# A short introduction to the electronic structure and magnetism of rare-earths

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# COLLABORATORS

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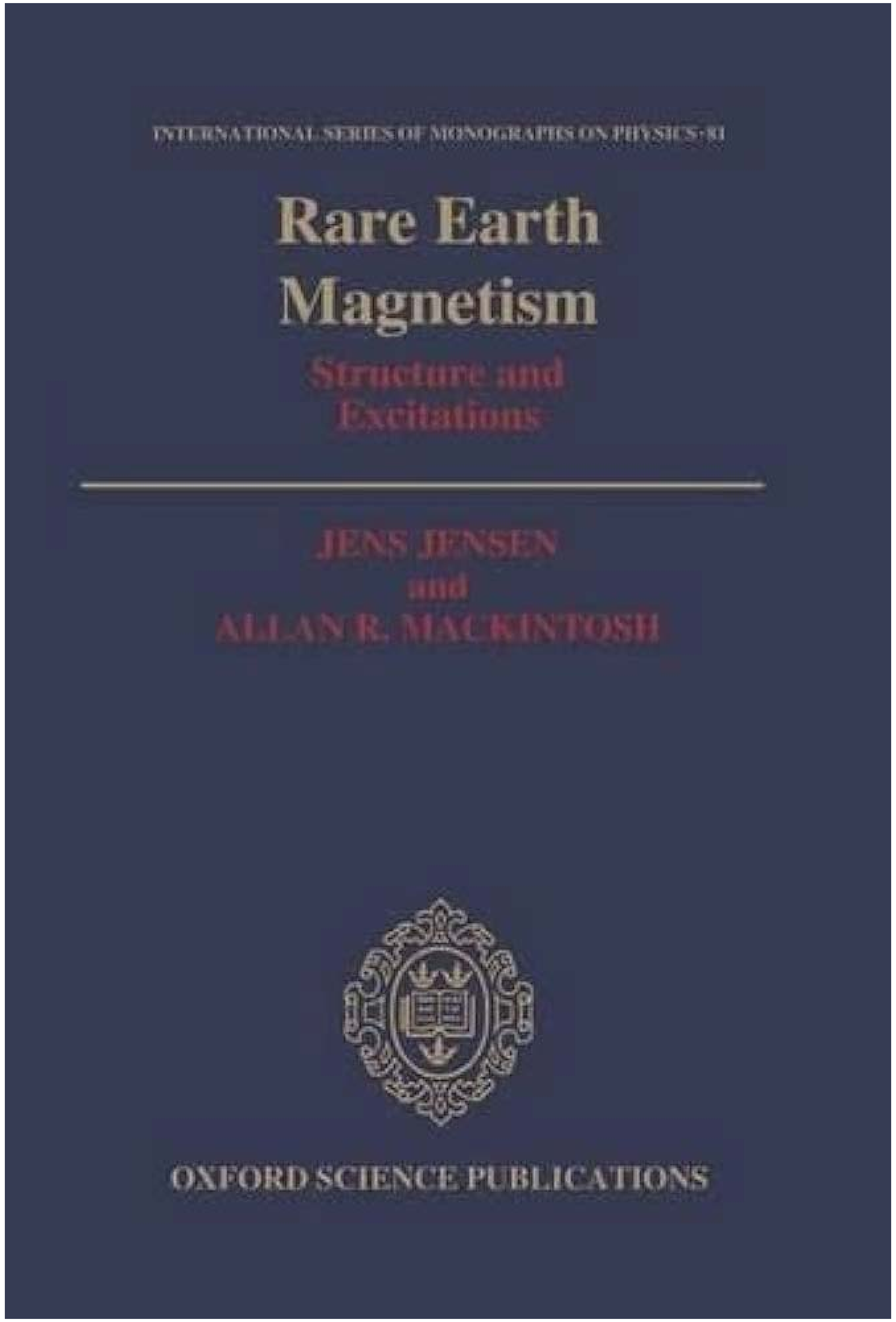
# Overview

- A short motivation
- DMFT and the Hubbard I approximation
- Electronic structure
- Magnetism and exchange
- Magneto calorics



INTERNATIONAL SERIES OF MONOGRAPHS ON PHYSICS · 81

Rare Earth
Magnetism

Structure and
Excitations

JENS JENSEN
and
ALLAN R. MACKINTOSH

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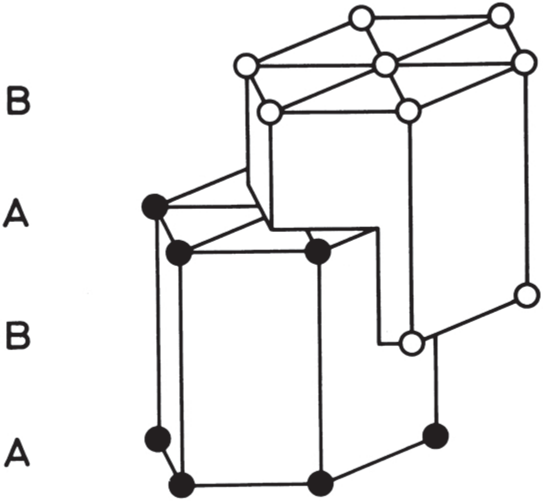
B
A
B
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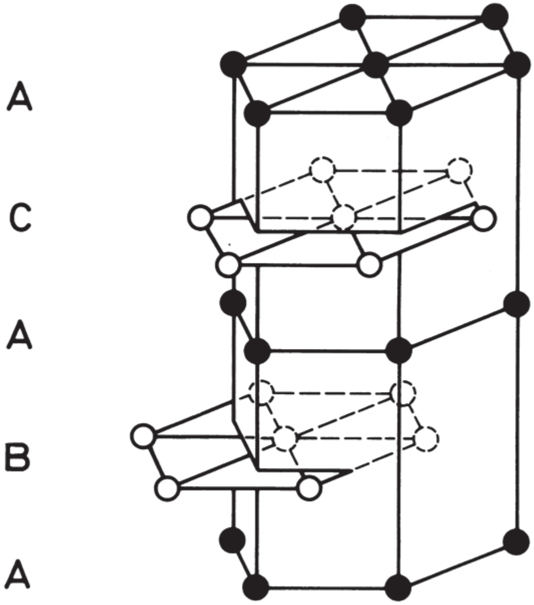
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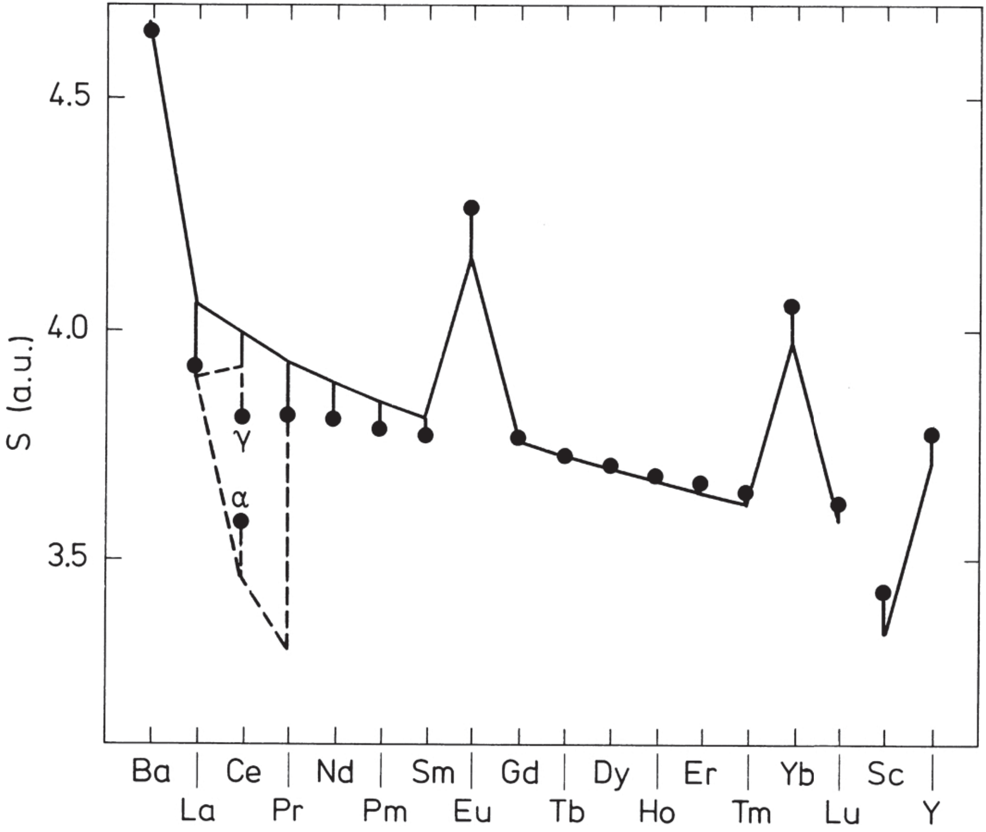


**Fig. 1.14.** The equilibrium atomic radii for the rare earth metals, after

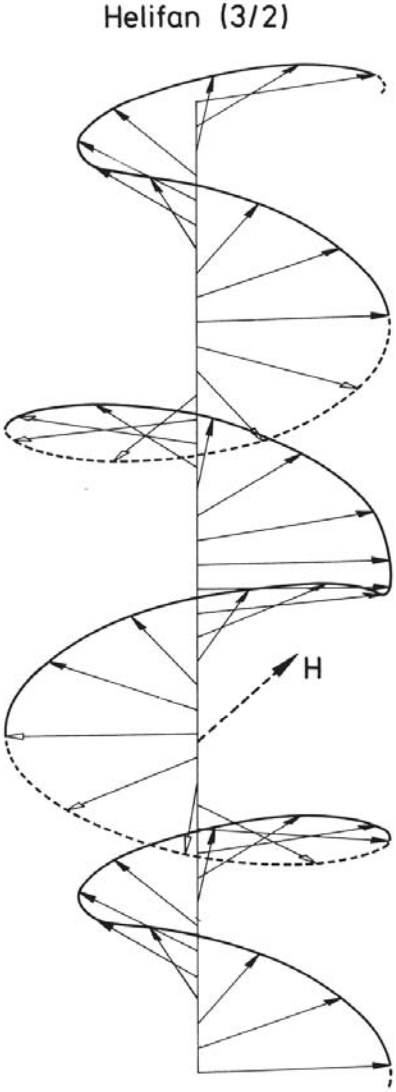
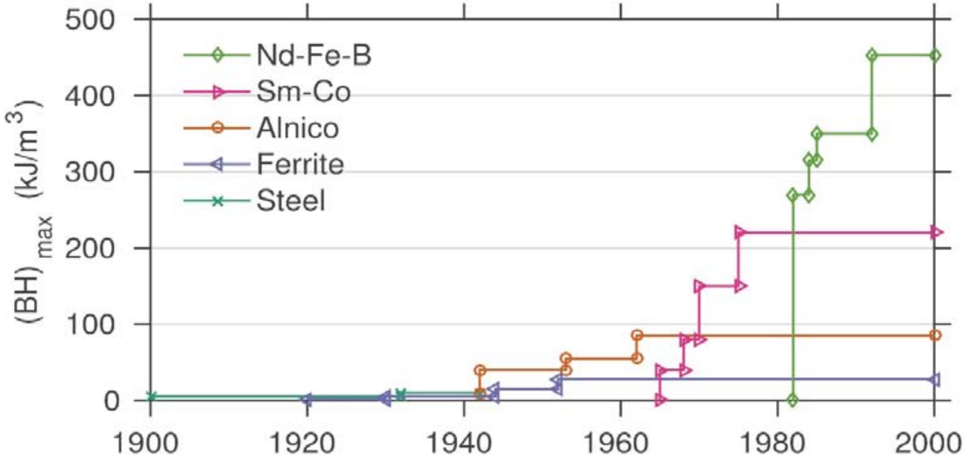
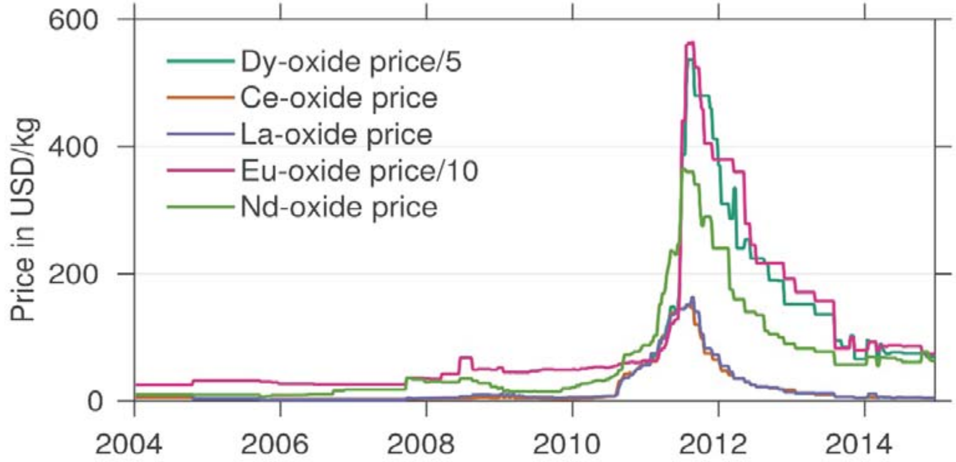


**Fig. 2.10.** The helifan(3/2) structure in Ho at 50 K. The moments lie in planes normal to the *c*-axis and their relative orientations are indicated by arrows. A magnetic field of 11 kOe is applied in the basal plane, and moments with components respectively parallel and antiparallel to the field are designated by filled and open arrow-heads. This component of the moments has a periodicity which is 3/2 that of the corresponding helix, and the helicity of the structure changes regularly.

