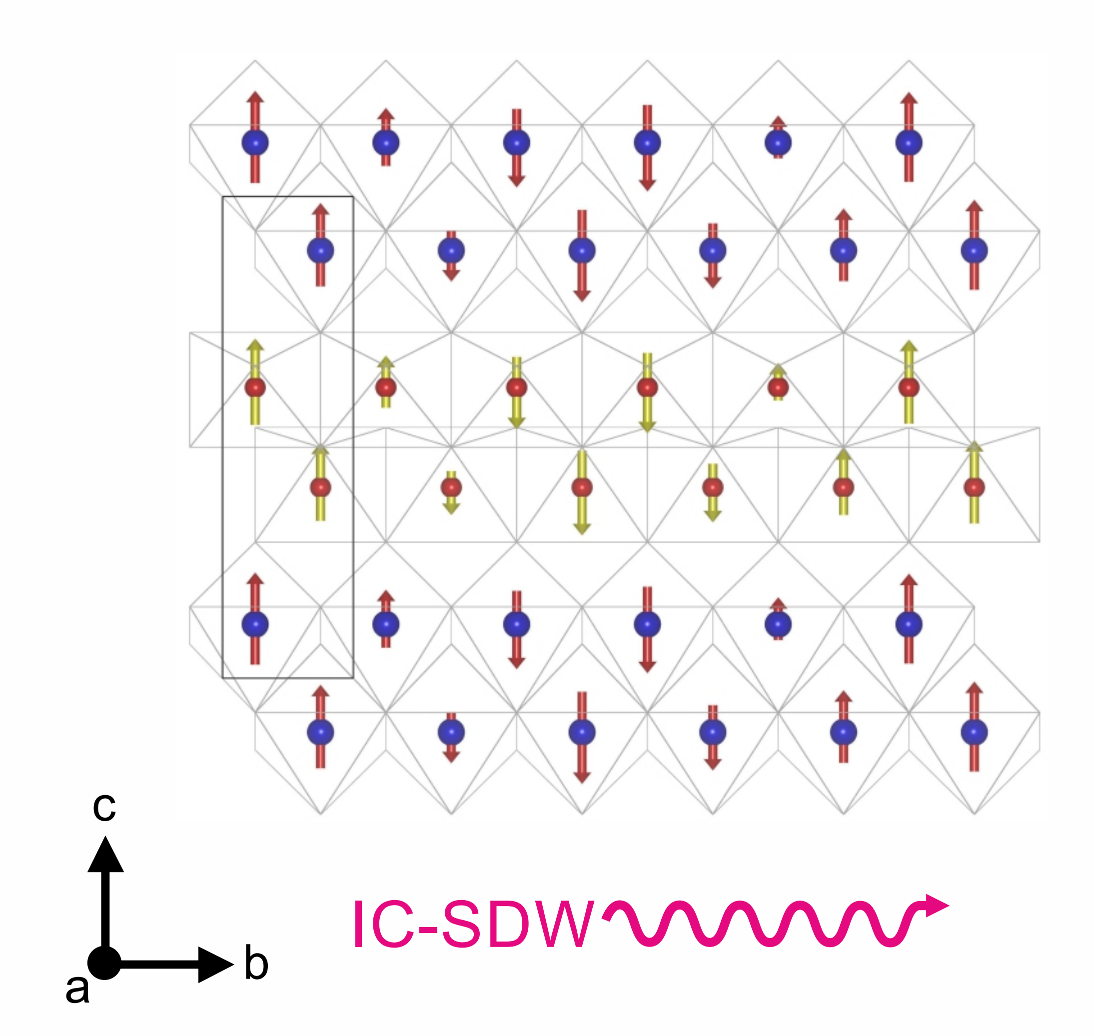
Physical Review B, 81, 100410(R) (2010)

Magnetic Order Parameter & Spin Structure

- **The magnetic order parameter obtained from temperature dependence of the neutron Bragg peak intensities clearly matches our previous results from muon spin rotation/relaxation.**
- **Order parameter is well fitted to a BCS typ equation, which is reasonable for a spin density wave (SDW) scenario.**
- **This is in perfect agreement to our NPD fits indicating an incommensurate (IC-) SDW along the b-axis, k = [0, 0.191, 0]**

Physical Review B, 81, 100410(R) (2010)





- **Note, this means:**

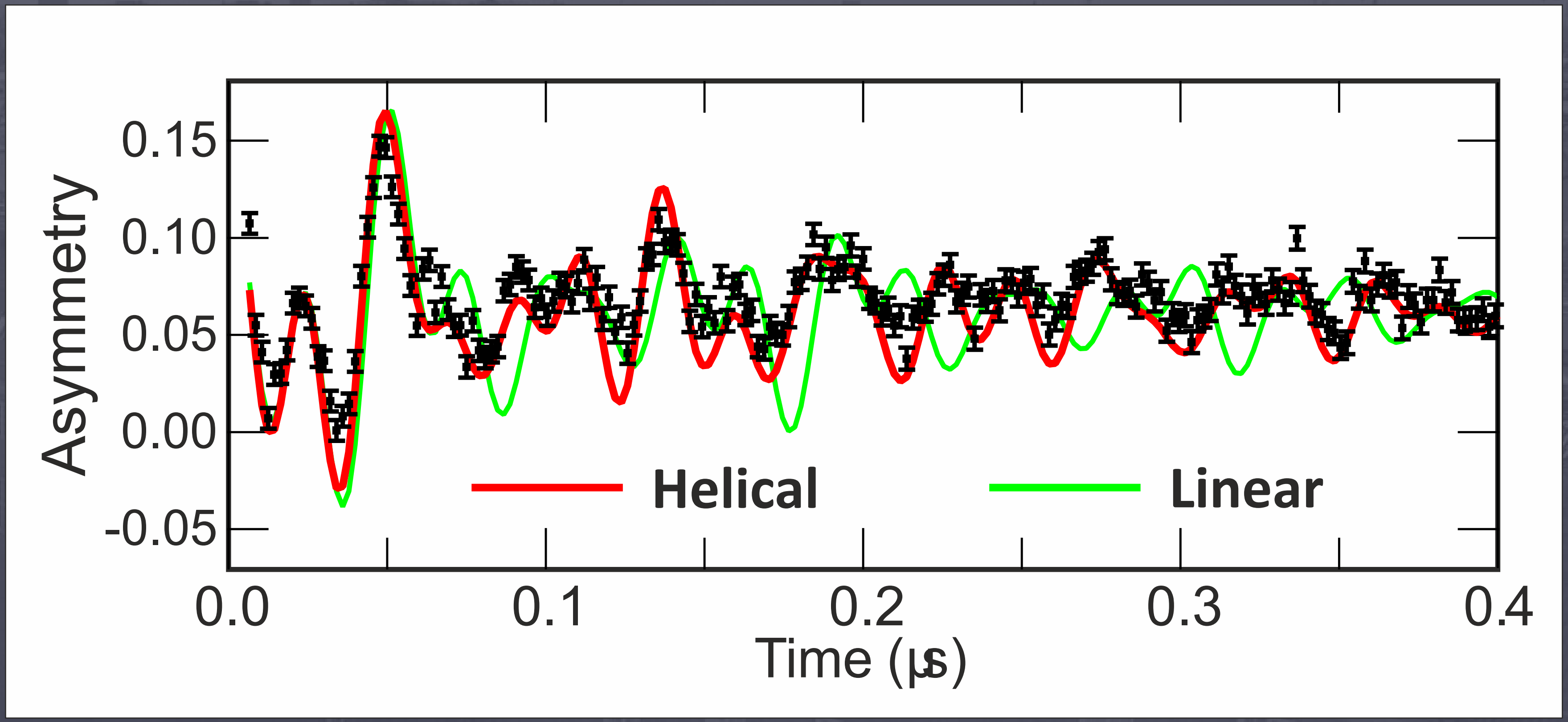
Intra-chain (J) AF
Inter-chain (J') FM

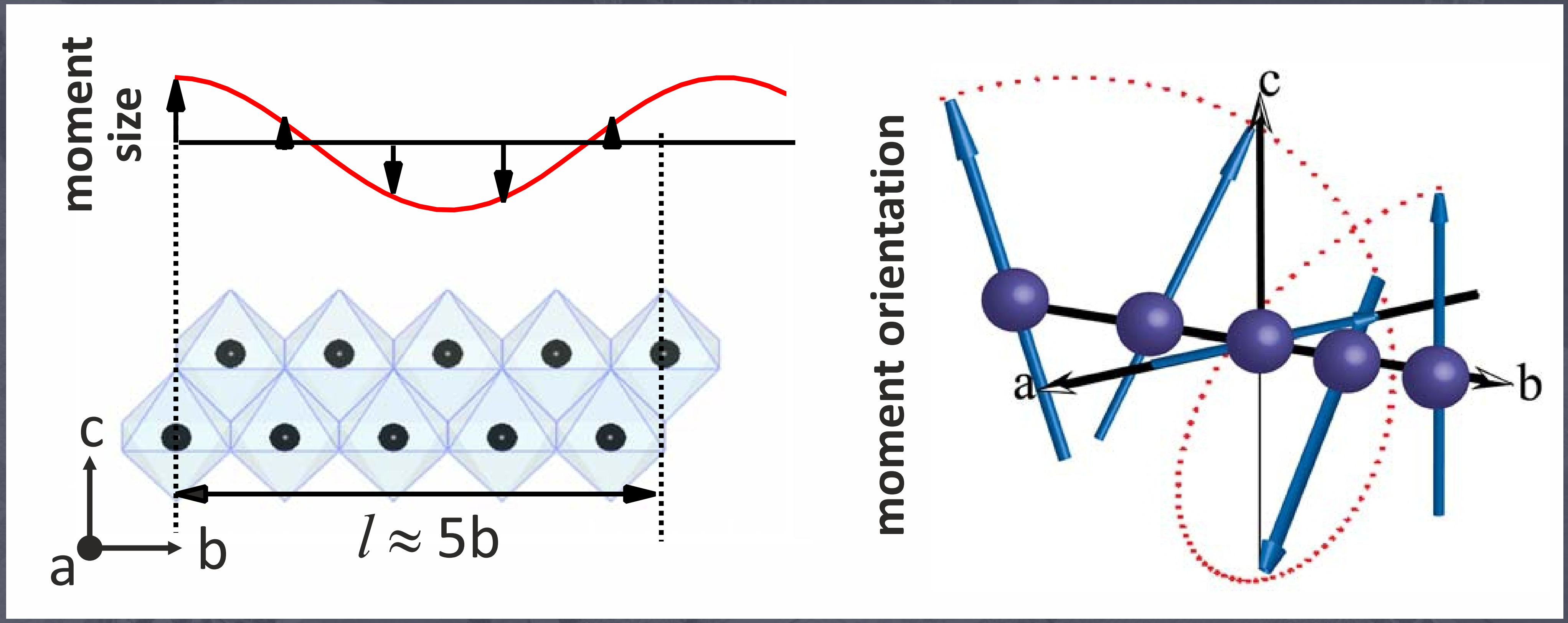
Opposite to what was previously indicated by bulk magnetic measurements !!!

$\mu^{+}SR$ - Revisited

Physical Review B 82, 094410 (2010)

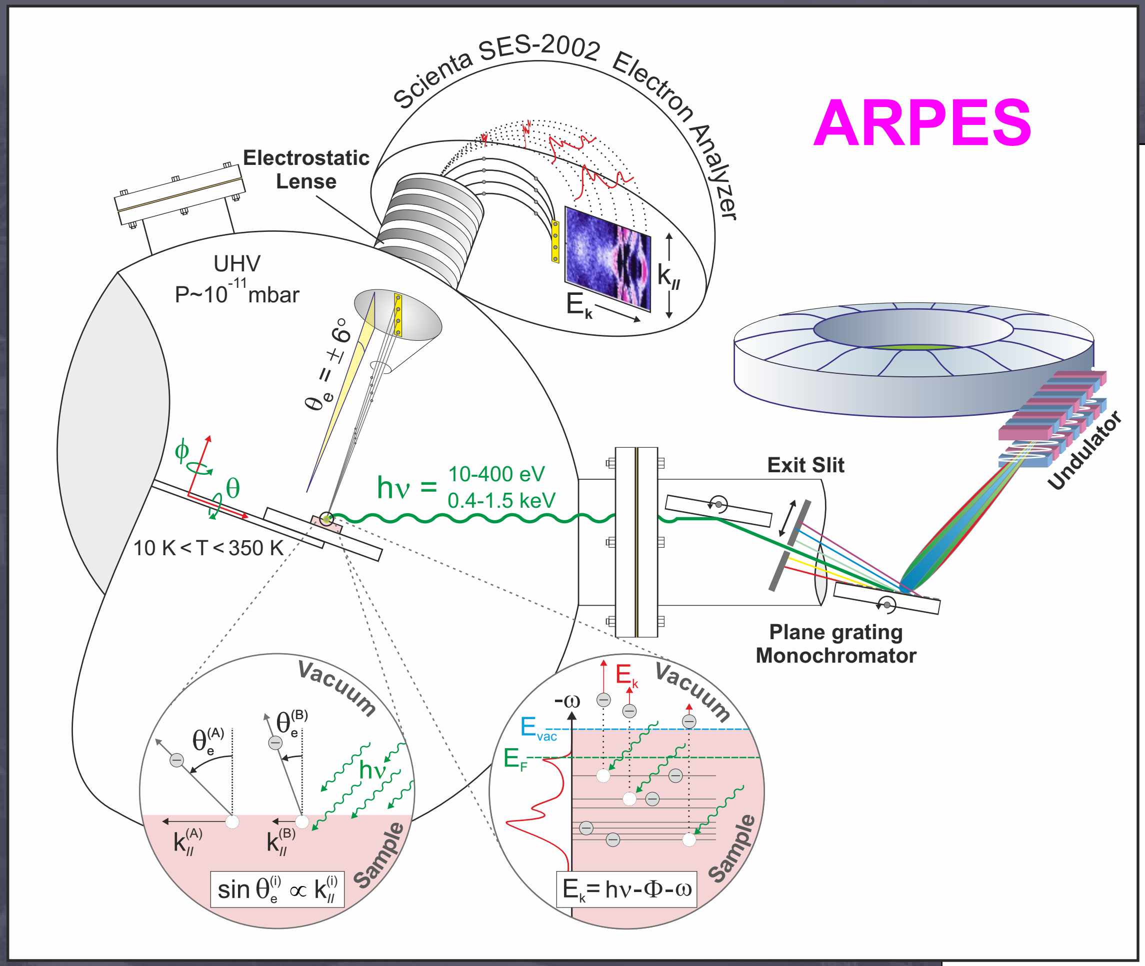
- With the knowledge concerning spin structure from NPD we can now go back to our muon data.
- Using XRD data + electrostatic potential calculations we obtain the muon stopping sites inside the lattice.
- Applying the spin structure and ratio between the different oscillation frequencies allow us to check for subtle details in the spin structure.
- We find that the simple linear IC-SDW model does not fully fit our muon data.
- We instead find that a helical IC-SDW (with same propagation vector) is more probable.

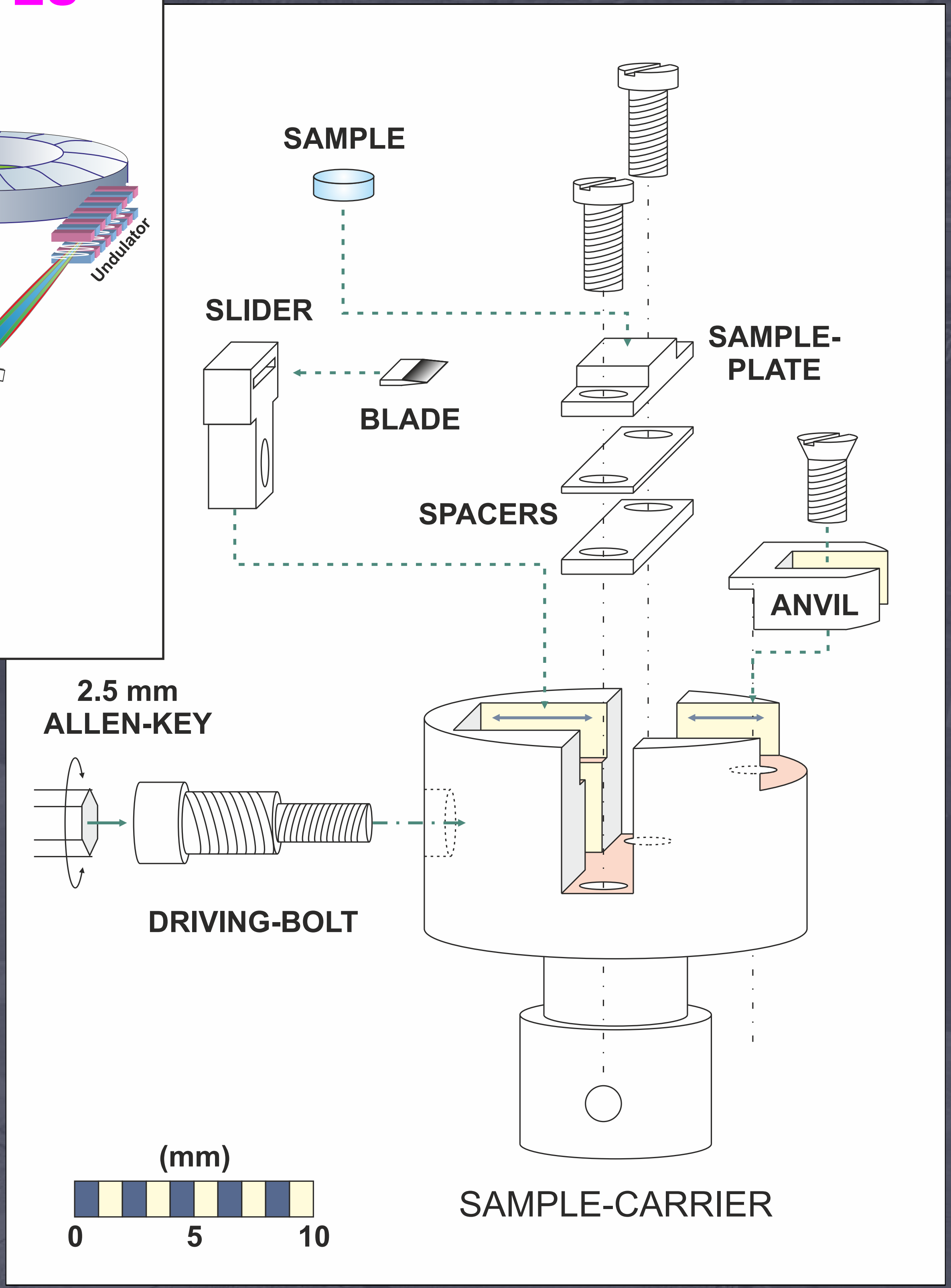




Electronic Band Structure - ARPES

- We used synchrotron ARPES to study of the electronic band structure of NaV_2O_4 single crystals.
- Crystals are tiny (500 μm) that needs to be cleaved inside UHV chamber for fresh surface (ARPES is an extremely surface sensitive technique, 5 Å !!!)
- For this purpose we used a specially designed *in situ* sample cleaver.
- ARPES data was acquired using 100 eV photons with circular polarization. T = 10 K and $p = 10^{-11}$ mbar (UHV).
- Data was reproduced using 3 different single crystals.

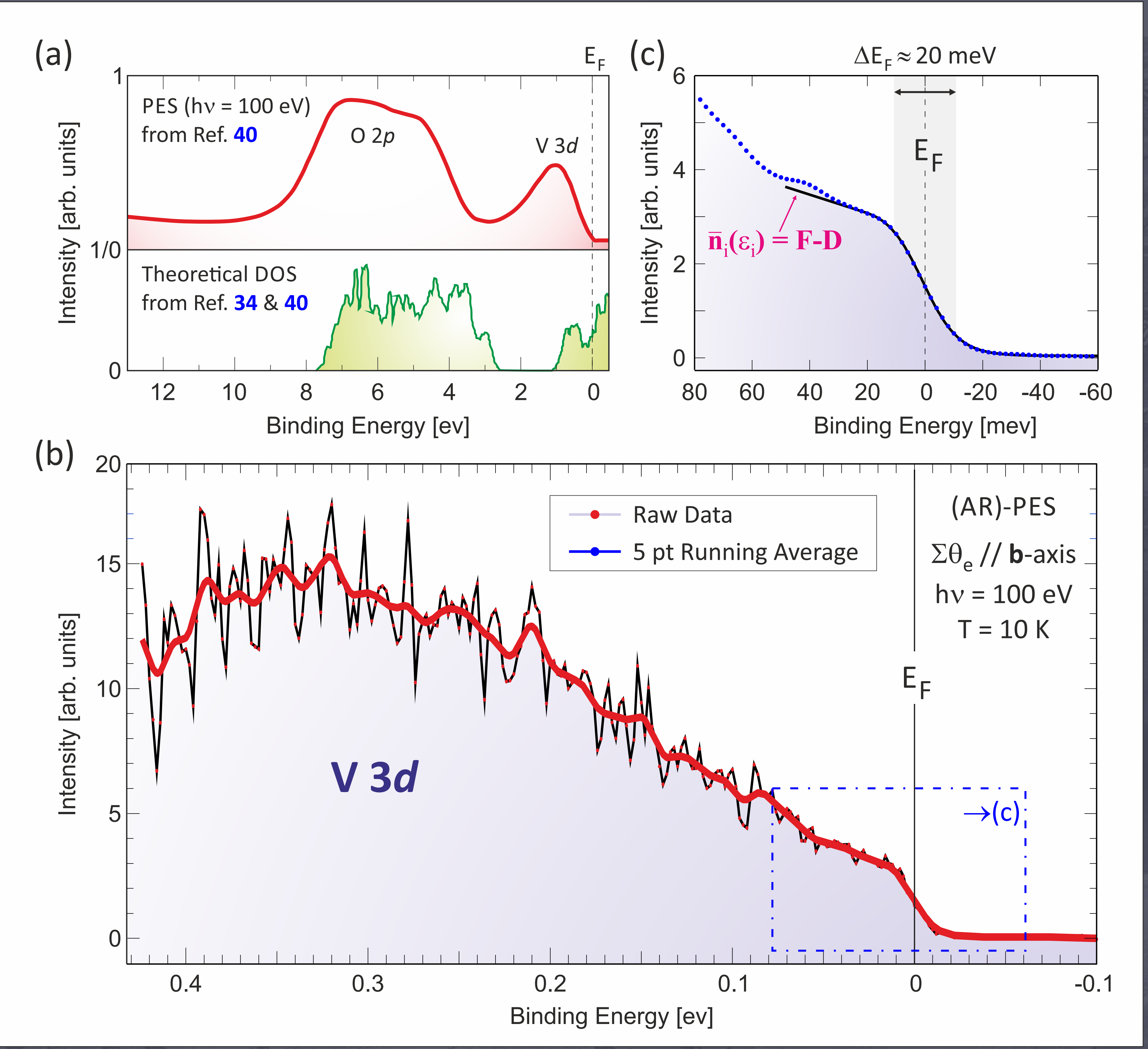




Månsson, Rev. Sci. Instr. 78, 076103 (2007)