# Hard magnets

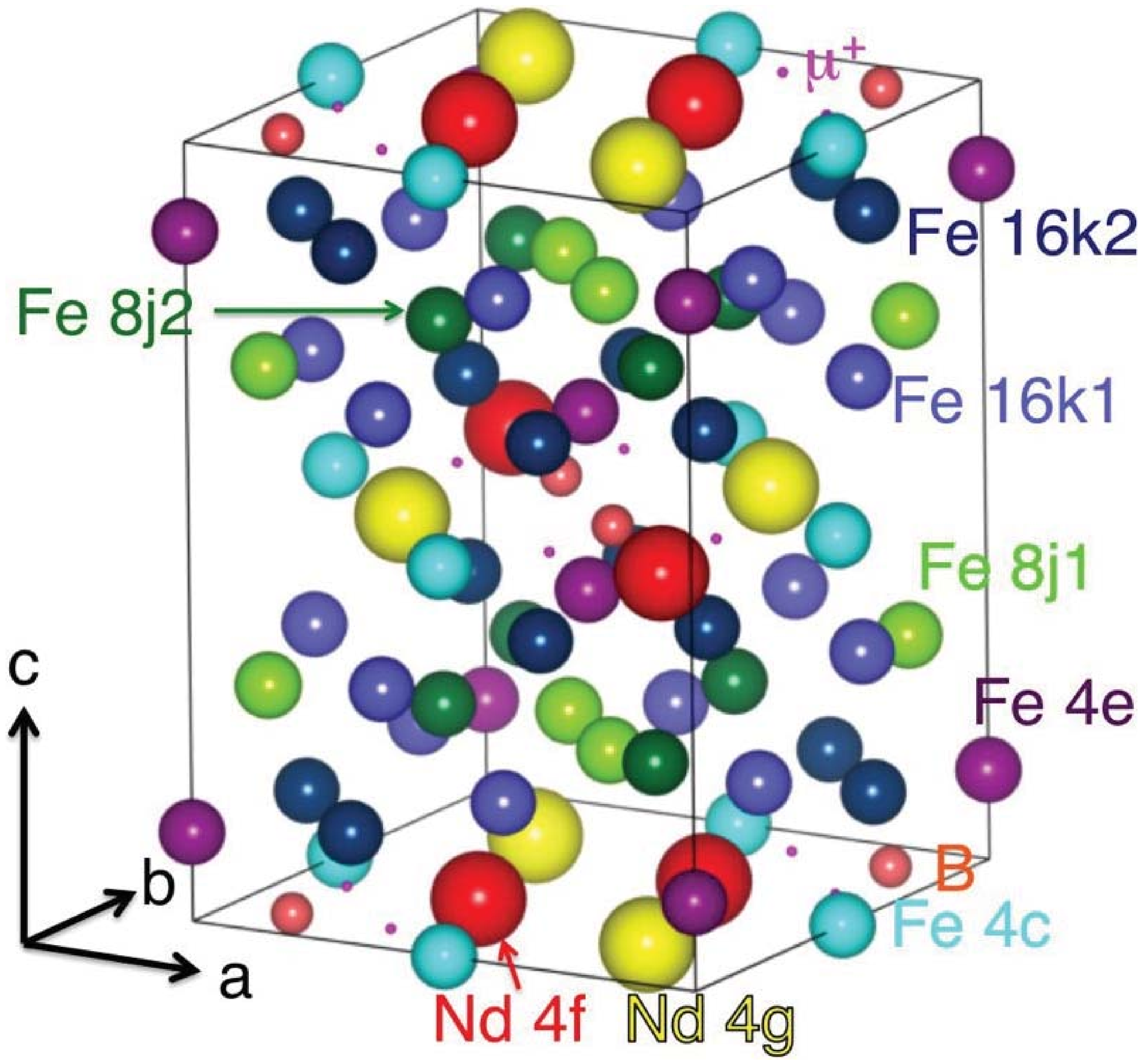


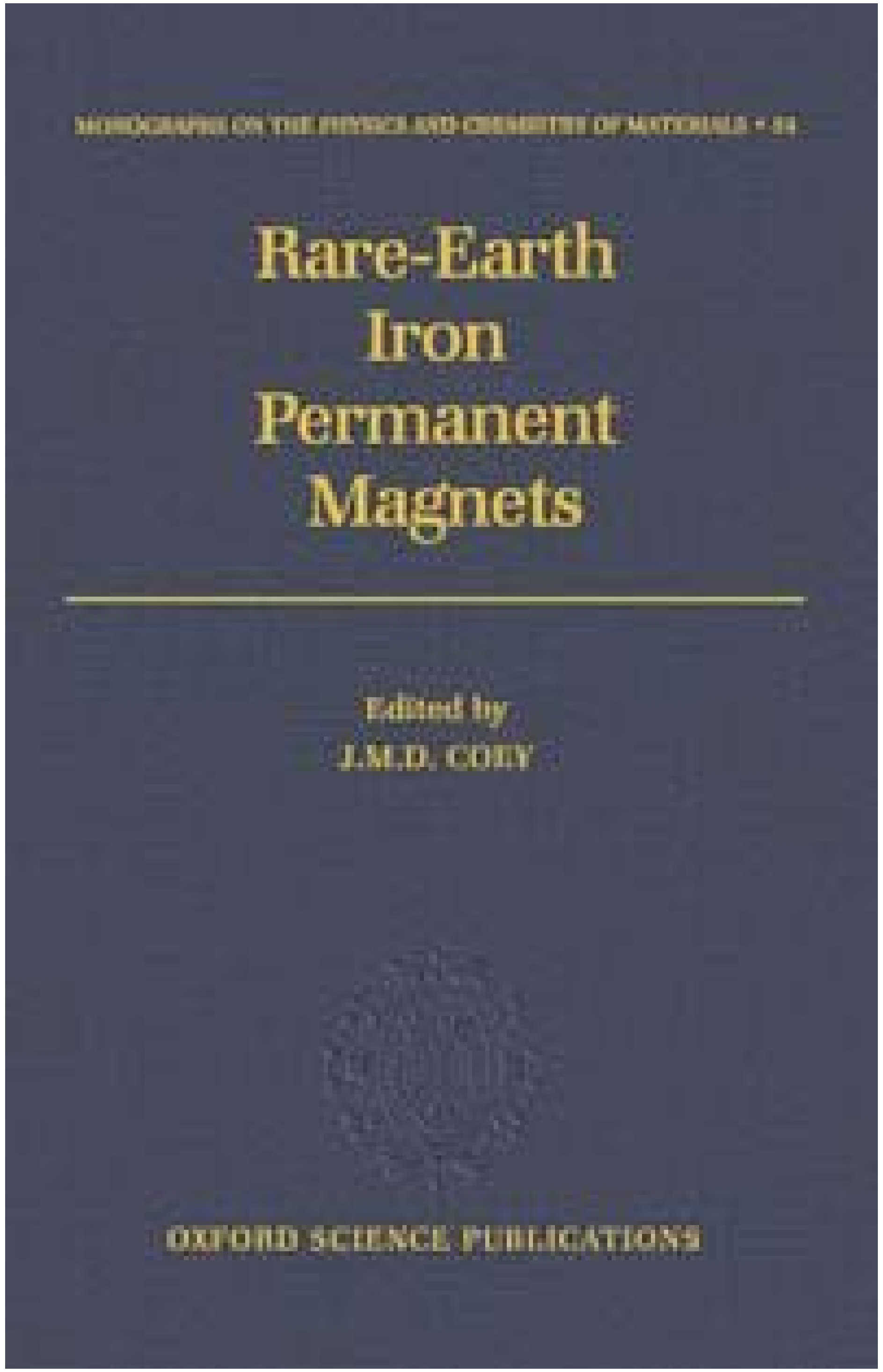
*(a)* Development of energy products of permanent magnets throughout the 20th century. Reproduced from Ref. [7, 23].



*(b)* Development in RE oxide prices with time from 2004 to 2014. Reproduced from Ref. [24].

# $Nd_2Fe_{14}B$ crystal structure





MONOGRAPHS ON THE PHYSICS AND CHEMISTRY OF MATERIALS • [illegible]

Rare-Earth
Iron
Permanent
Magnets

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# Bloch states and bands

$$H_{one} = \frac{-\nabla^2}{2} + V_{eff}$$

$$H_{one}\psi(\mathbf{r}) = \epsilon\psi(\mathbf{r})$$

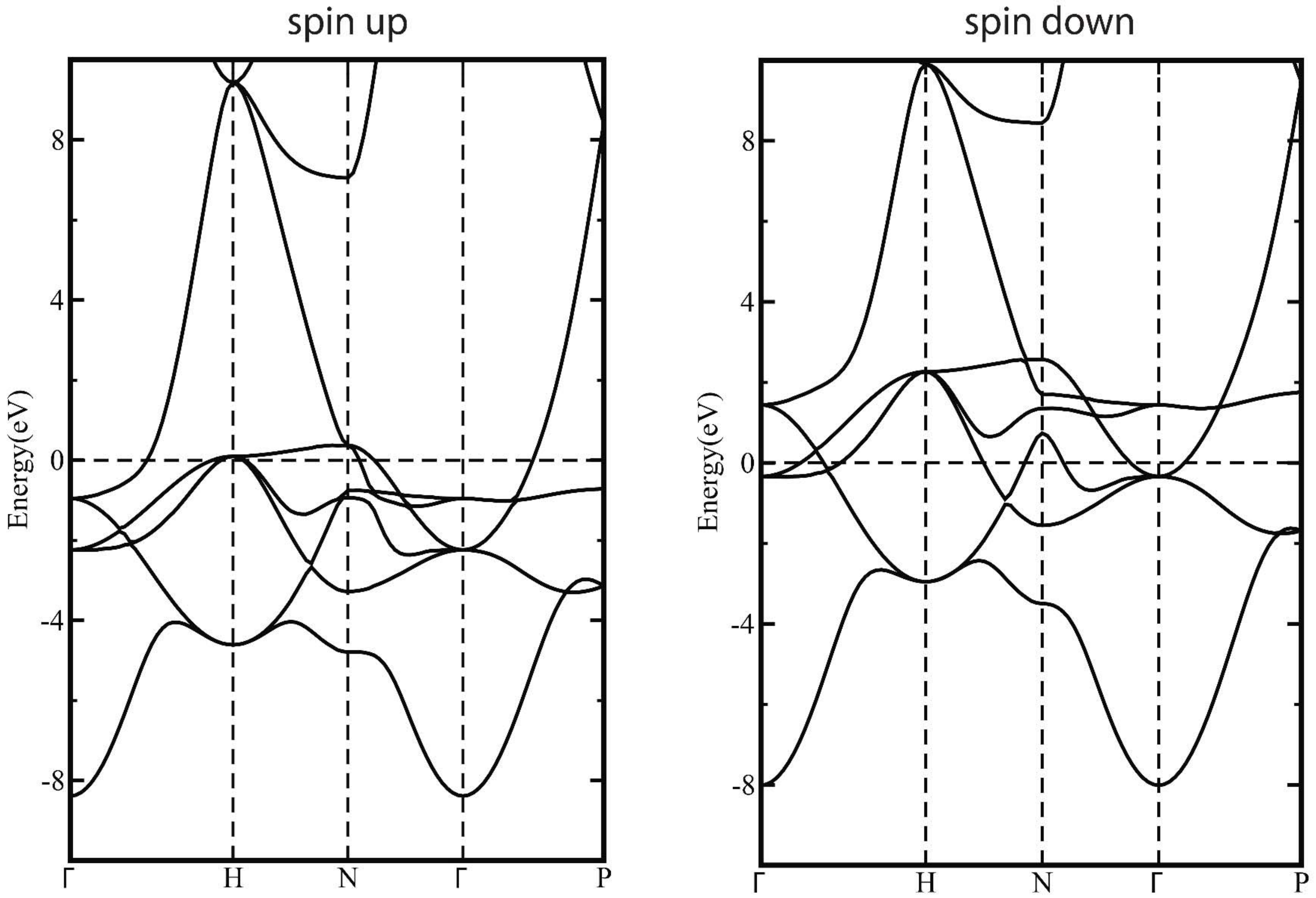
$$\psi(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u(\mathbf{r})$$