Initial PES data

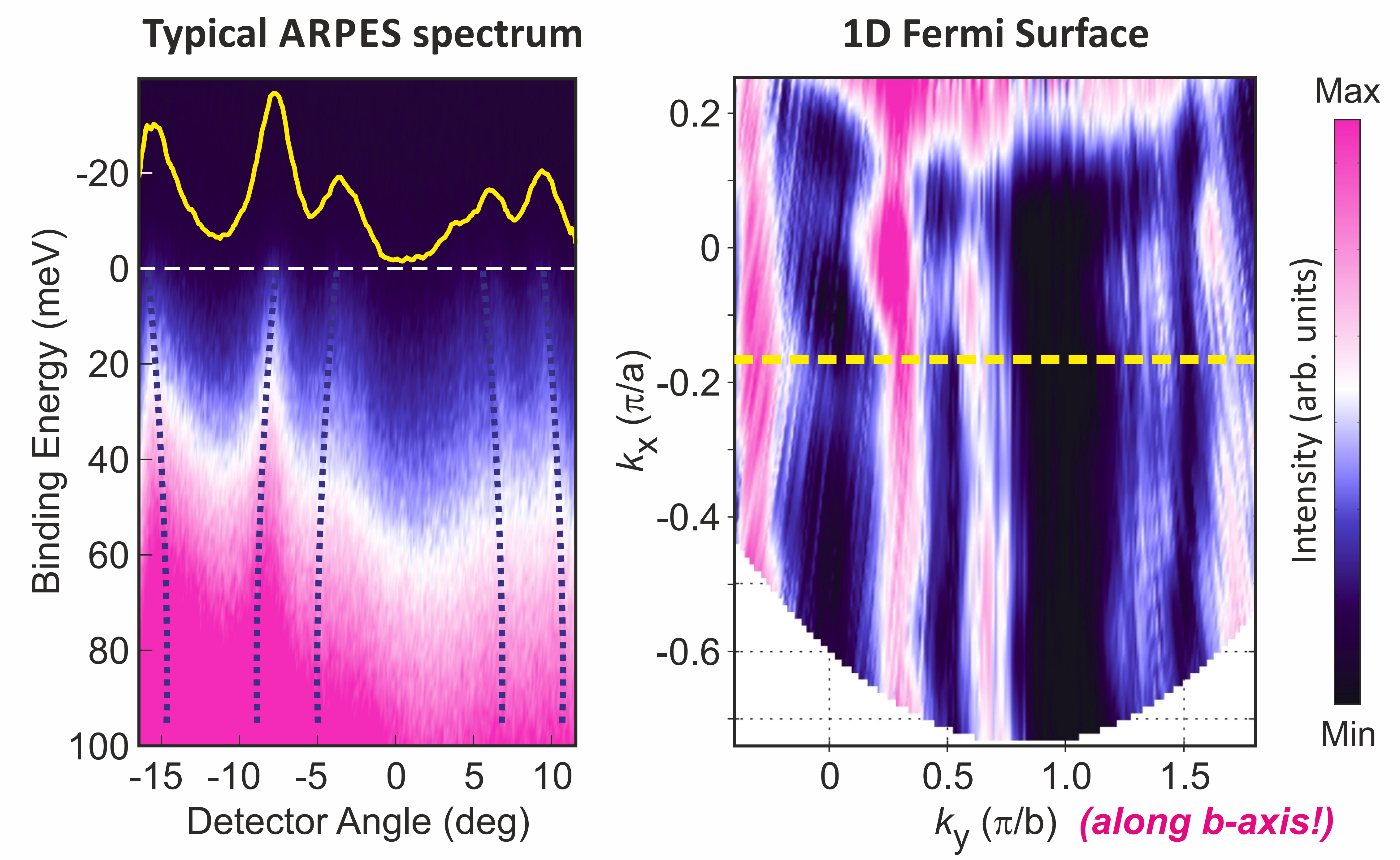
- **Angle-integrated PES data clearly show broad features corresponding to the O-2*p* and V-3*d* bands.**
- **This is coherent with what is expected from theoretical DOS calculations.**
- **Further, it is clear that the sample is metallic at 10 K (as expected) since we have a sharp step function at the Fermi level (E_F)**



Journal of Electron Spectroscopy and Related Phenomena 224, 79 (2018)

ARPES Data

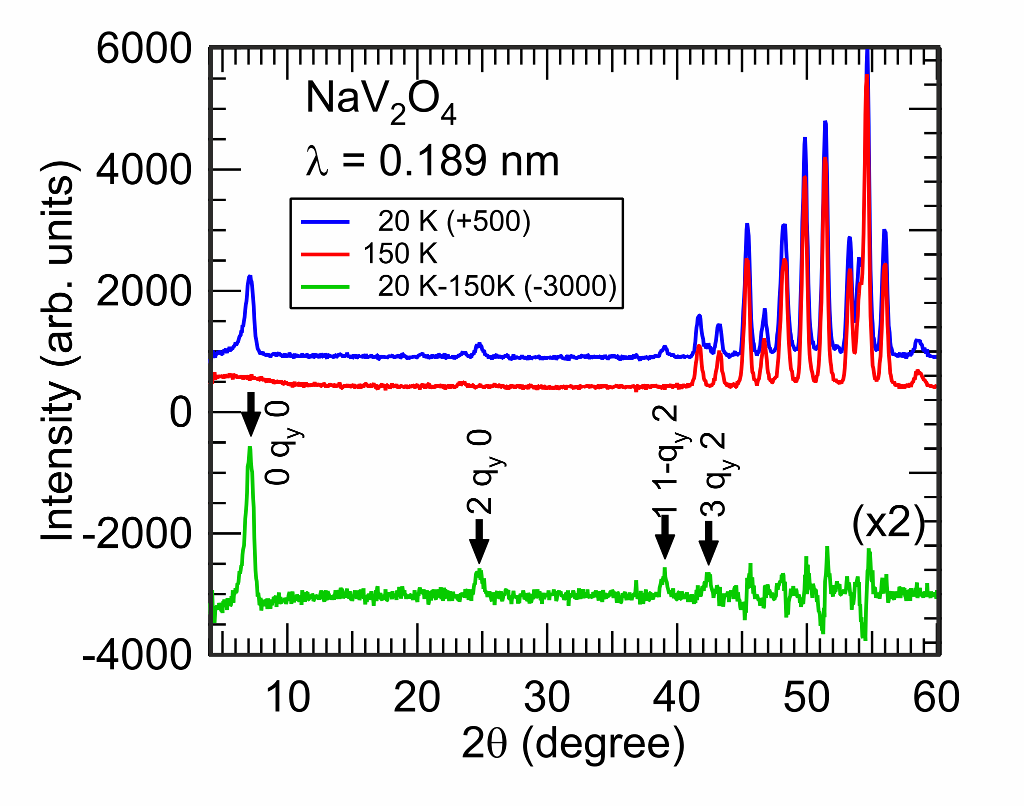
- We also recorder the very first ARPES data from NaV_2O_4, showing clear dispersing electronic bands crossing the Fermi level that are visble both in 2D map and MDC.
- By performing several measurements for different crystal orientations we were able to map out the Fermi surface.
- As expected from the crystal structure, the Fermi surface is highly 1D in its nature, indicating strong nesting (SDW!)



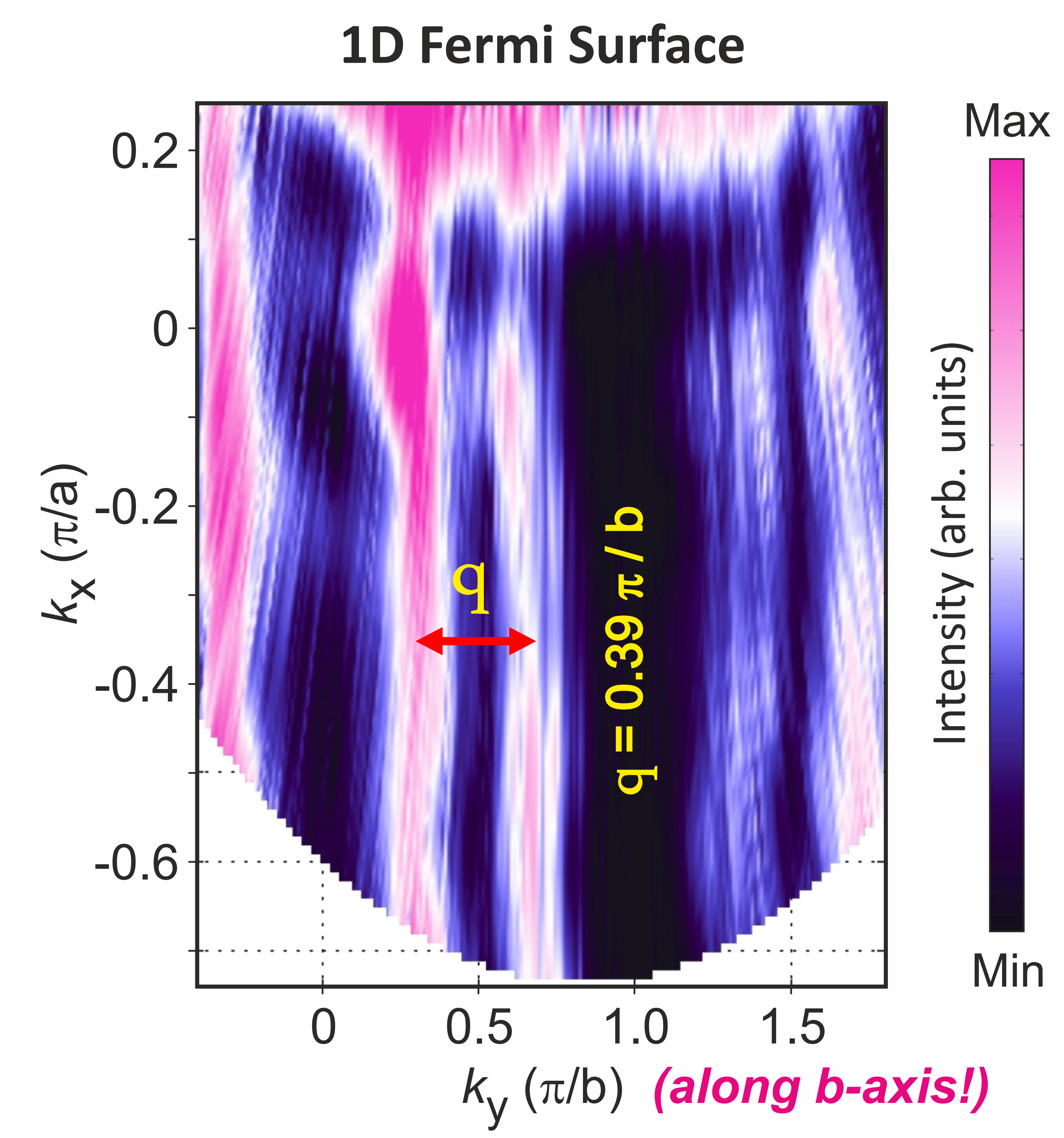
Y. Sassa, M. Månsson, *et al.*, Publication in Progress (2025)

Nesting Vector

- The nesting vector can be extracted from the Fermi surface as **q = [0 0.39 0]** in units of **π/b**.
- Translated to propagation vector this equals **k = [0 0.195 0]**, which is almost exactly the same as obtained from NPD



Physical Review B, 81, 100410(R) (2010)

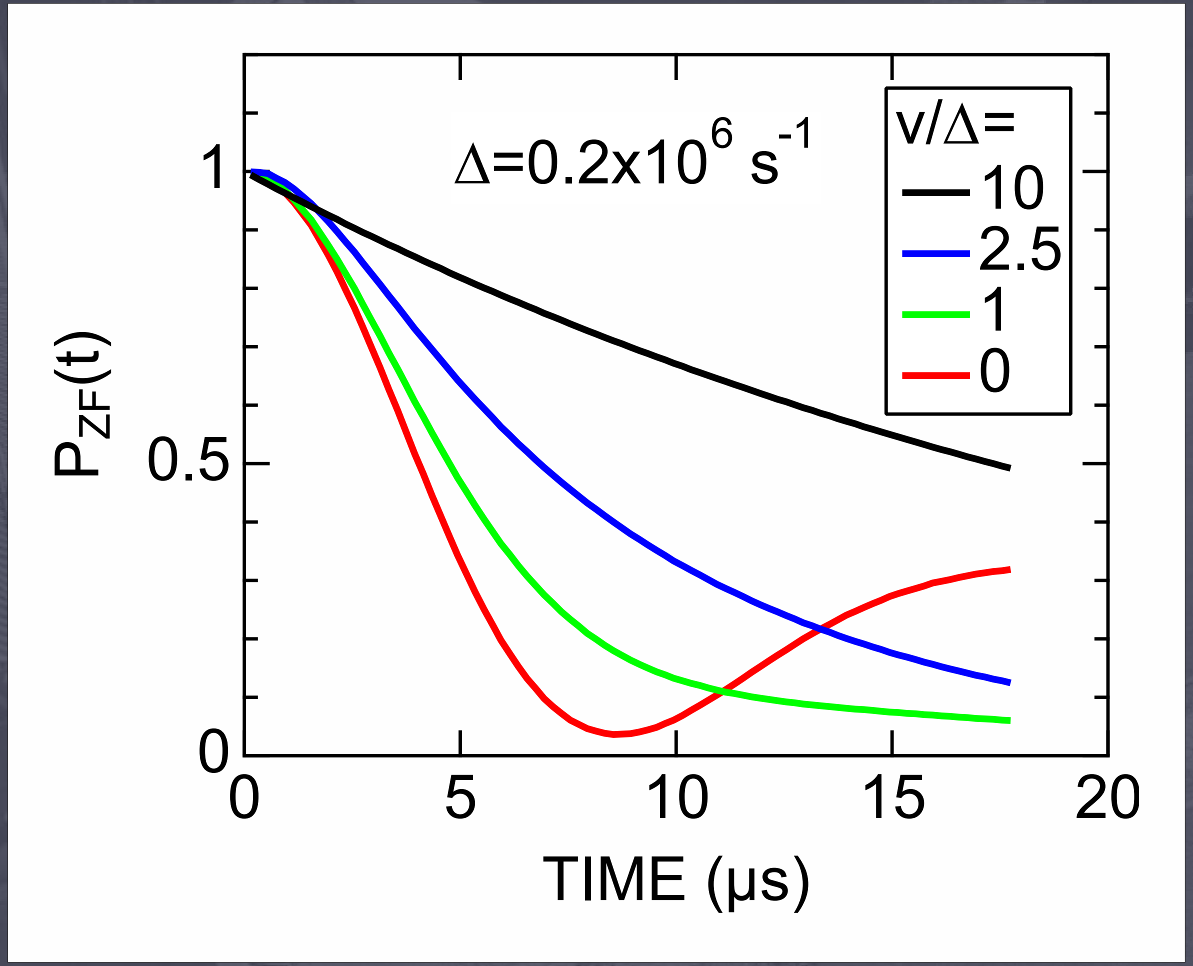


Y. Sassa, M. Månsson, *et al.*, Publication in Progress (2025)

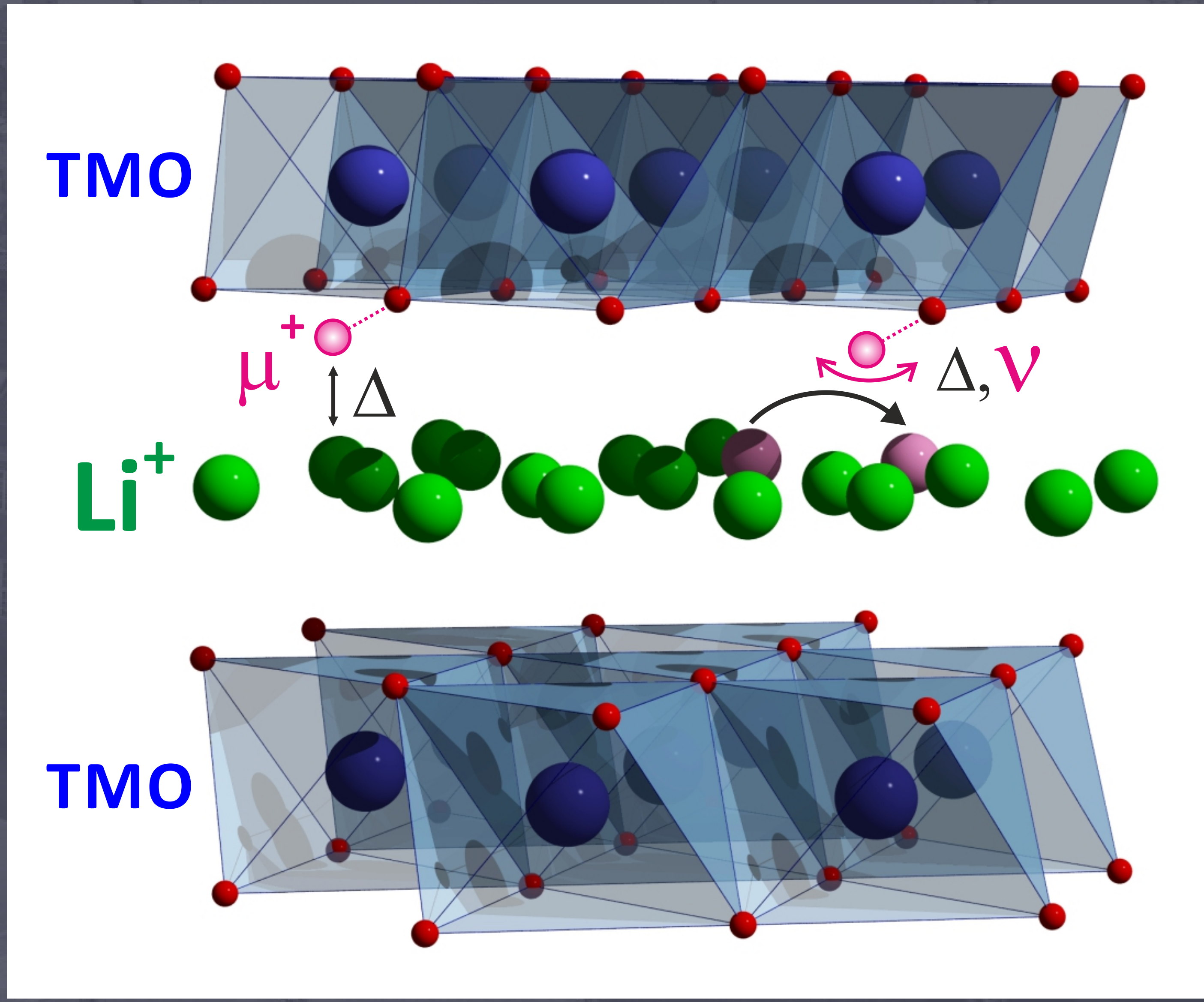
Ion Diffusion by $\mu^{+}SR$

Sugiyama and Mansson
Phys. Rev. Lett. 103, 147601 (2009)
Phys. Scr. 88 068509 (2013)

- Muons are very sensitive probes of local internal fields
- In the paramagnetic state, muons feel mainly the random nuclear dipole fields (of Li) $\rightarrow \Delta$
- Implanted μ^{+} bind strongly to O^{-} within the crystal lattice
- If Li-ions are immobile the mSR time-spectrum is described by a static Kubo-Toyabe function



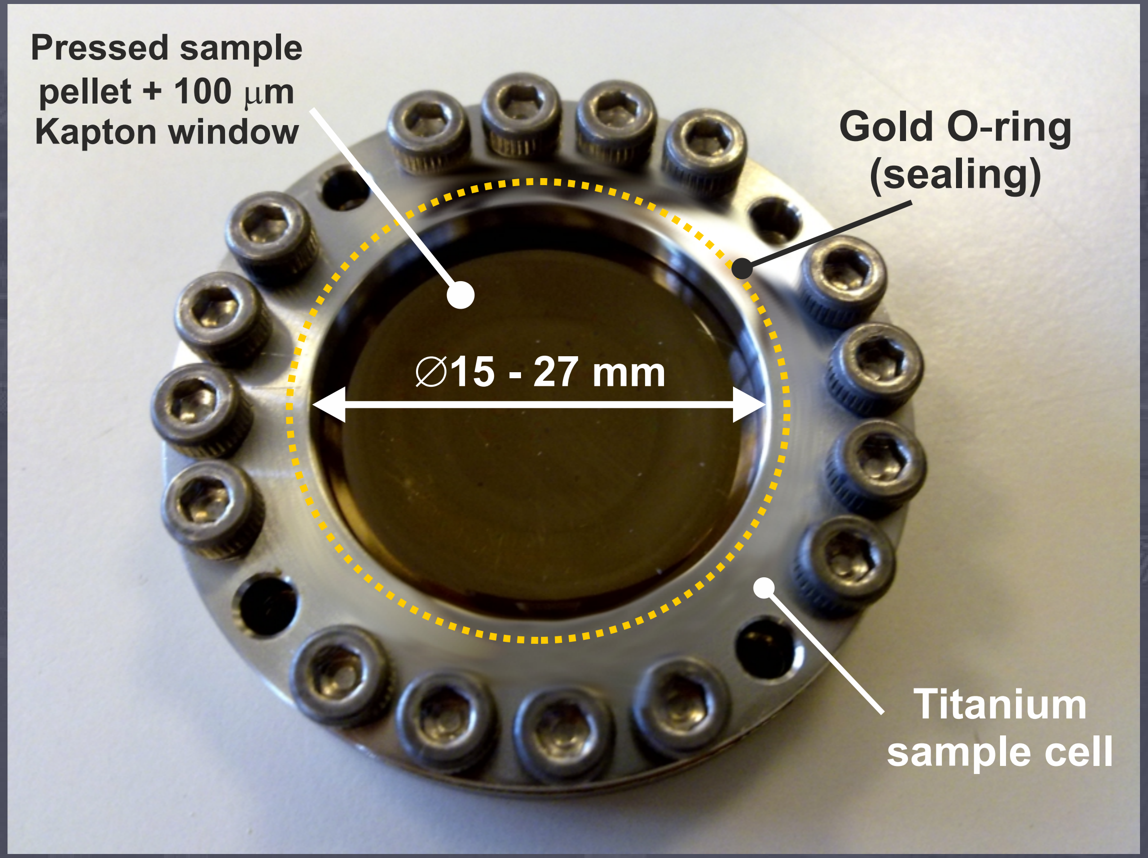
- If ion-diffusion is present, the muons will detect a dynamic contribution to the dipole field.