with $u(\mathbf{r})$ having the same periodicity as the lattice

$$\psi(\mathbf{r}) \rightarrow \psi_{\mathbf{k}}(\mathbf{r})$$

$$\epsilon \rightarrow \epsilon_{\mathbf{k}}$$

# Spin-polarised energy dispersion for Fe



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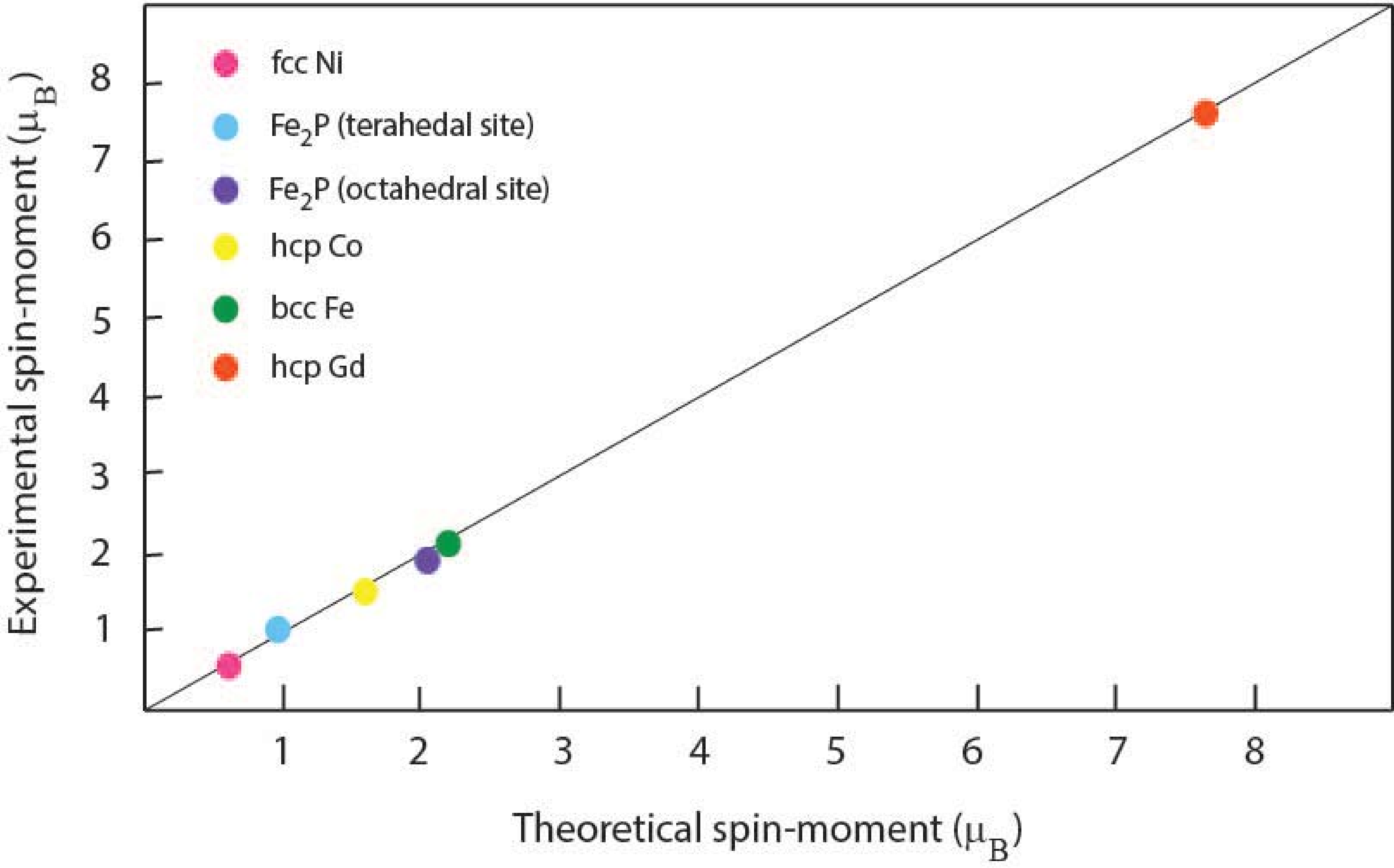

fcc Ni
Fe2P (terahedal site)
Fe2P (octahedral site)
hcp Co
bcc Fe
hcp Gd
Experimental spin-moment (μB)
Theoretical spin-moment (μB)
1
2
3
4
5
6
7
8
1
2
3
4
5
6
7
8

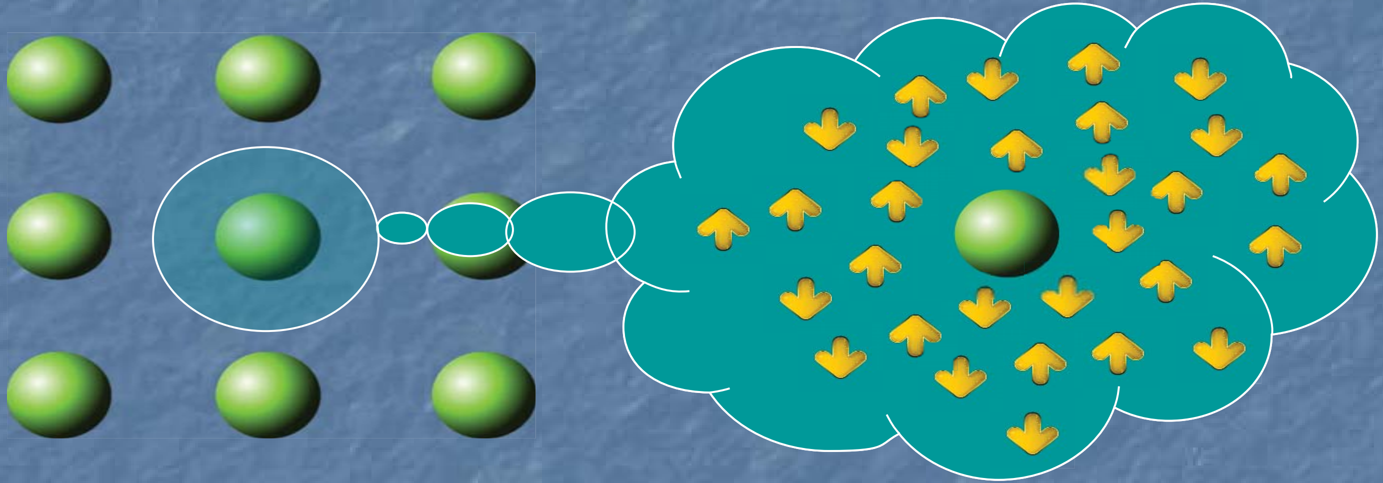
# Dynamical Mean Field Theory and the Hubbard-I Approximation

# Dynamical mean field theory

$$H = H_{LDA} + \sum_{R} \sum_{\xi_1\xi_2\xi_3\xi_4} U_{\xi_1\xi_2\xi_3\xi_4} c^{\dagger}_{R\xi_1} c^{\dagger}_{R\xi_2} c_{R\xi_3} c_{R\xi_4}$$

U-matrix expressed in terms of Slater integrals

The Hubbard model is mapped into an Anderson Impurity Model



FICTITIOUS SYSTEM REPRODUCING THE DYNAMICS

The mapping is made with the condition of preserving the local Green's function and is exact in the limit of infinite nearest neighbors

# Exact Diagonalization Solver

The finite size problem can be solved exactly with a direct construction of all the accessible many-body states.

N=5 electrons in K=10 orbitals:

$$\begin{aligned} |\Psi_1^5\rangle &= |1111100000\rangle, \\ |\Psi_2^5\rangle &= |1111010000\rangle, \\ &\vdots \\ |\Psi_M^5\rangle &= |0000011111\rangle. \end{aligned}$$

M corresponds to $\binom{K}{N}$

Too large for standard computational resources!

Block diagonalization $\longrightarrow$ up to 30 bath states!

# Exact Diagonalization Solver

The finite size problem can be solved exactly with a direct construction of all the accessible many-body states.

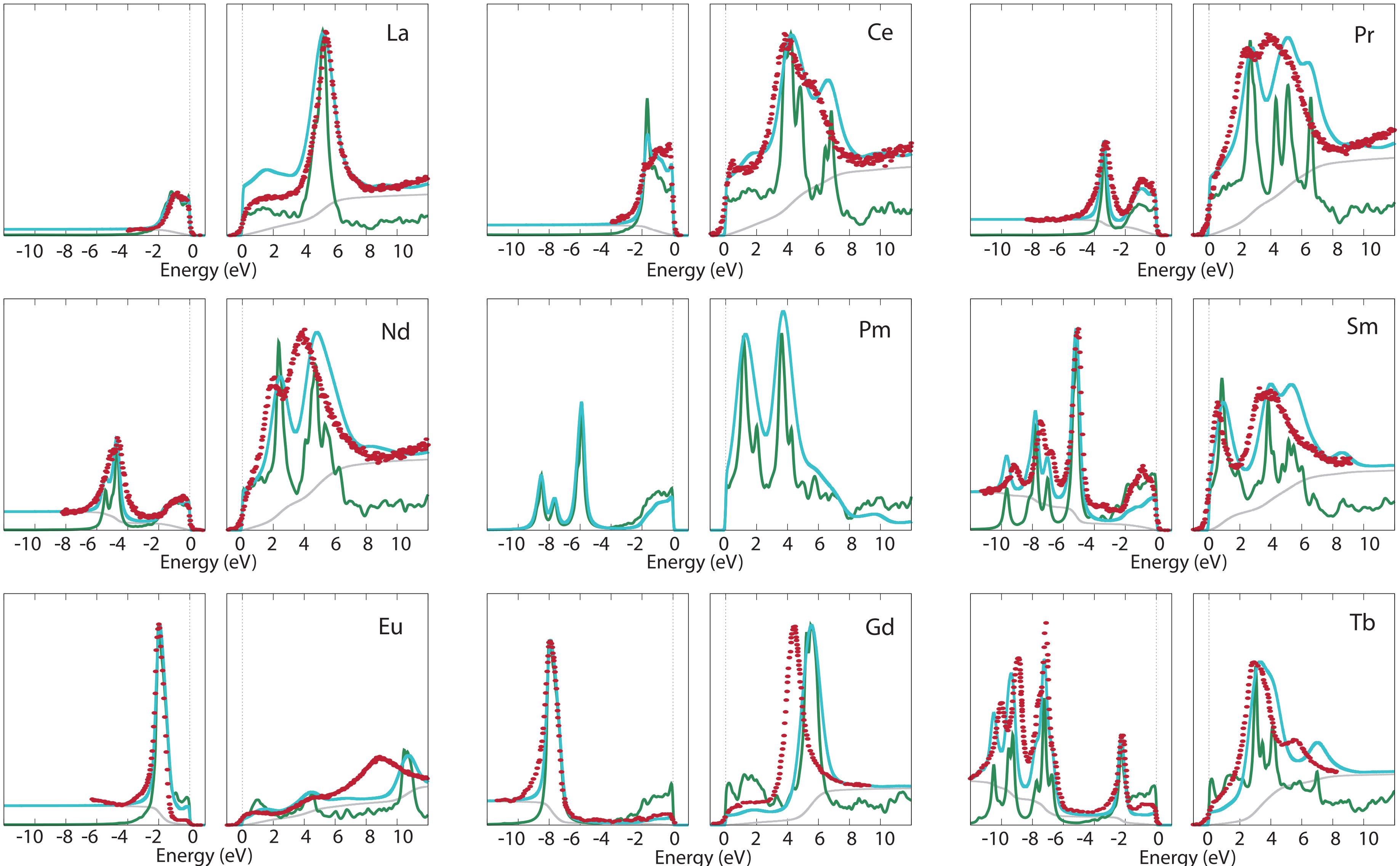
N=5 electrons in K=10 orbitals:

Once the many-body states have been determined, the one-particle Green's function can be obtained through the Lehmann representation

$$G^{\mathrm{ED}}(i\omega)_{\xi_1\xi_2} = \frac{1}{Z}\sum_{\nu\mu}\frac{\langle\mu|\hat{c}_{\xi_1}|\nu\rangle\langle\nu|\hat{c}^{\dagger}_{\xi_1}|\mu\rangle}{i\omega+E_{\mu}-E_{\nu}}\left(e^{-\beta E_{\mu}}+e^{-\beta E_{\nu}}\right)$$

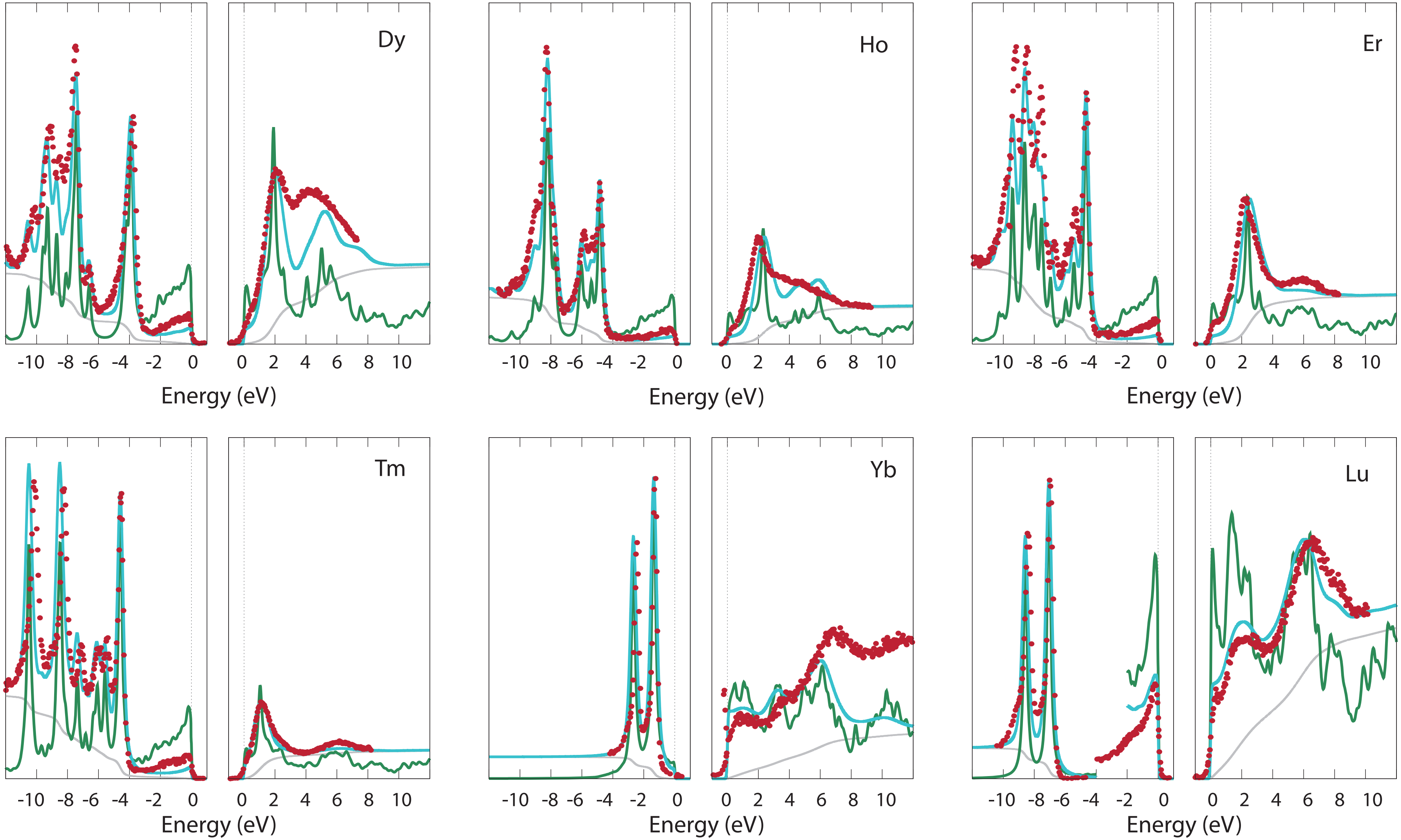
# Valence band spetra of rare-earths

(Loch et al. PRB 2016)

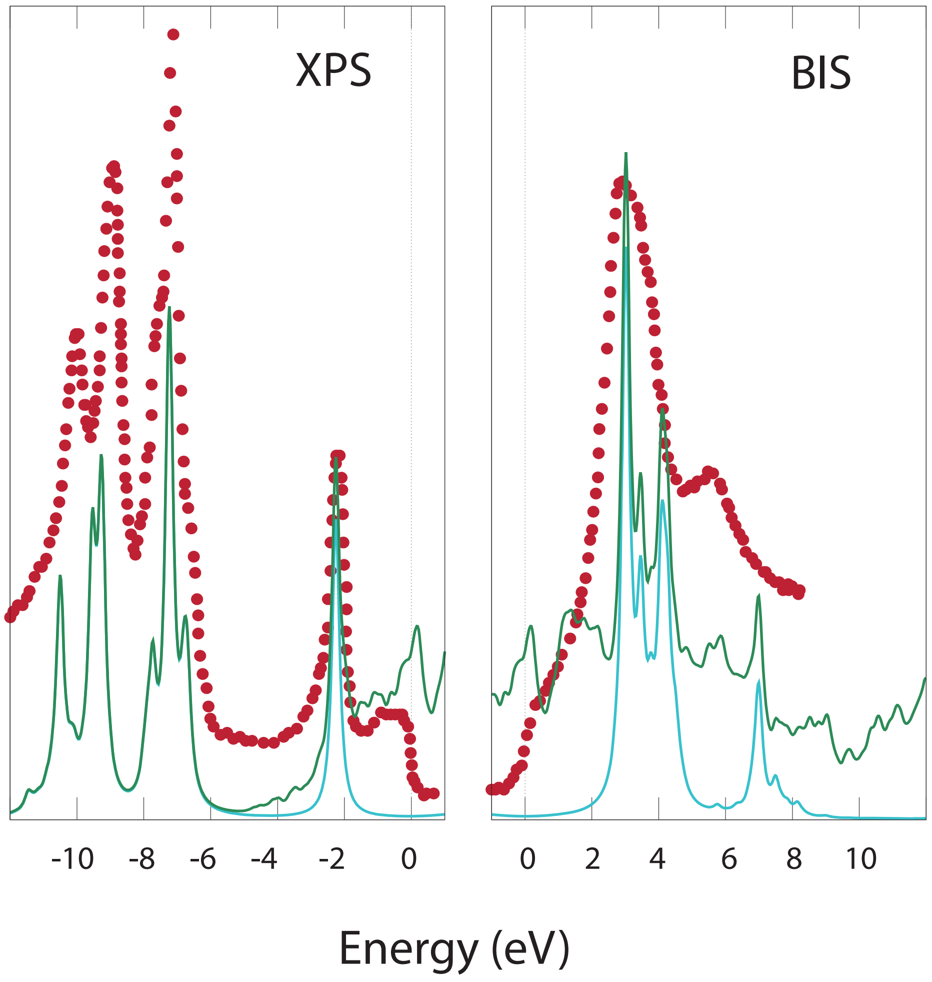


# Valence band spetra of rare-earths

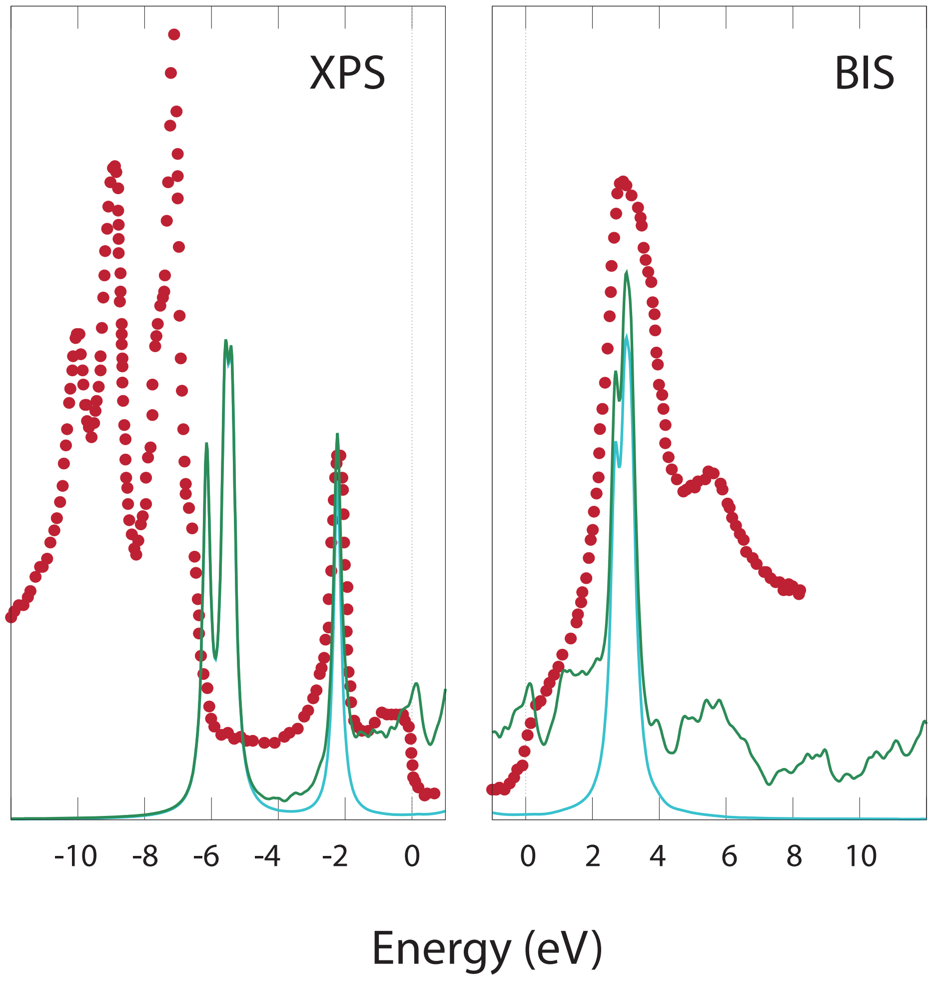
(Loch et al. PRB 2016)