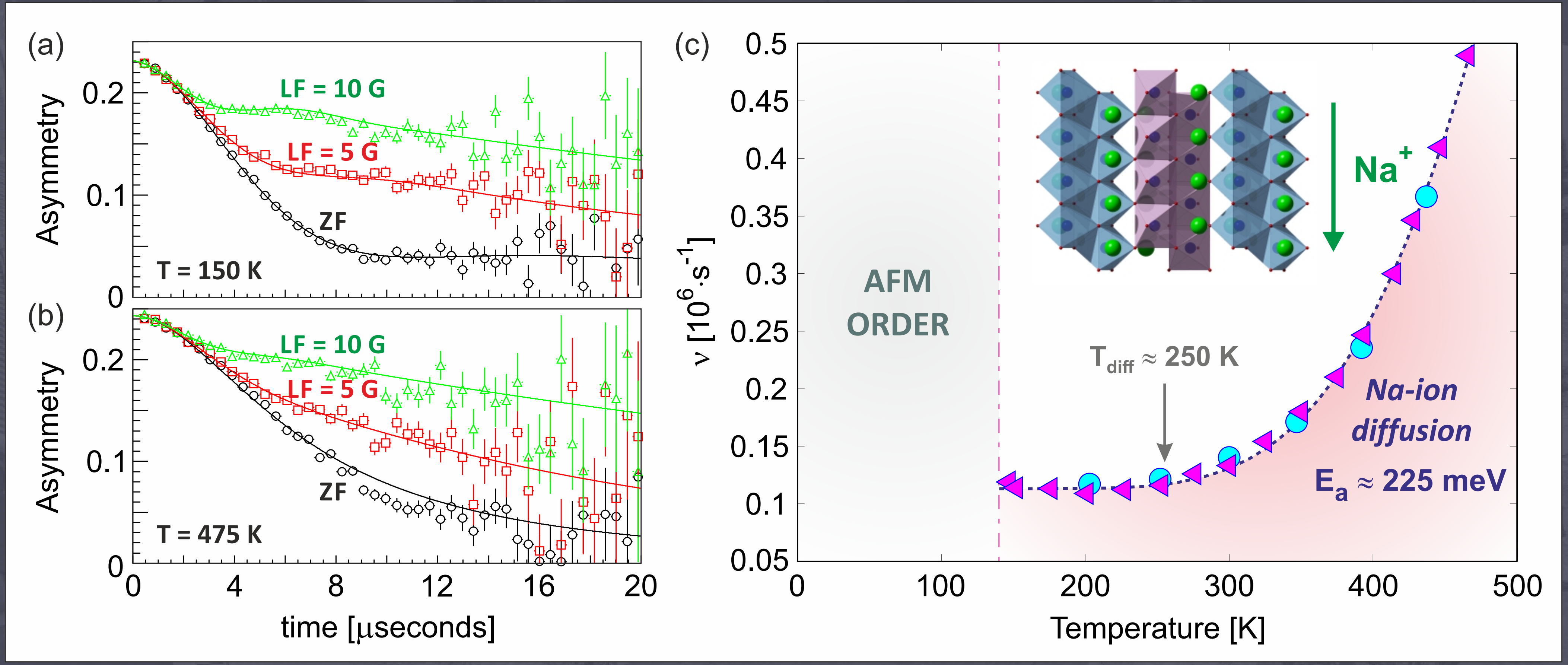


- Data is now described by a dynamic KT function that includes the parameter: ion hopping rate (ν)
- From *T*-dependence $\nu(T)$, the ion self-diffusion coefficient (D_{ion}) is extracted

Na-ion Diffusion in NaV_2O_4 by μ^+SR

- 1.2 g powder sample pressed into a 1.5 mm thick sample pellet
- Introduced into a ∅ = 25 mm Titanium cell with thin kapton window and Ag O-ring sealing.
- A series of μ^+SR spectra are collected at each temperature → global fit = robust results for Na-ion hopping rate: $\nu(T)$

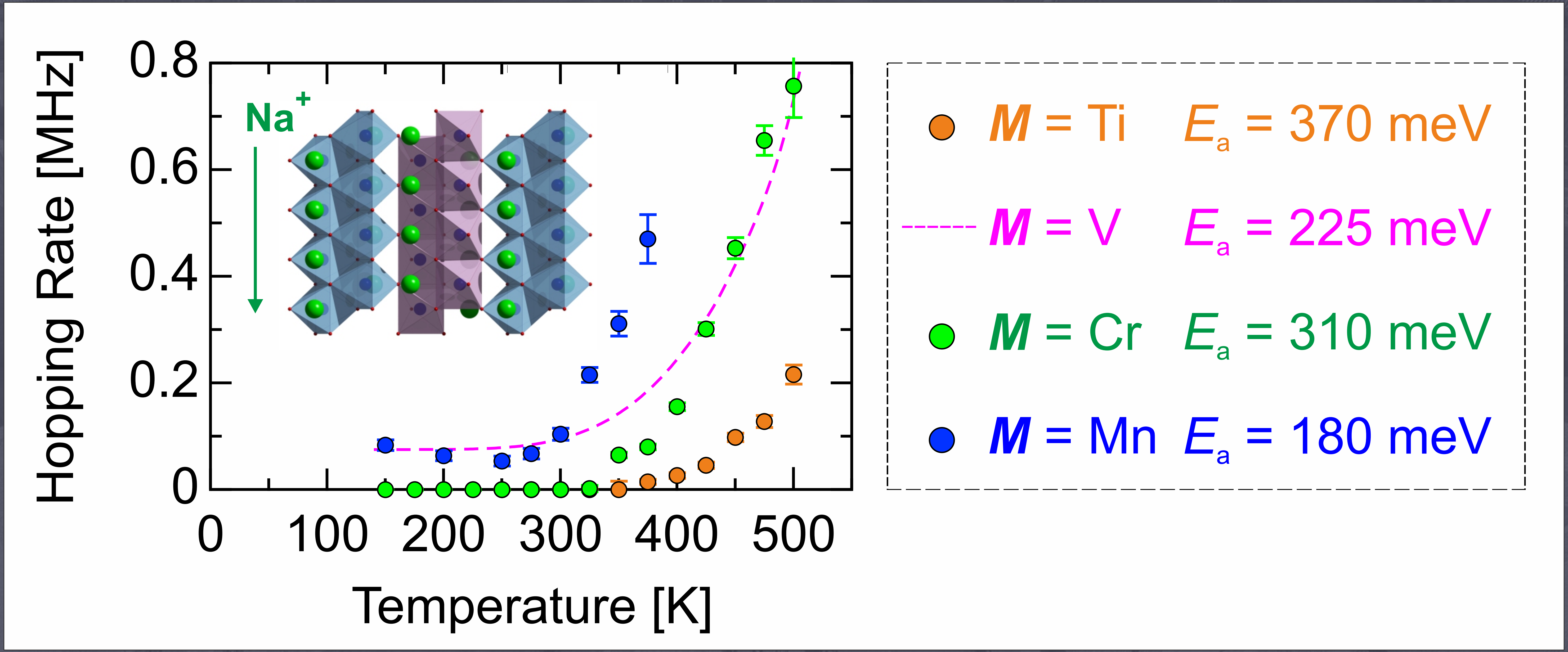




- $\nu(T)$ show exponential increase for T > 250 K, thermally activated process.
- Fits well to an Arrhenius type equation for diffusion.
- Can extract an activation energy for the diffusion process: E_a = 225 meV