# GGA+HIA and GGA+U for Tb

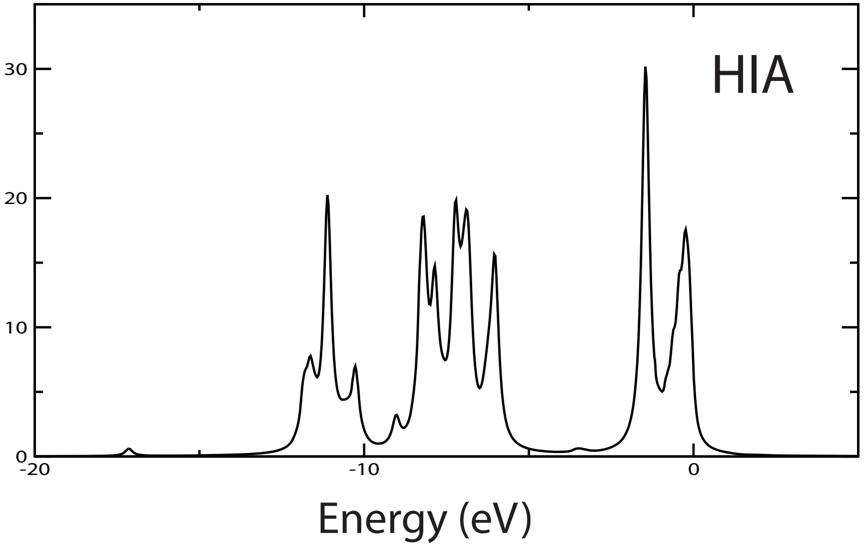


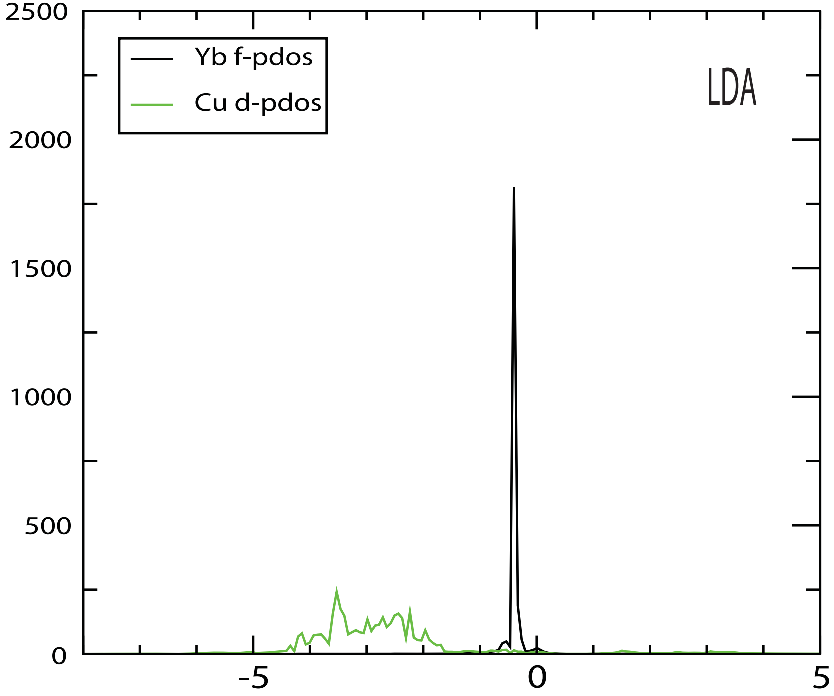
(a)HIA



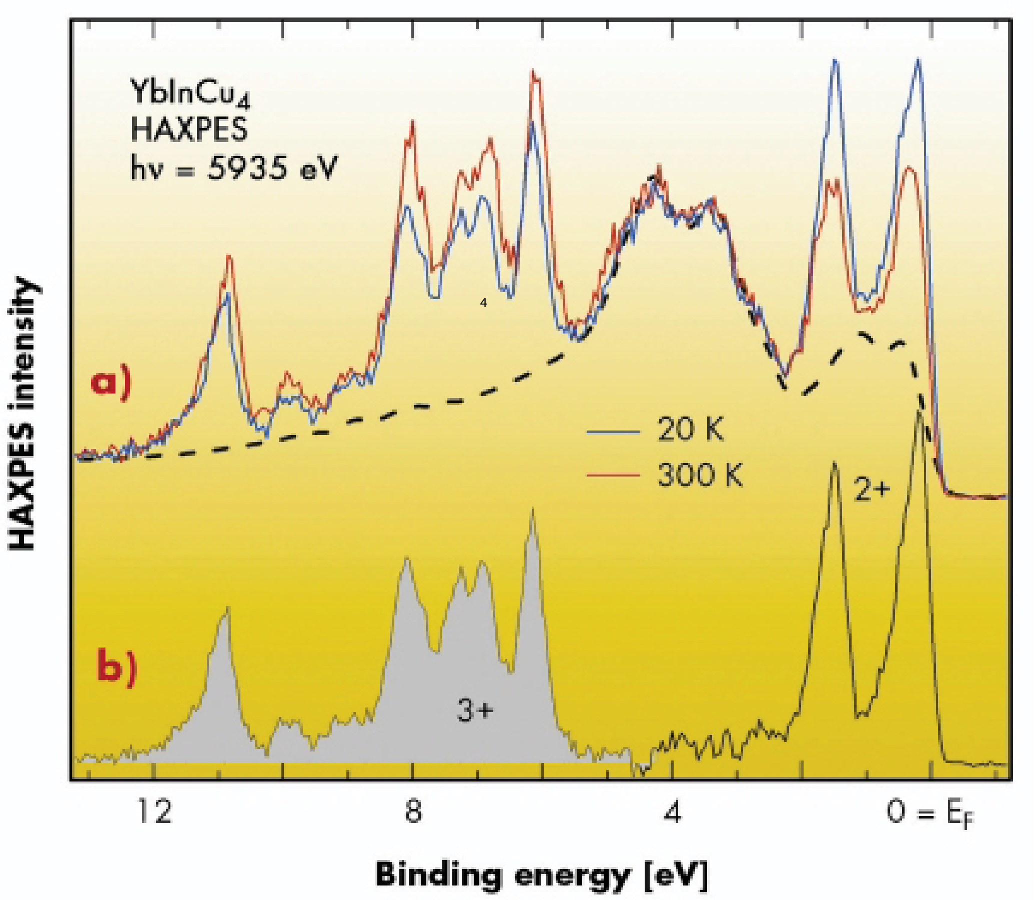
(b)LDA+U

# Spectral properties from a mixed valent compound: $YbInCu_4$





## Experimental XPS spectrum



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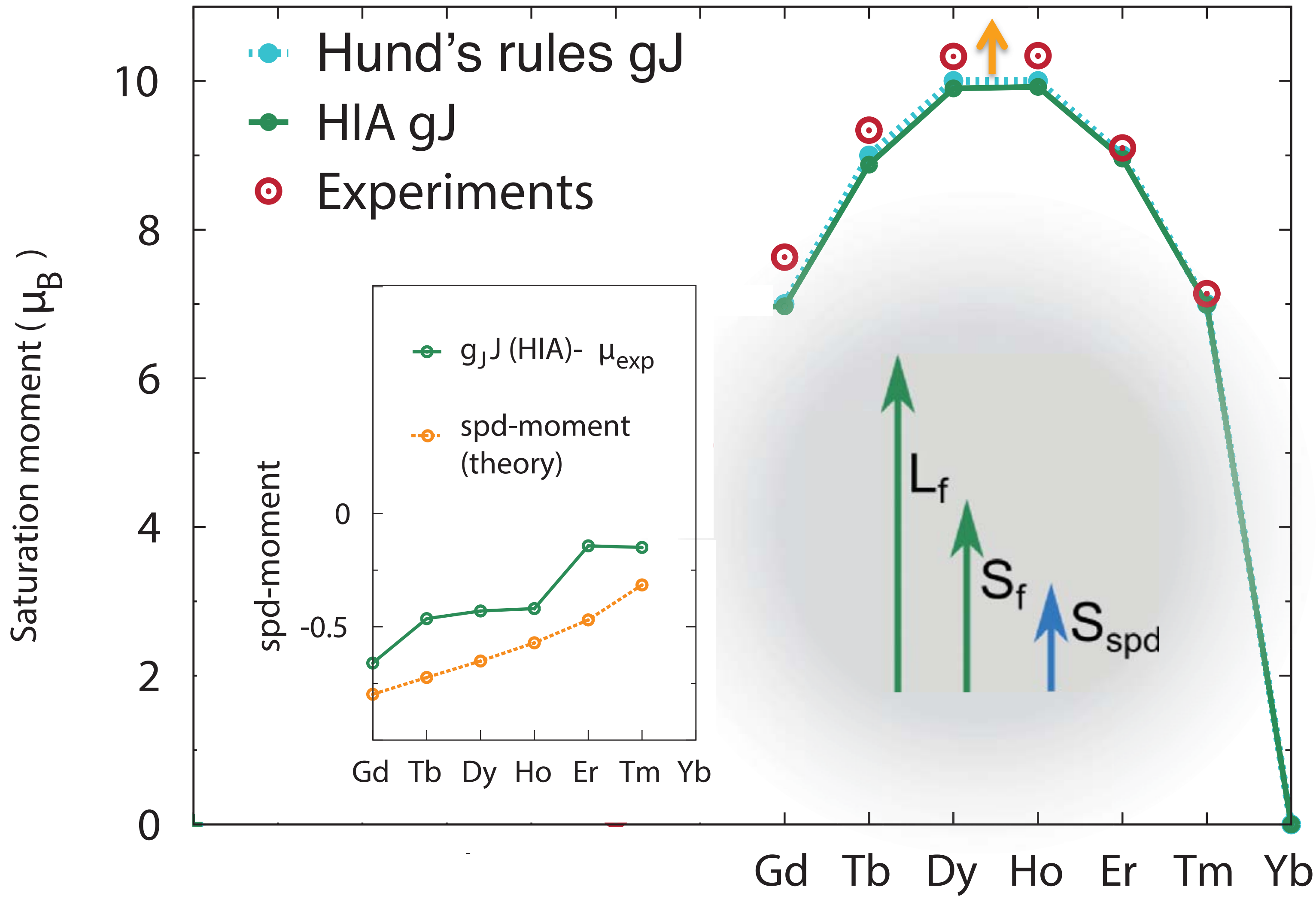
# Magnetic properties



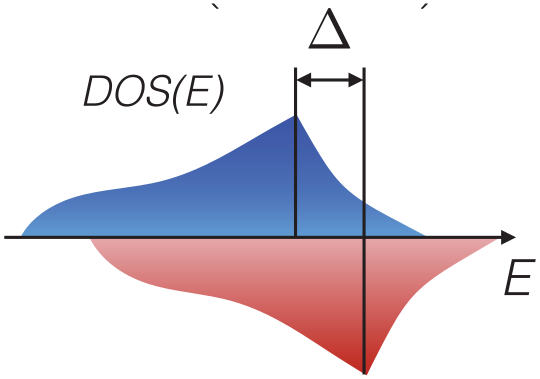
# Exchange parameters

Expansion of the Hamiltonian in $\delta\vec{\theta}_i$ and $\delta\vec{\theta}_j$ gives

$$J_{ij} = \frac{-1}{4\pi}\int_{-\infty}^{E_\mathrm{F}} \delta\epsilon\,\mathrm{Tr}_m\left[\Delta_i \cdot G_{ij}^{\uparrow}(\epsilon)\cdot\Delta_j\cdot G_{ij}^{\downarrow}(\epsilon)\right]$$

Local exchange field

$$\Delta_i = (\hat{H}_i^{\uparrow} - \hat{H}_i^{\downarrow})$$

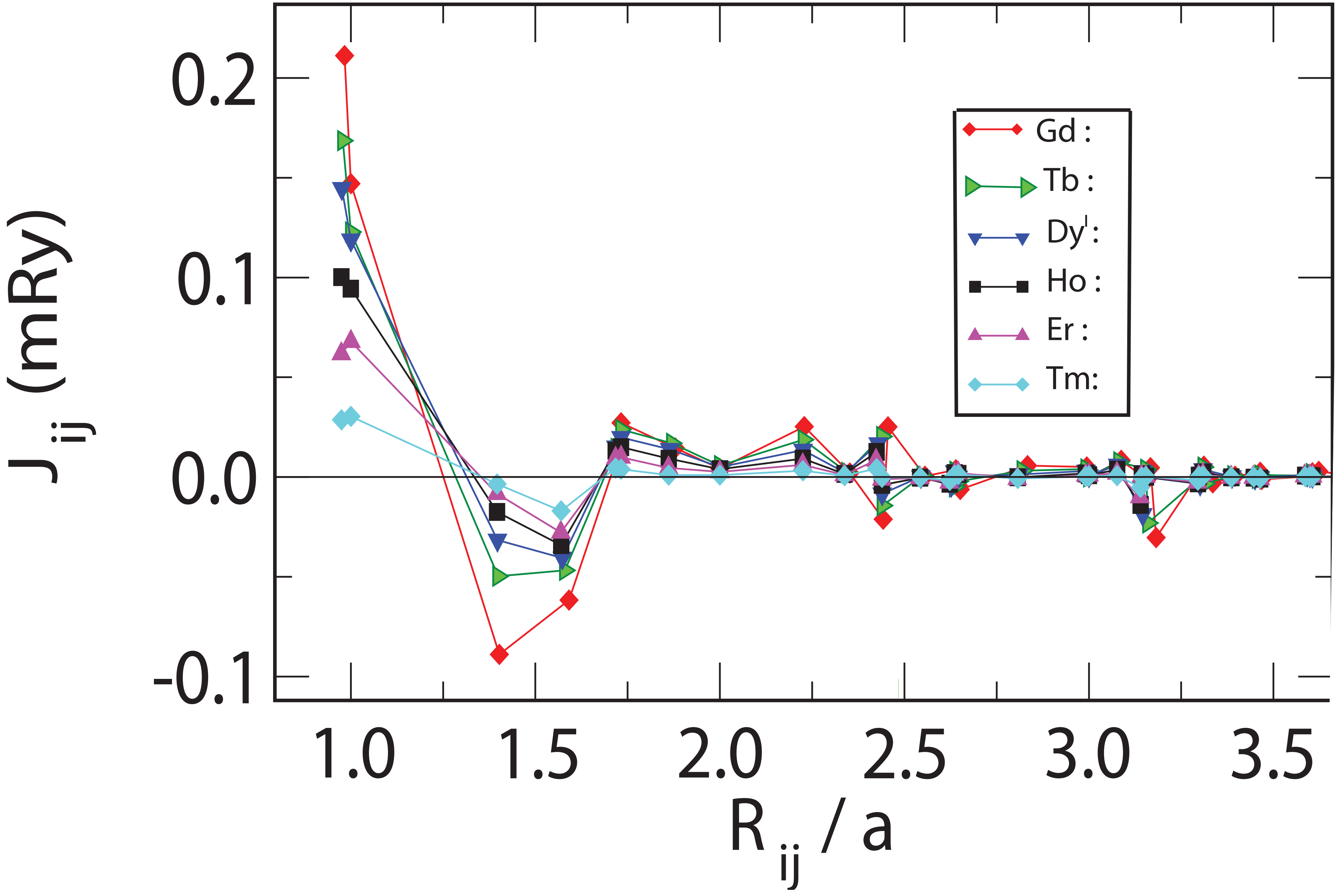


Inter-site Greens function

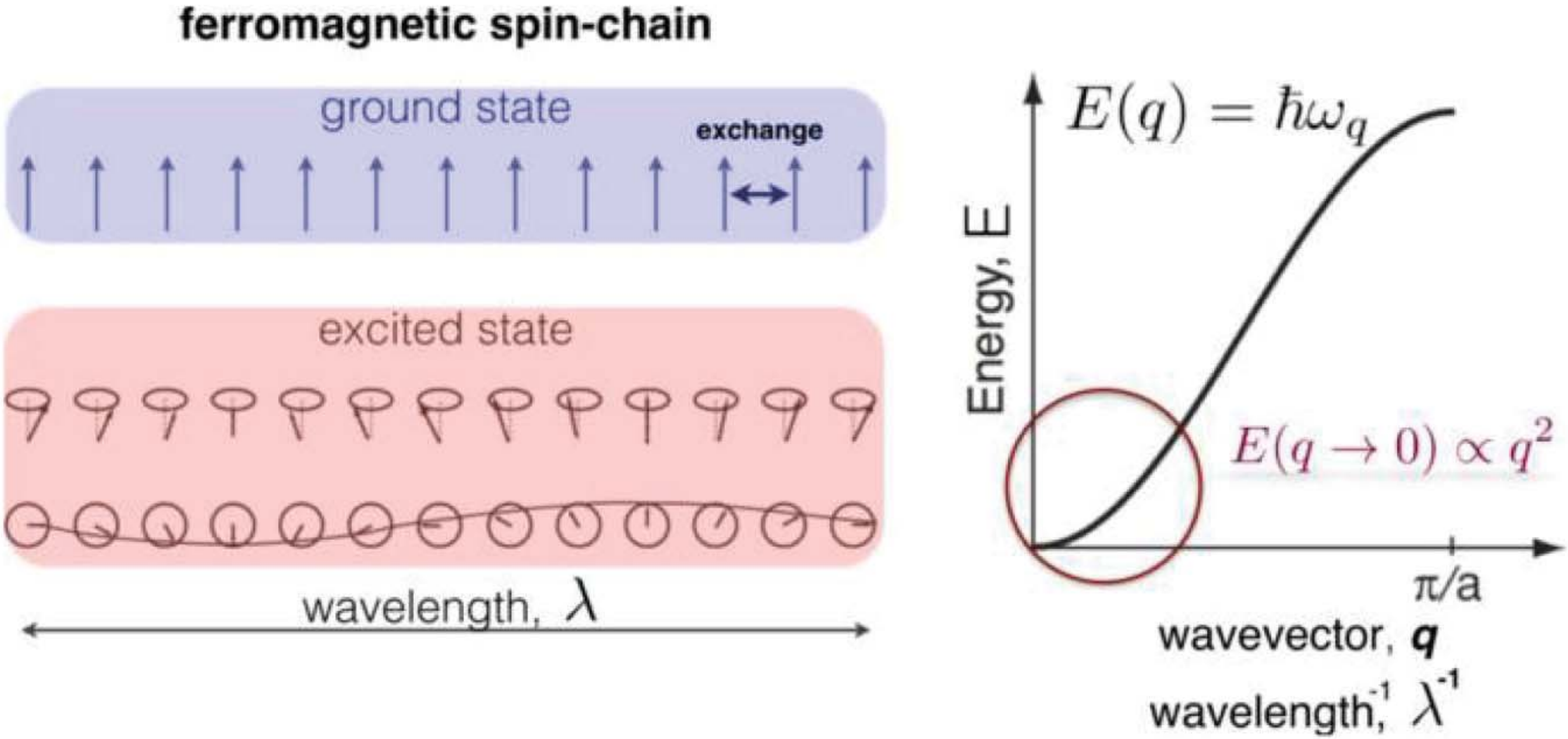
$$G_{ij}^{\sigma} = \left\langle i \middle| \hat{G}(z) \middle| j \right\rangle = \left\langle i \middle| \frac{1}{z-\hat{H}^{\sigma}} \middle| j \right\rangle$$

Lichtenstein *et al* JMMM **67** 65 (1987),
Katsnelson *et al* PRB **61** 8906 (2000),
Kvashnin *et al* PRB **91** 125133 (2015)

# Exchange parameters



# Magnons



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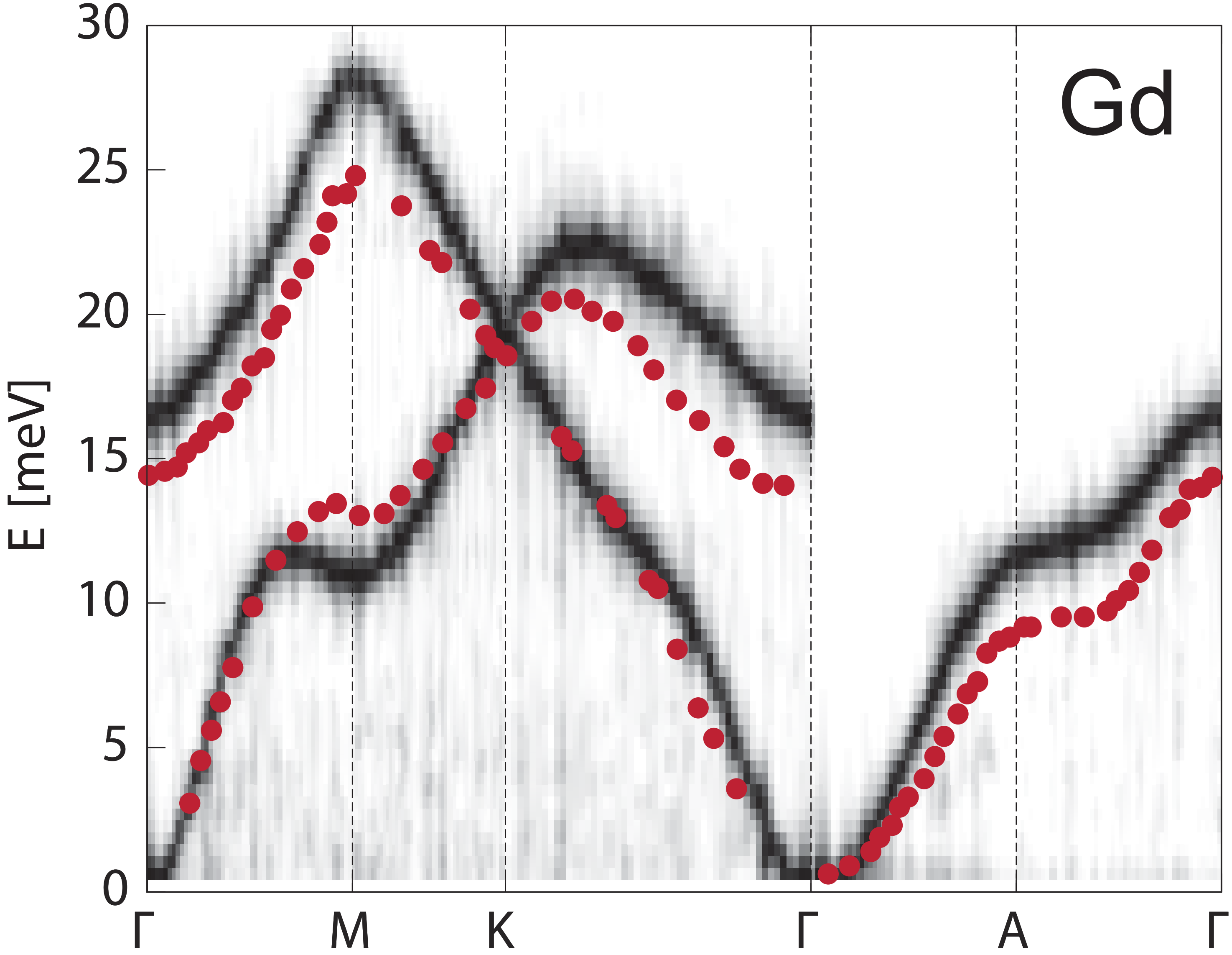
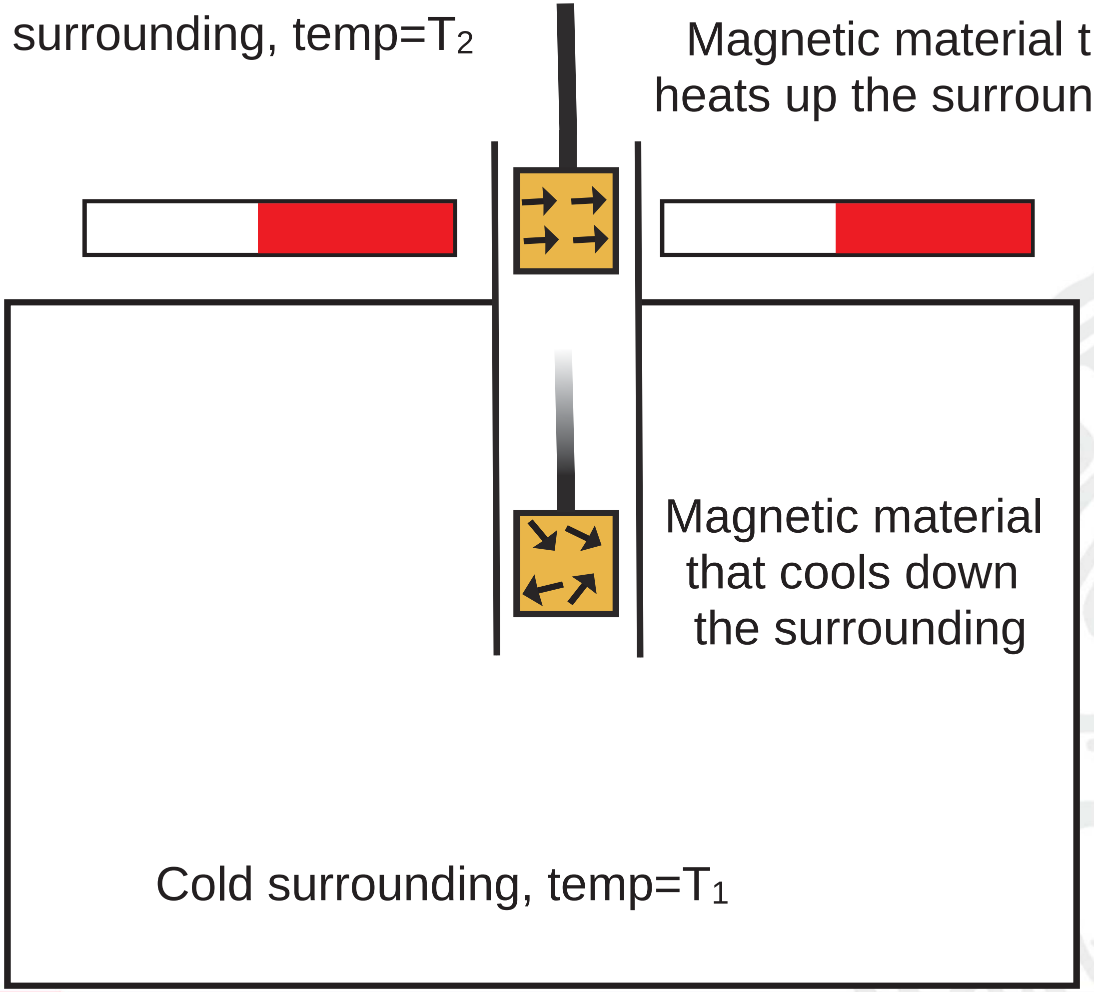
# Spin wave dispersion spectrum



# Magnetic refrigeration I



Warm surrounding, temp=$T_2$

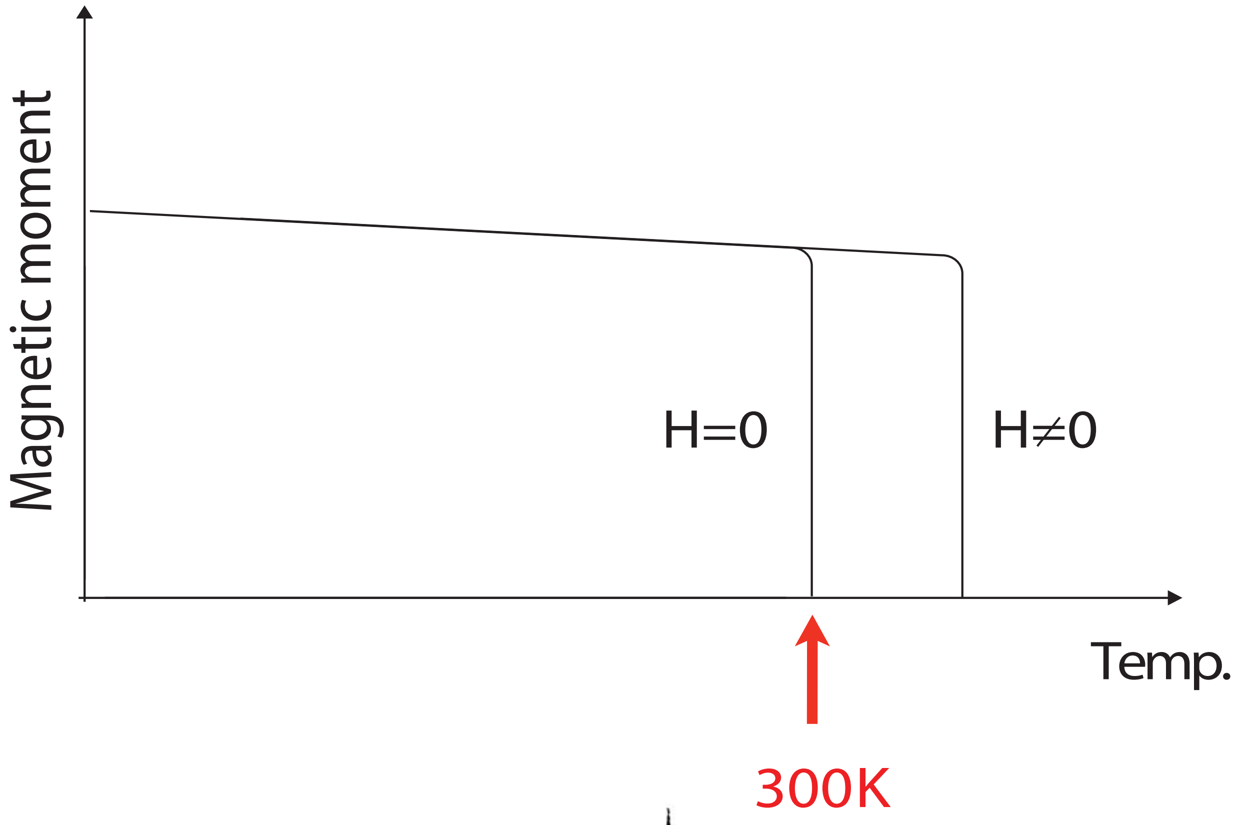
Magnetic material that heats up the surrounding

Magnetic material that cools down the surrounding

Cold surrounding, temp=$T_1$

# Magnetocalorics

$$\Delta S_m = \mu_0 \int_0^{H_f} \left( \frac{\partial M(T,H)}{\partial T} \right)_H dH$$



# Relevant equations

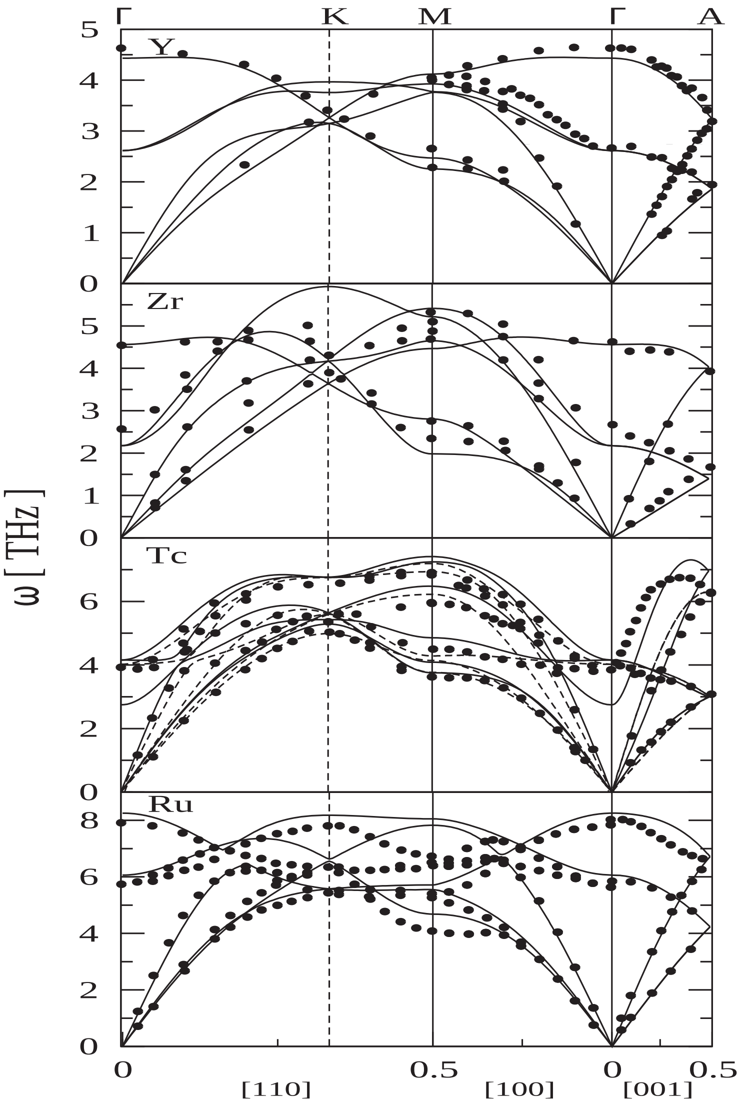
$$S_{tot} = S_{el} + S_{lat} + S_{mag}$$