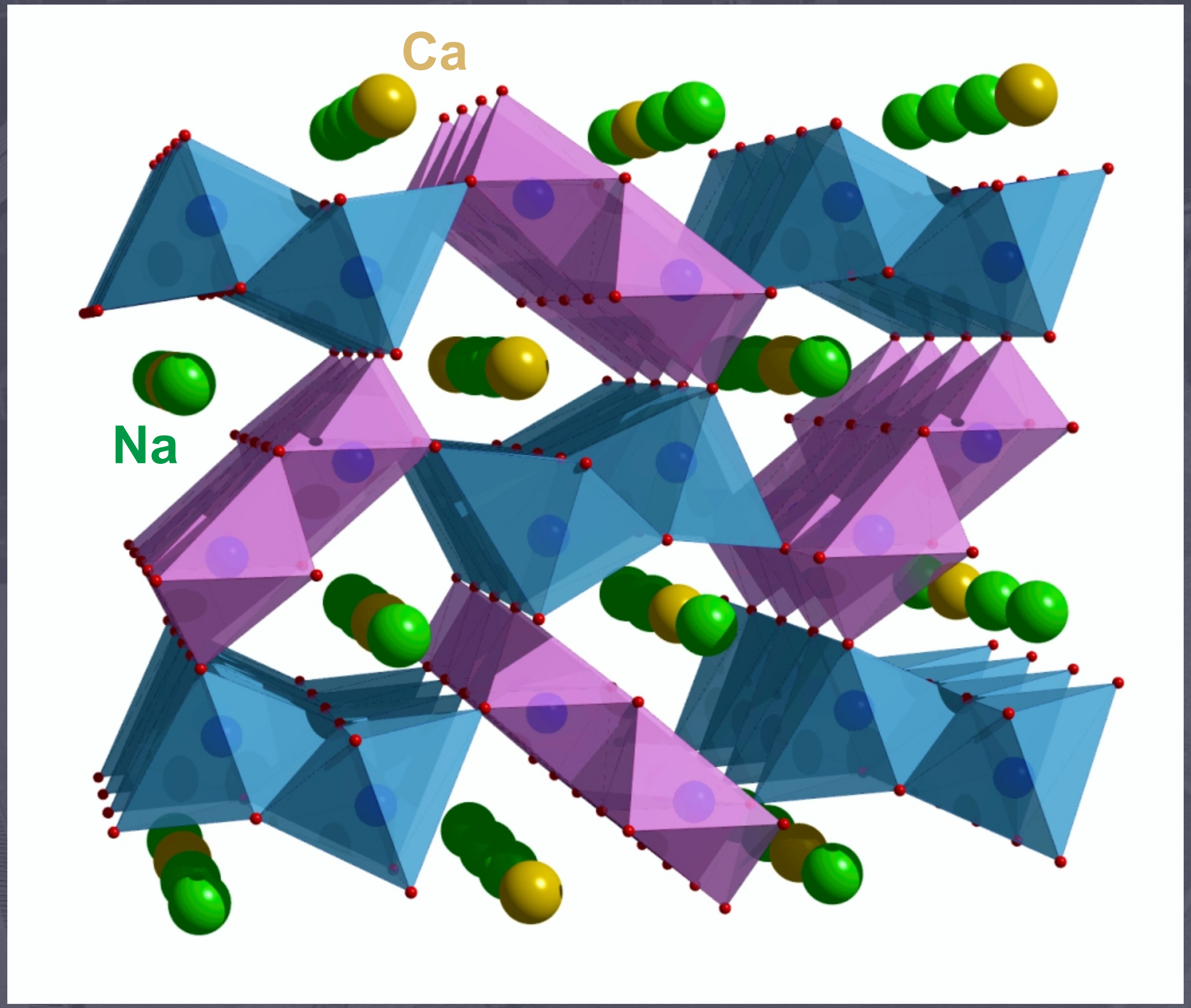
Na-ion Diffusion in NaM_2O_4 by μ^+SR

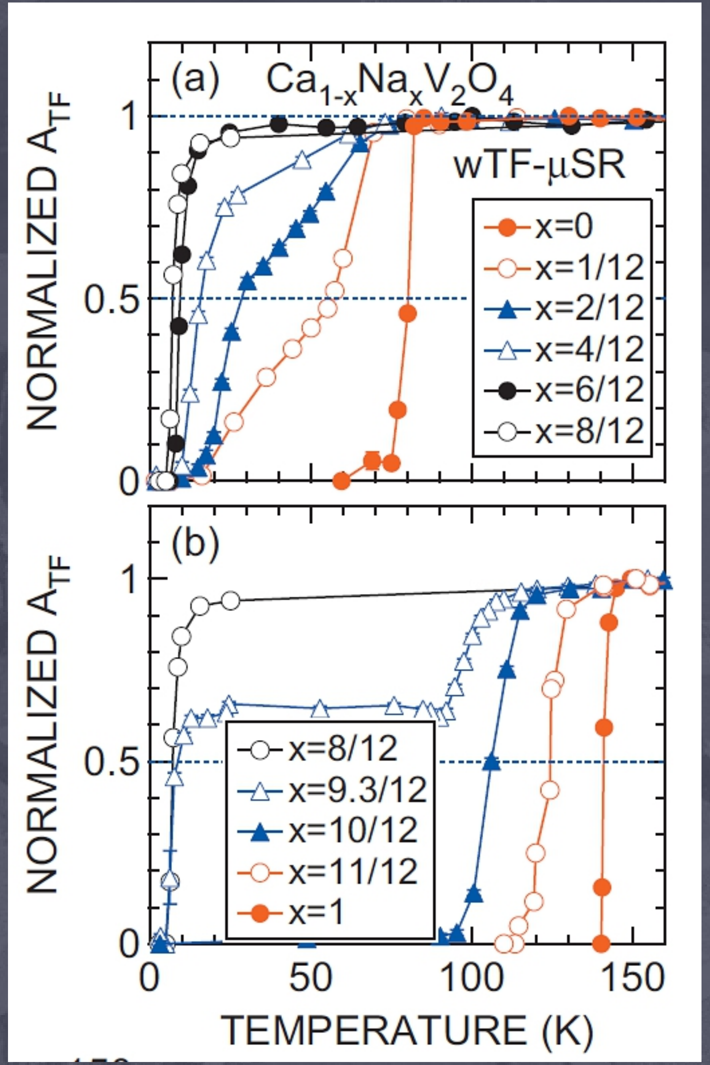
- Similar studies of Na-ion diffusion have been performed also for the entire NaM_2O_4 series
- We find a strong dependence on the activation energy with ***M***, where the Mn compound seems to be the most interesting for application point of view.

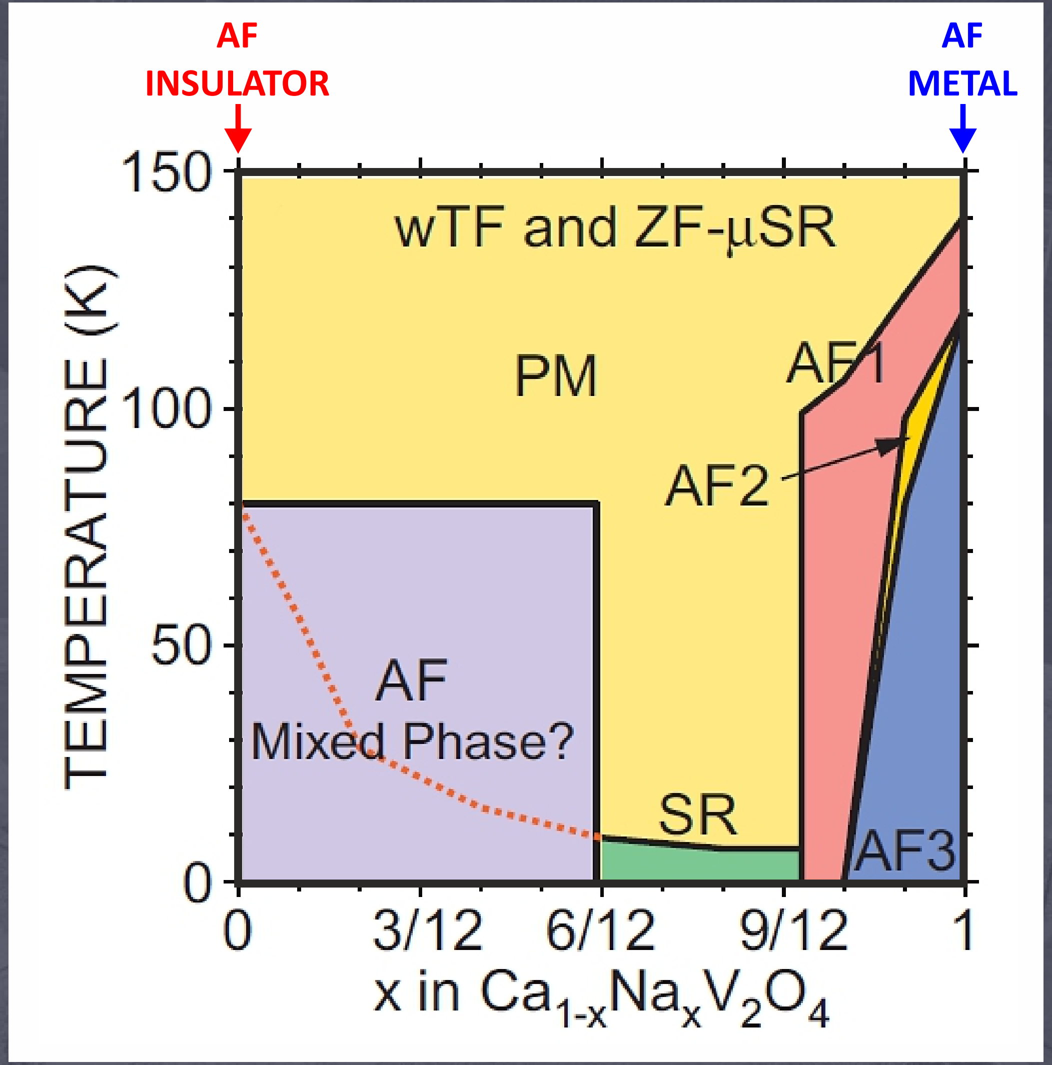


Introducing Ca "defects"

- The compounds containing Na and Ca can be of interest for both spin order and ion diffusion.
- A complex magnetic phase diagram is found by μ^+SR (AF Metal ⇒ AF Insulator !!!).
- The addition of Ca into the Q1D Na-ion channels can be seen as point defects (c.f. LFPO)
- Ca has no nuclear moment ⇒ "invisible" to the muons i.e. ideal setup for such studies