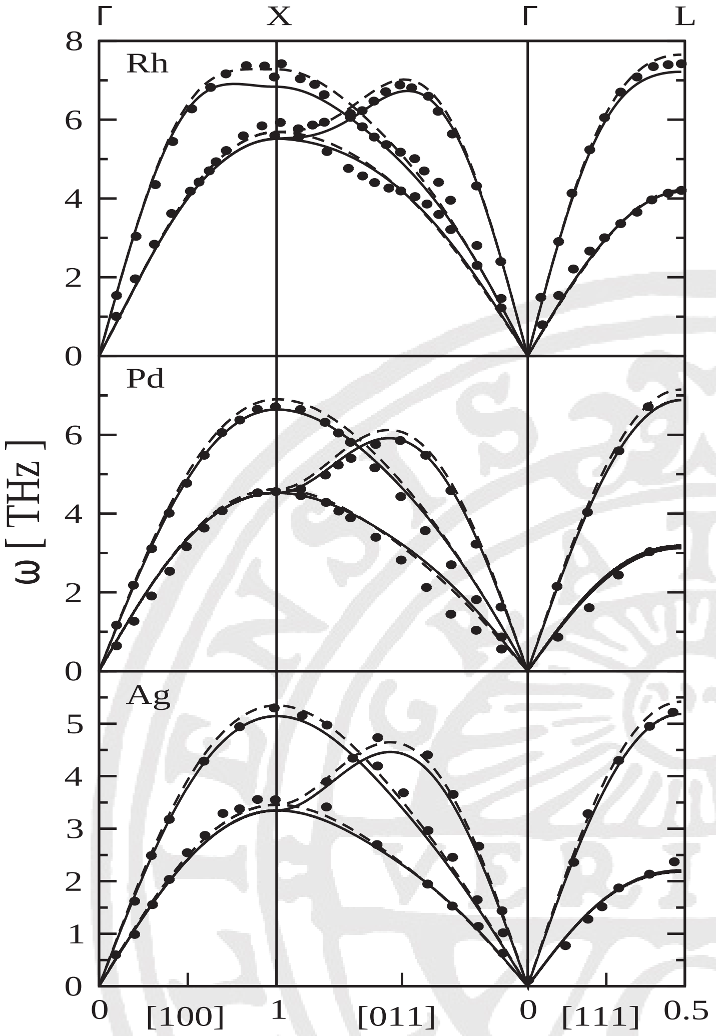
$$S_{el} = -k_B \int D(e)([1 - f(e,T)]ln[1 - f(e,T)] + f(e,T)lnf(e,T))de$$

$$S_{lat} = k_B \int g(e)([1 + n(e,T)]ln[1 + n(e,T)] + n(e,T)ln[n(e,T)])de$$

$$S_{mag}(T) = \int_0^T \frac{C(H,T')}{T'}dT'$$

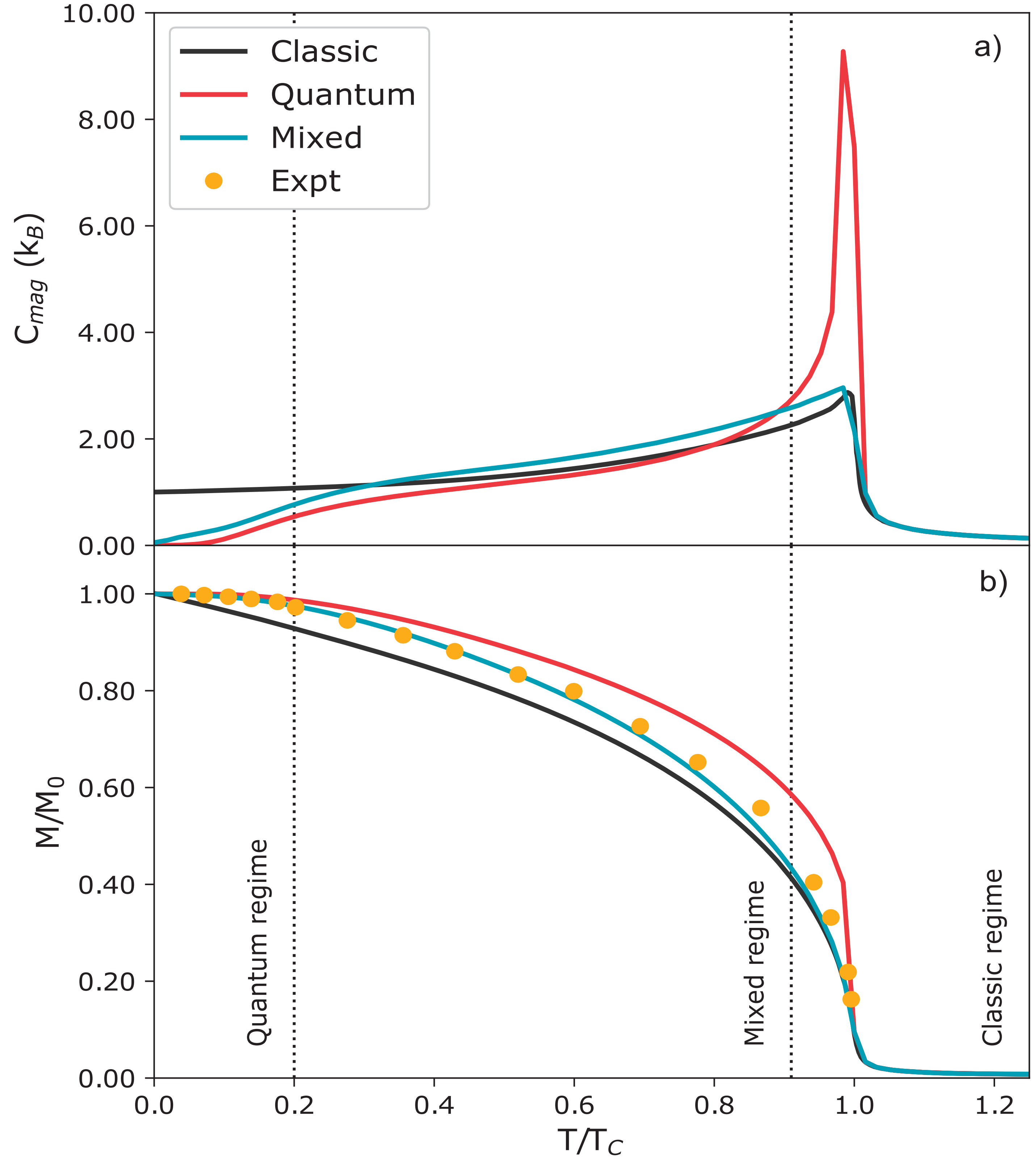
# Phonons of transition metals

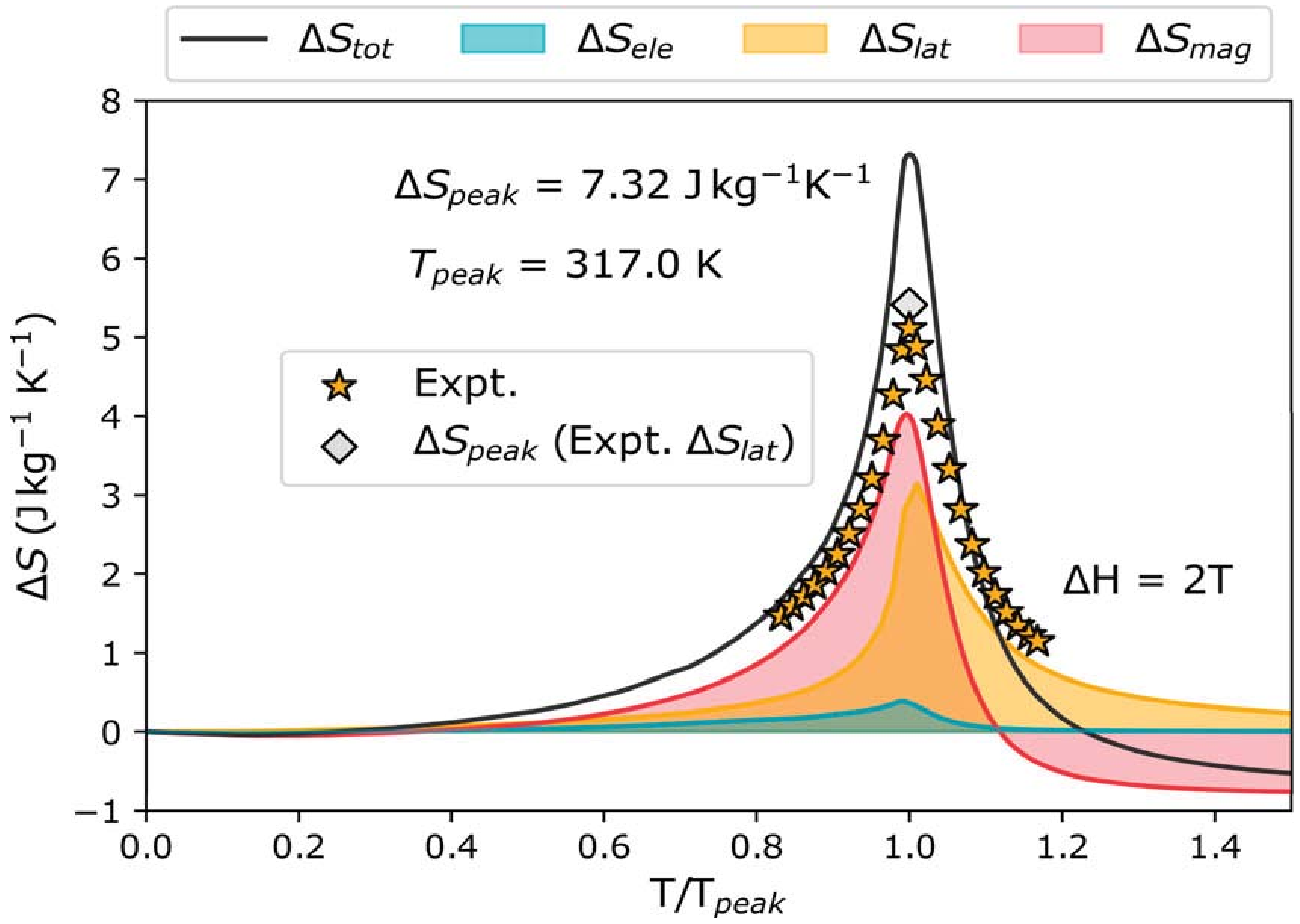




Souvatzis et al., PRB 77, 24110 (2008)

# Data for hcp Gd





Expt: Gottschall et al. Energy Materials 9, 1901322 (2019)
Theory: Vieira et al. Mat. Res. Lett. 10:3, 156 (2022)

# Spin glass state of Nd

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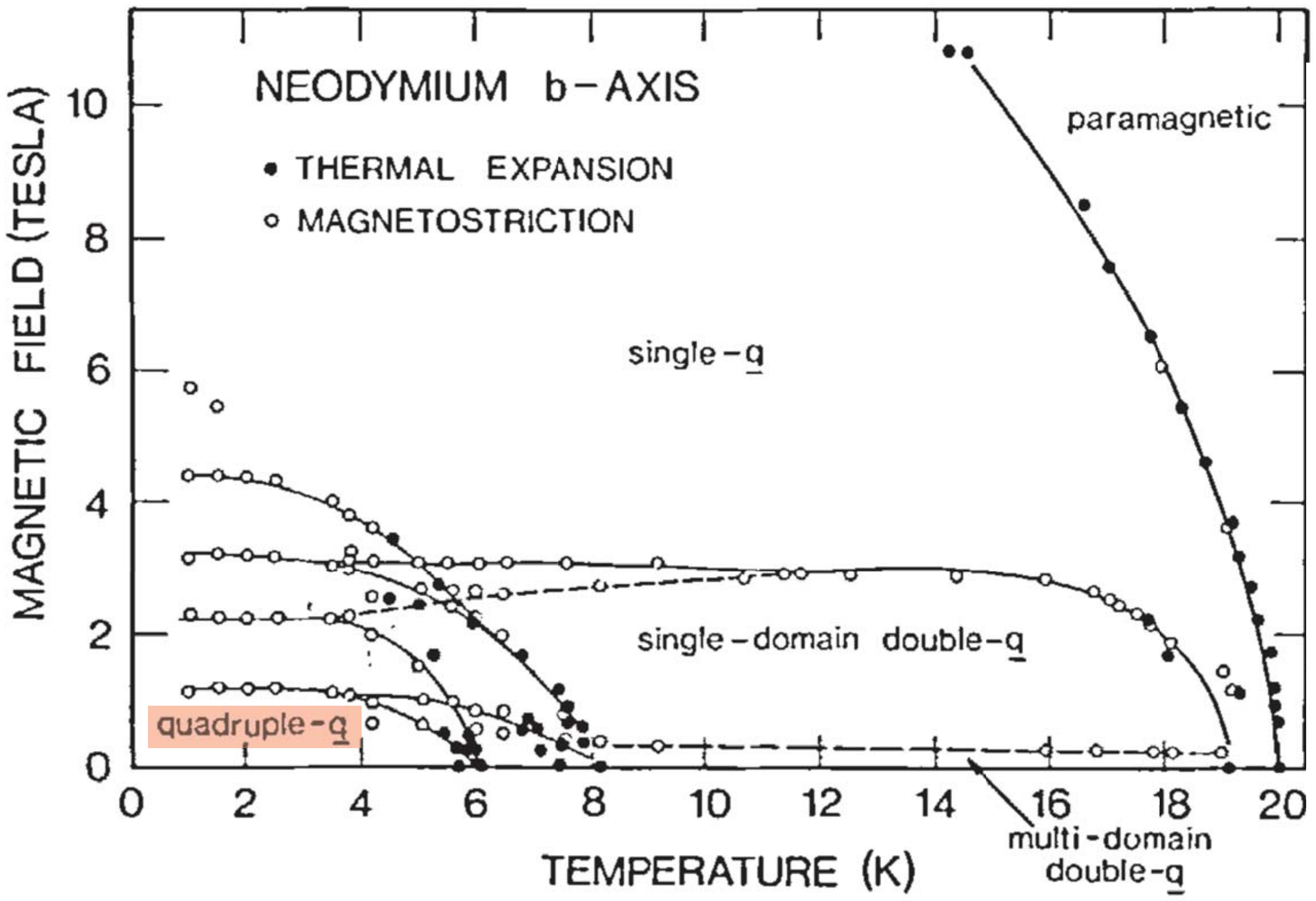
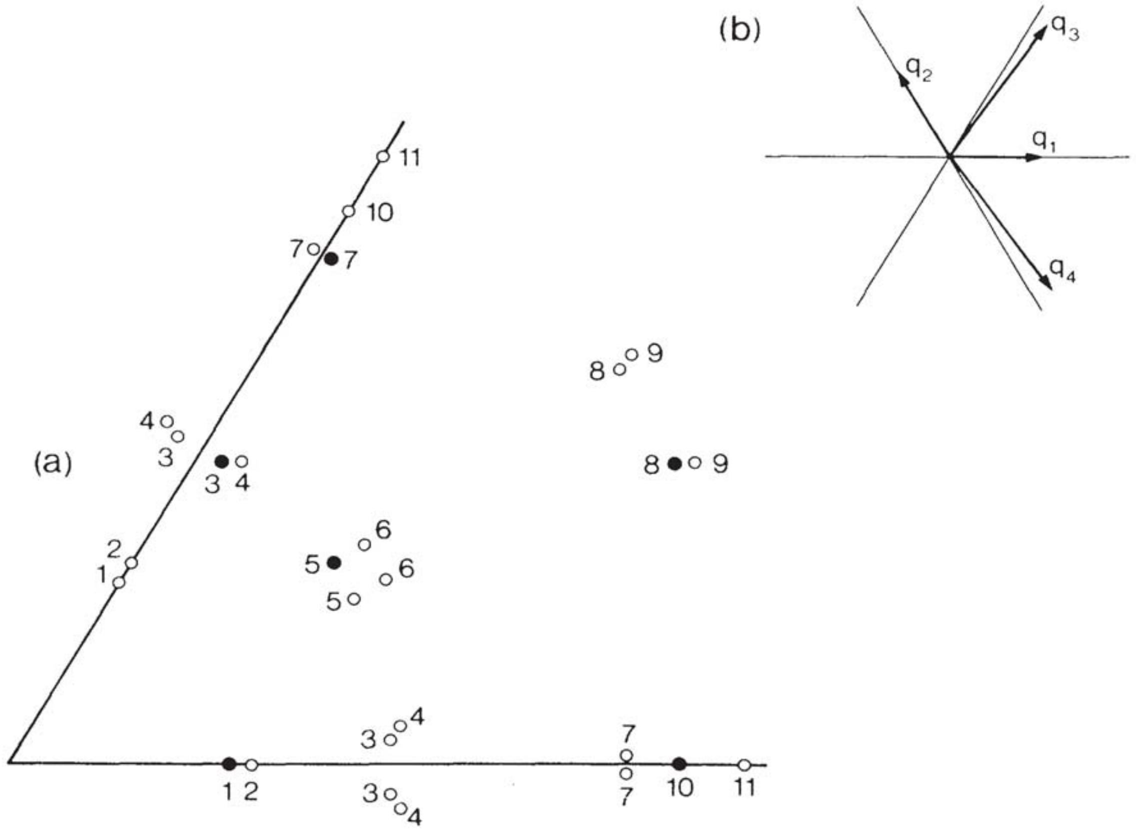
# Magnetic phases of Neodymium