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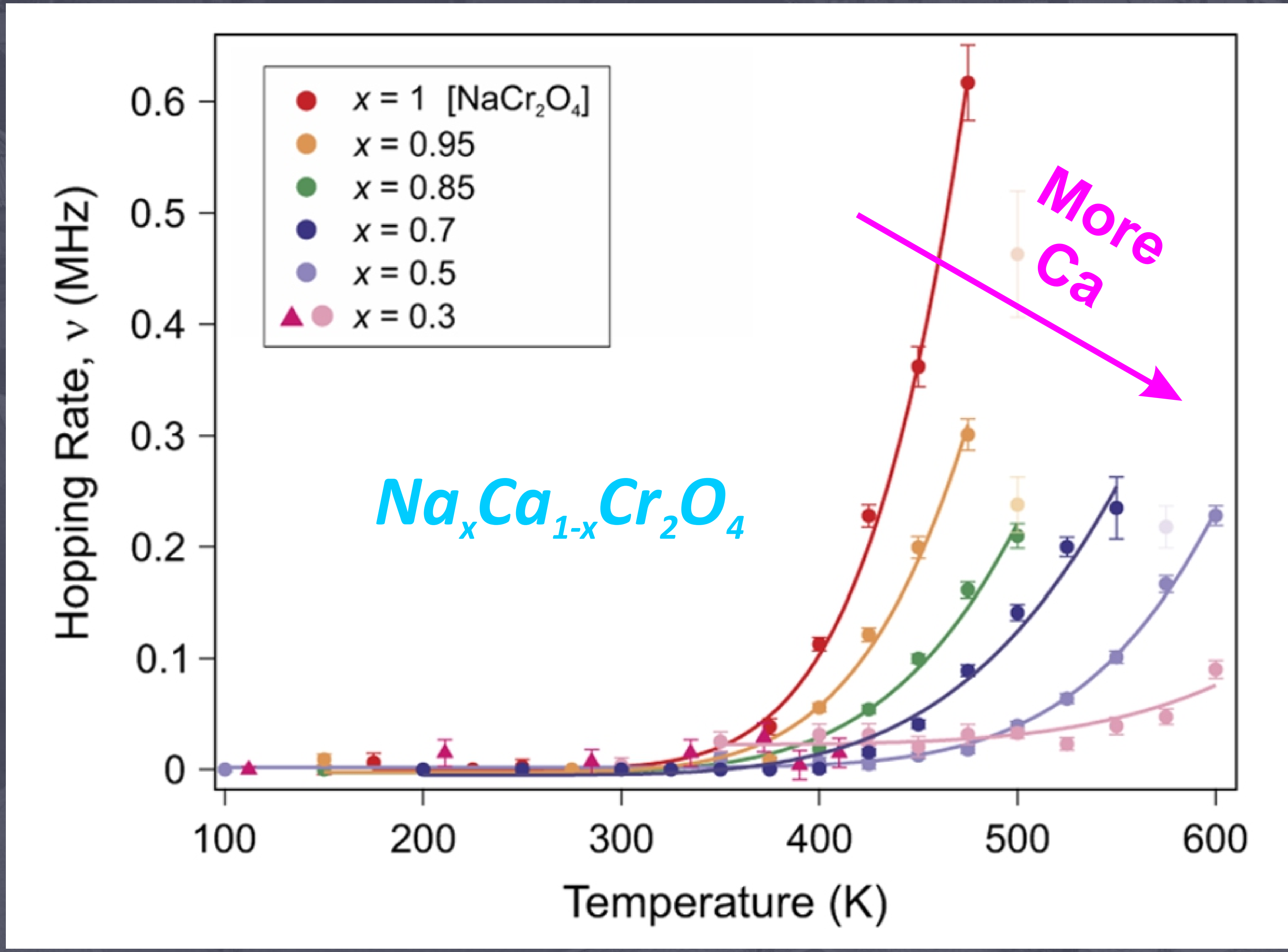
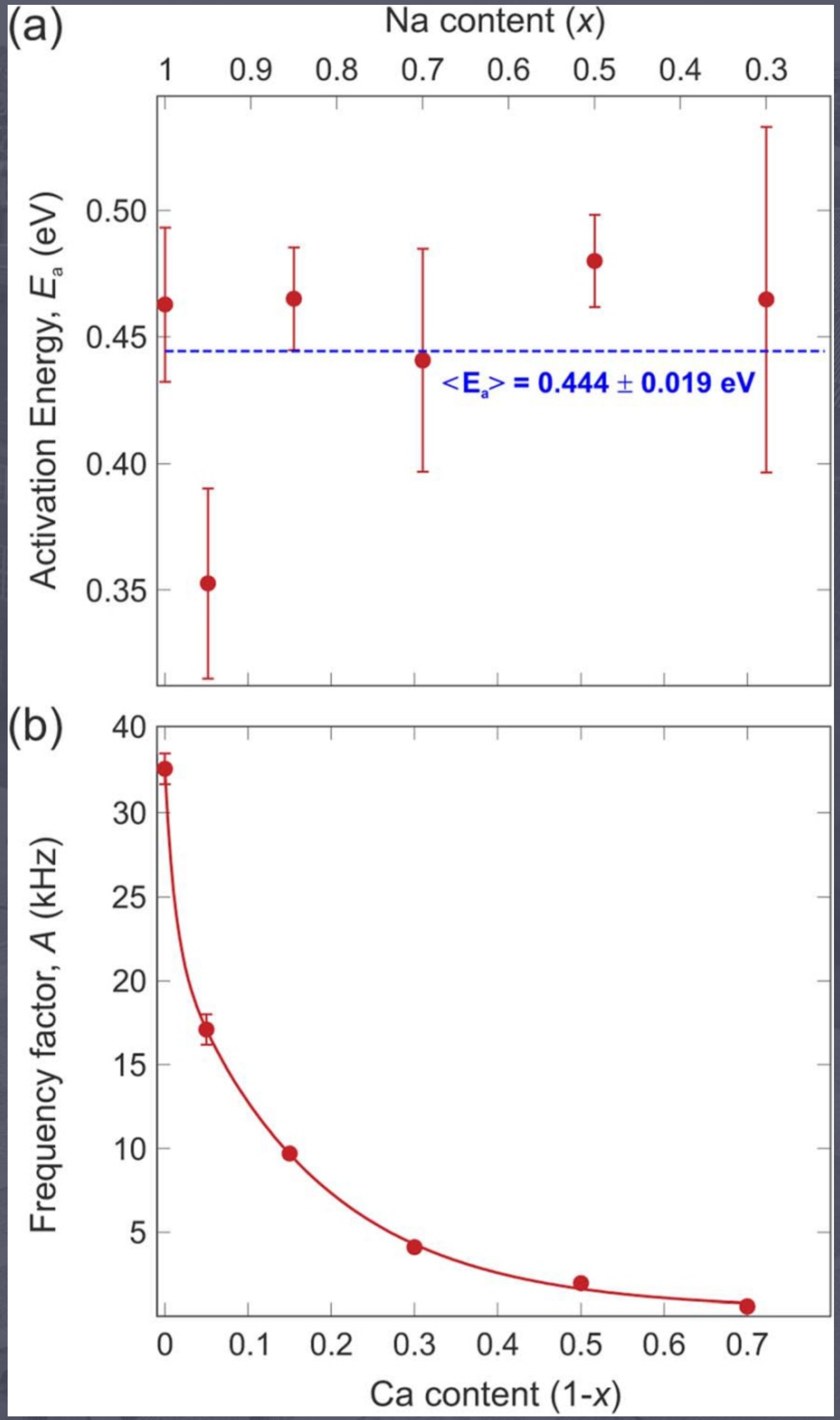
Defects in 1D ion-diffusion Channels

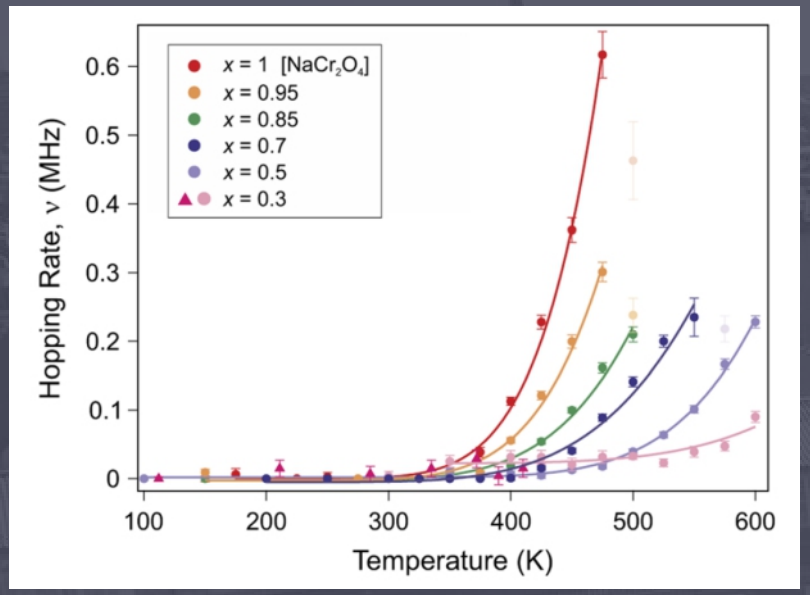
μ^+SR

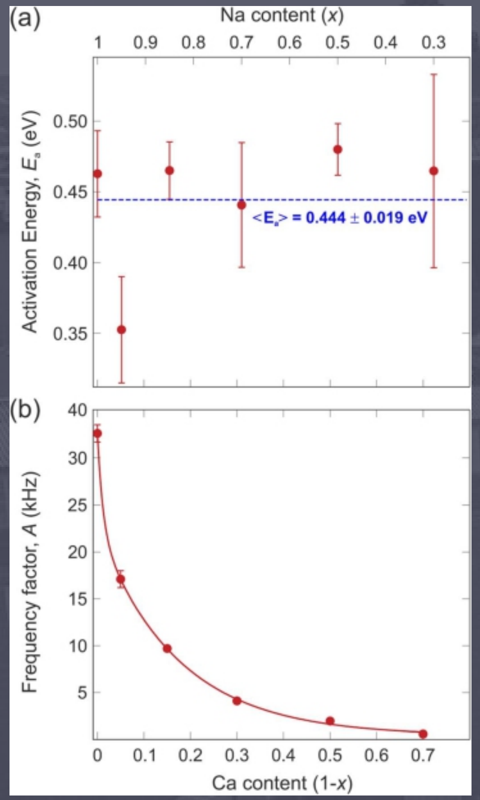




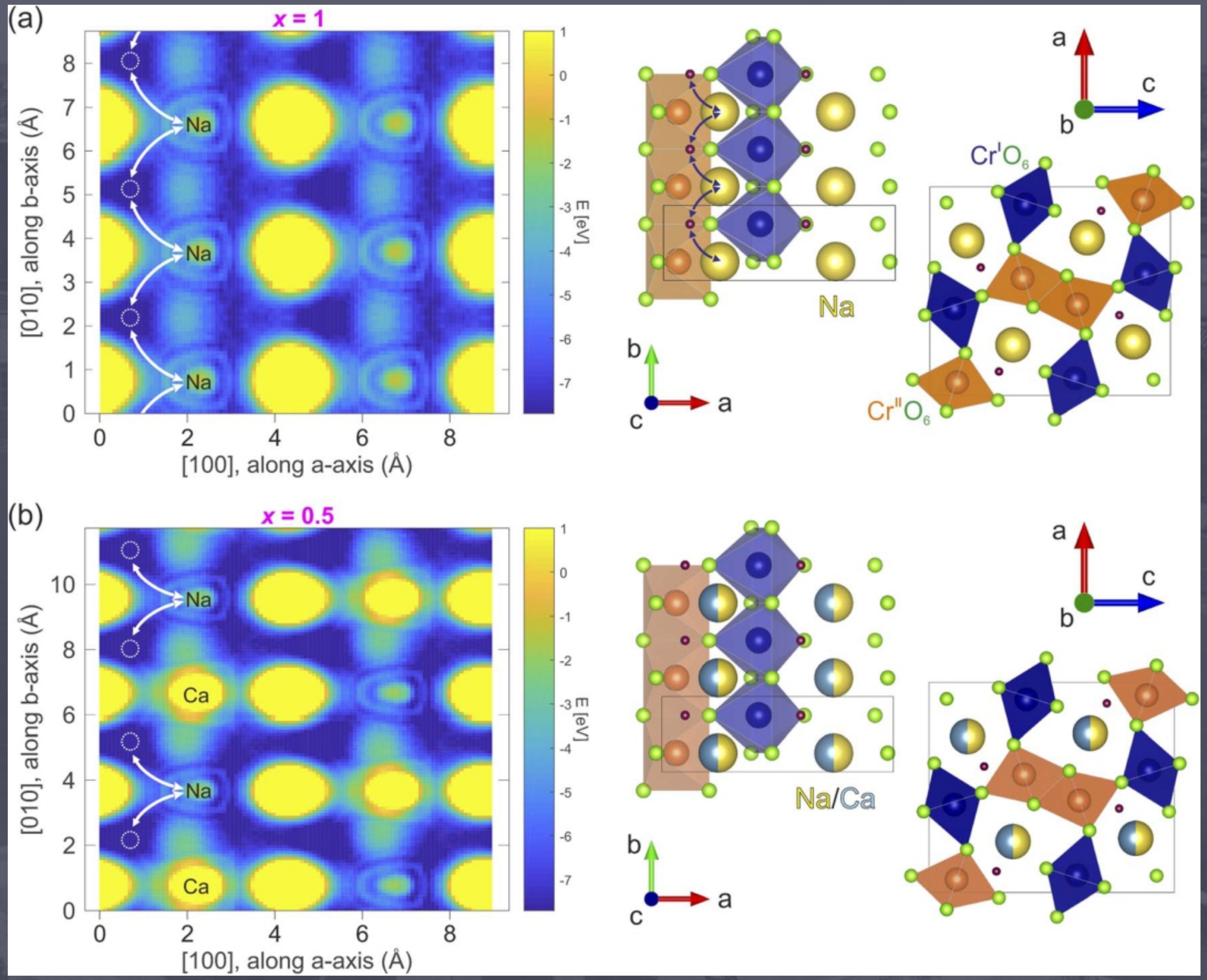
Defects in 1D ion-diffusion Channels

μ^+SR

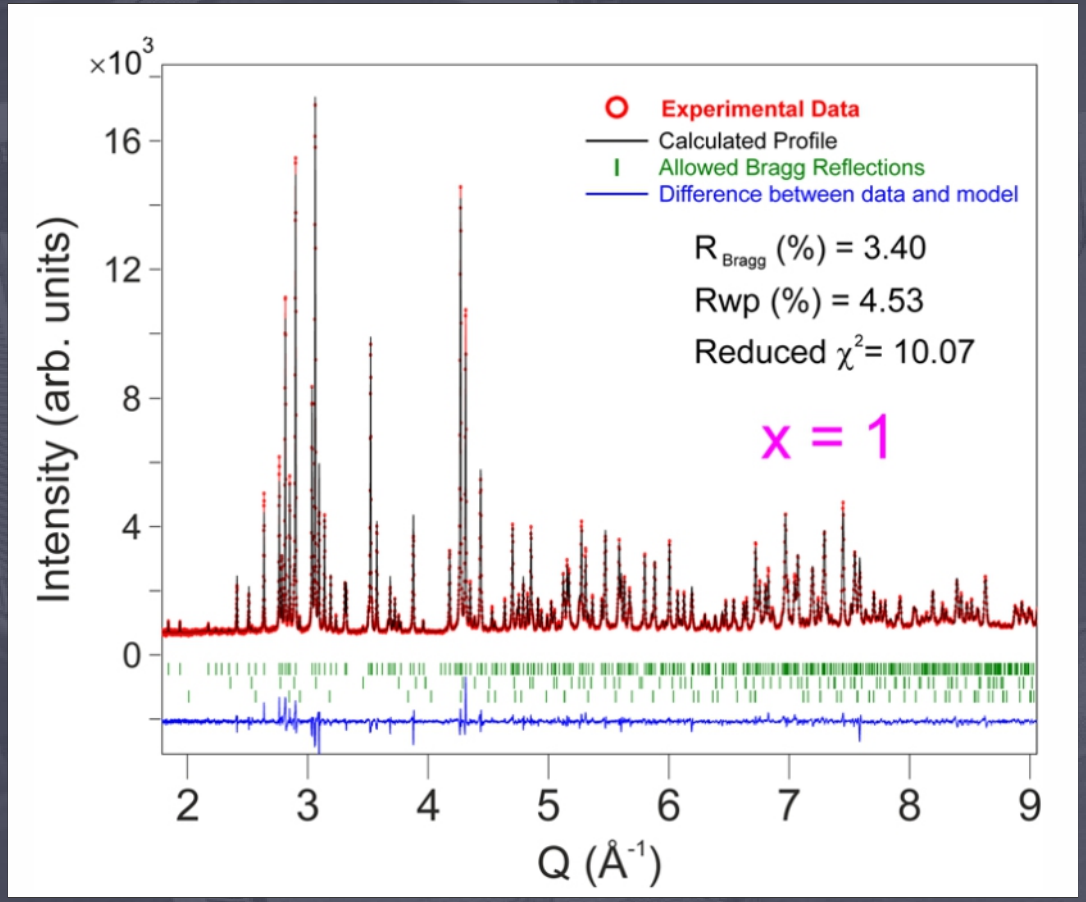




Modeling



NPD



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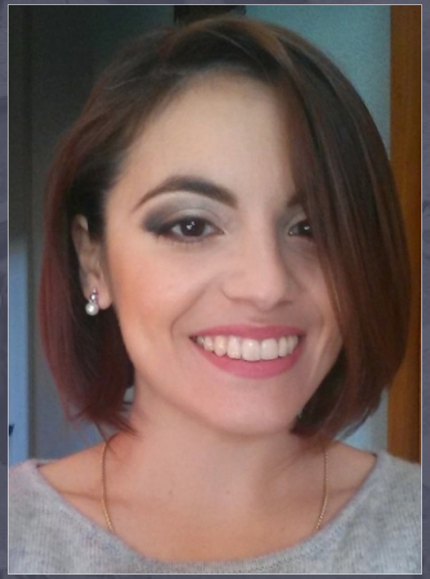

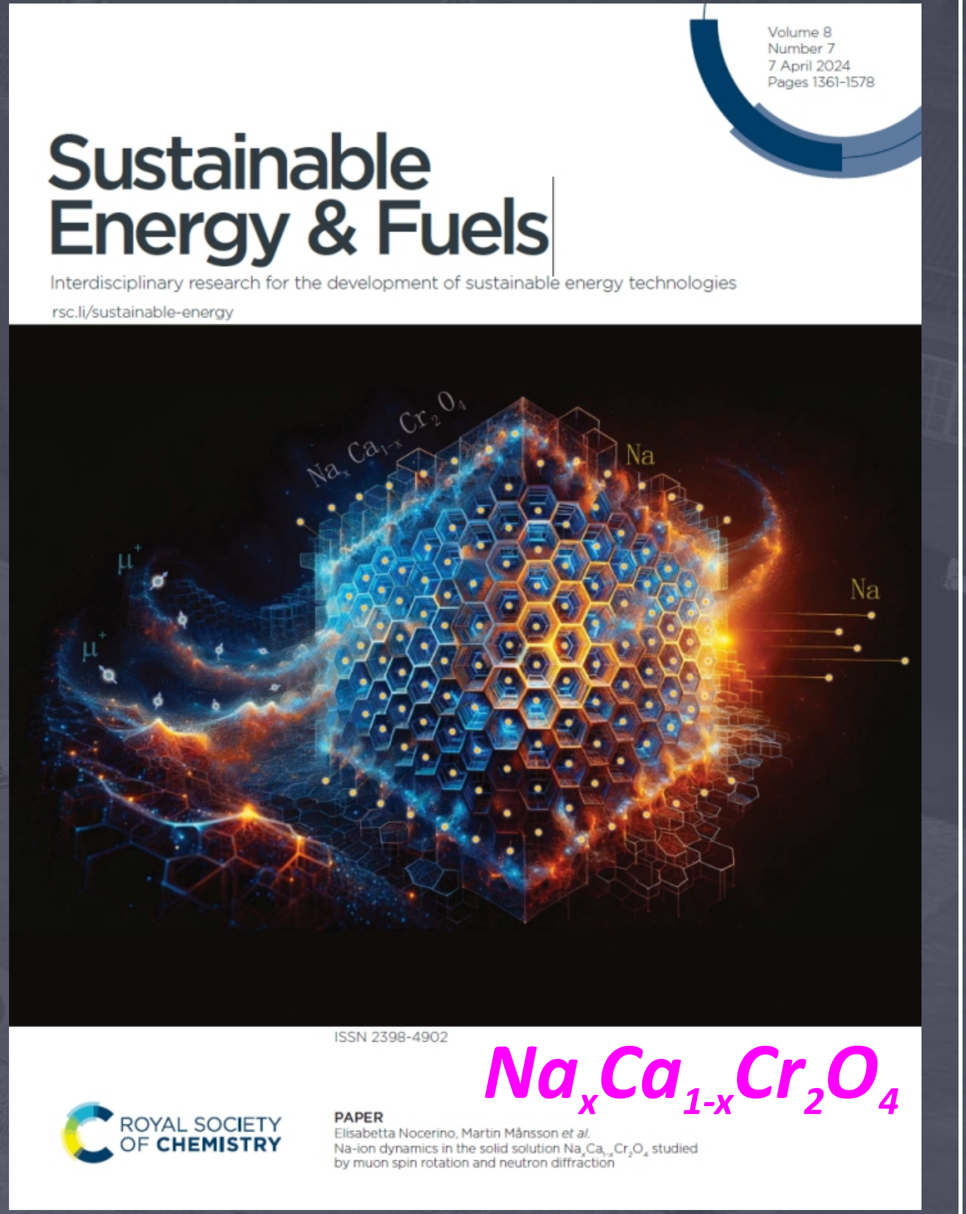

$Na_xCa_{1-x}Cr_2O_4$

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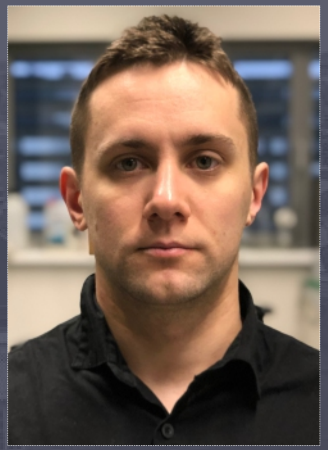

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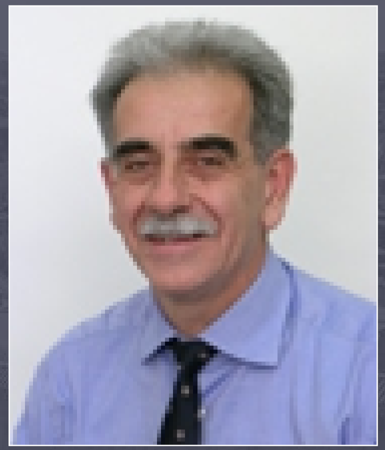

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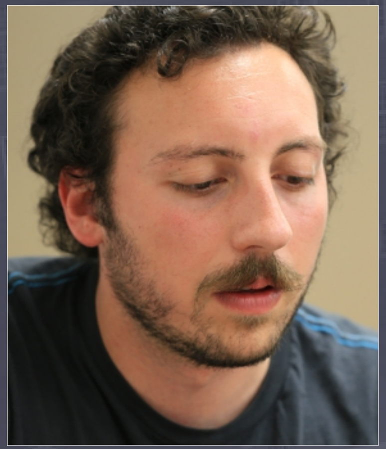

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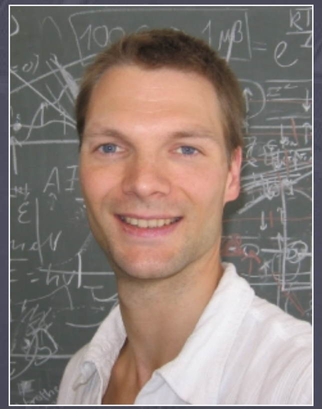

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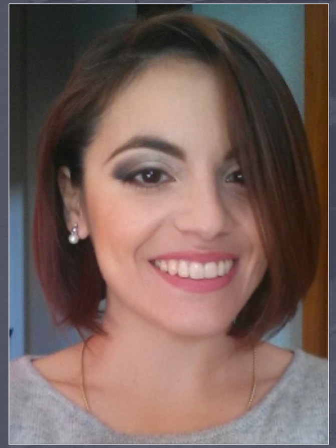

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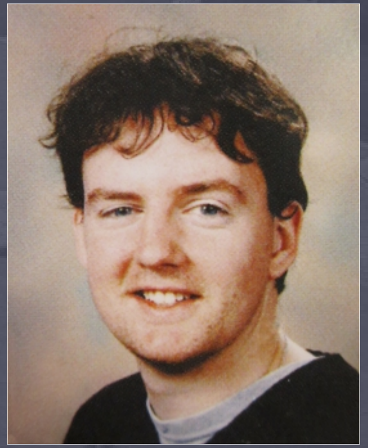

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