Phase diagram



McEwen and Zochowski, JMMM **90** 94 (1990)

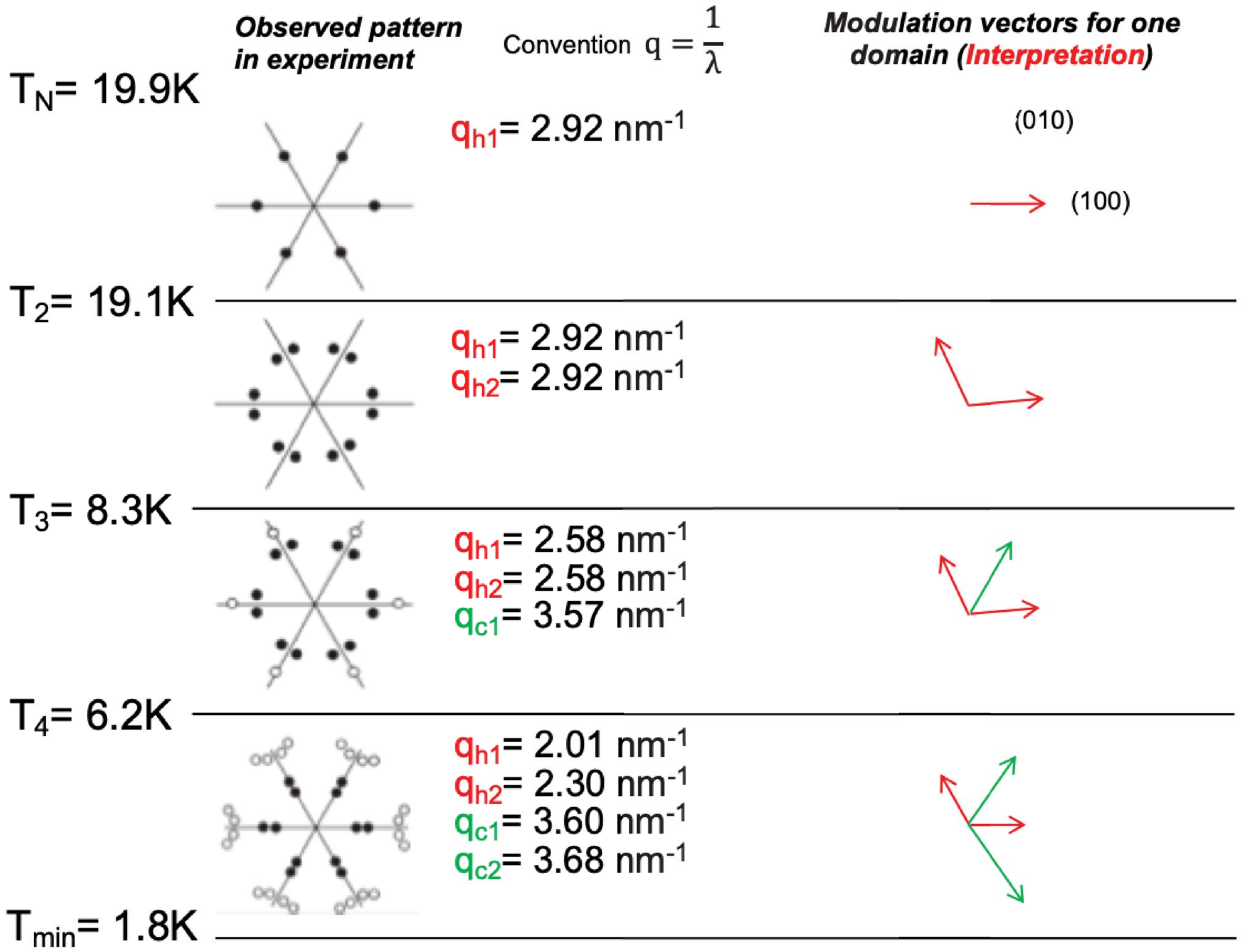
Neutron scattering peaks: multi-q



Forgan et. al, PRL **62** 470 (1989)

See also: Moon et al. JAP **35** 1041 (1964), Bak et al. PRL **40** 800 (1978)

# Magnetism of Nd



***Observed pattern in experiment***

Convention $q = \frac{1}{\lambda}$

***Modulation vectors for one domain (Interpretation)***

$T_N$= 19.9K

$q_{h1}$= 2.92 nm$^{-1}$

(010)

(100)

$T_2$= 19.1K

$q_{h1}$= 2.92 nm$^{-1}$
$q_{h2}$= 2.92 nm$^{-1}$

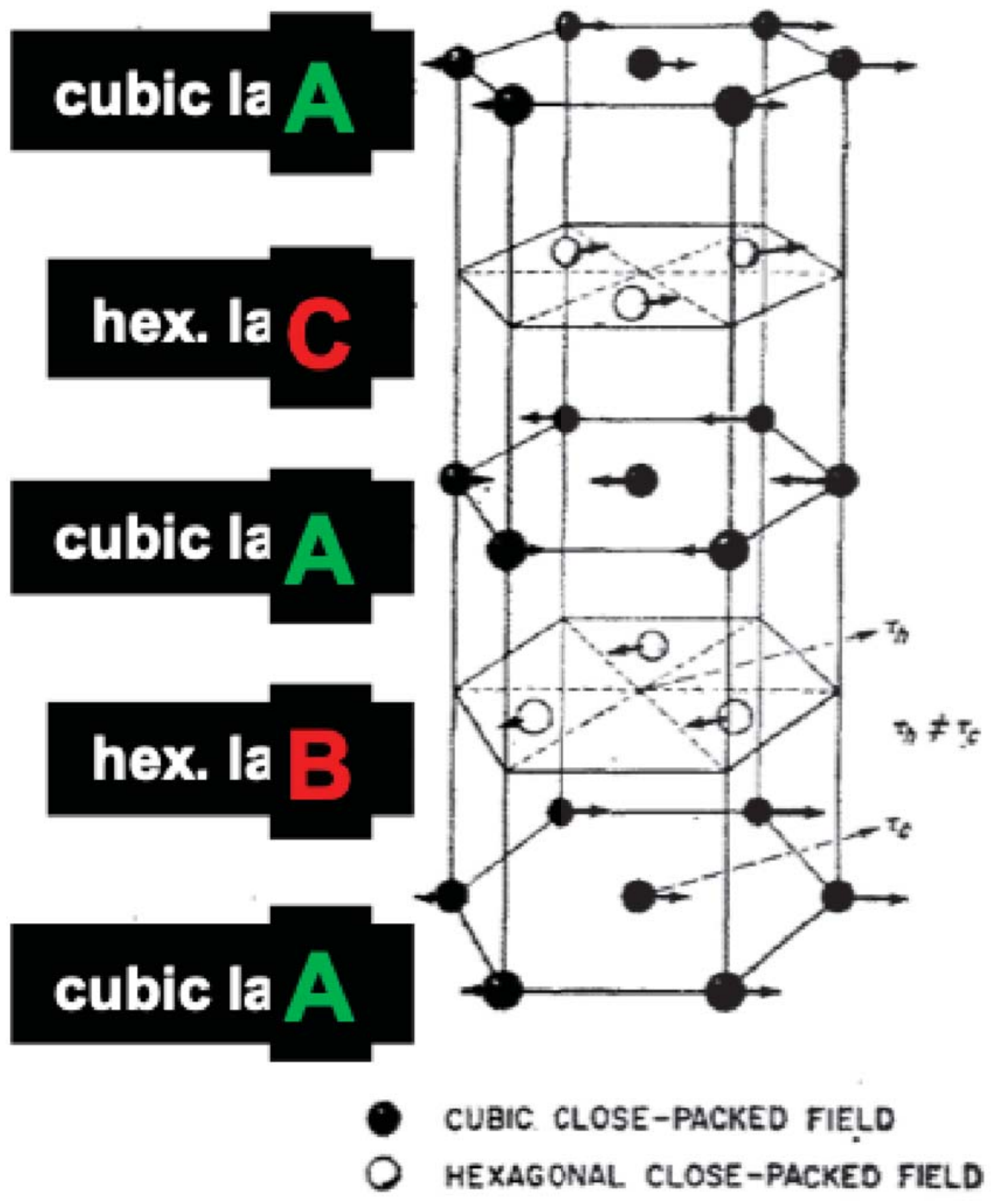
$T_3$= 8.3K

$q_{h1}$= 2.58 nm$^{-1}$
$q_{h2}$= 2.58 nm$^{-1}$
$q_{c1}$= 3.57 nm$^{-1}$

$T_4$= 6.2K

$q_{h1}$= 2.01 nm$^{-1}$
$q_{h2}$= 2.30 nm$^{-1}$
$q_{c1}$= 3.60 nm$^{-1}$
$q_{c2}$= 3.68 nm$^{-1}$

$T_{min}$= 1.8K



E.M. Forgan *et al.*, PRL **62**, 470 (1989).
E.P. Gibbons *et al.*, Physica B **180**, 91 (1993).
R. M. Moon, J. Magn. Magn. Mater. **104**, 1485 (1992).
R. M. Moon *et al.*, J. Magn. Magn. Mater. **100**, 139 (1991).

# A new look : SP-STM

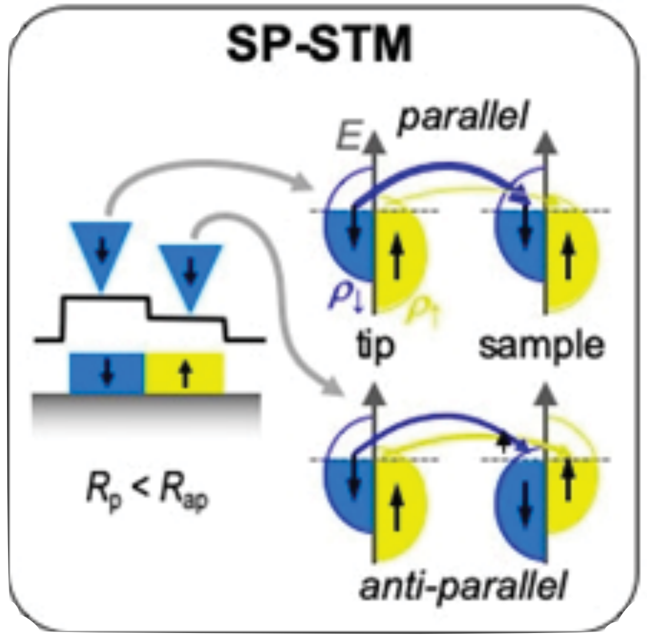
Thick (> 50ML) films of dhcp Nd(0001) grown on W(110)

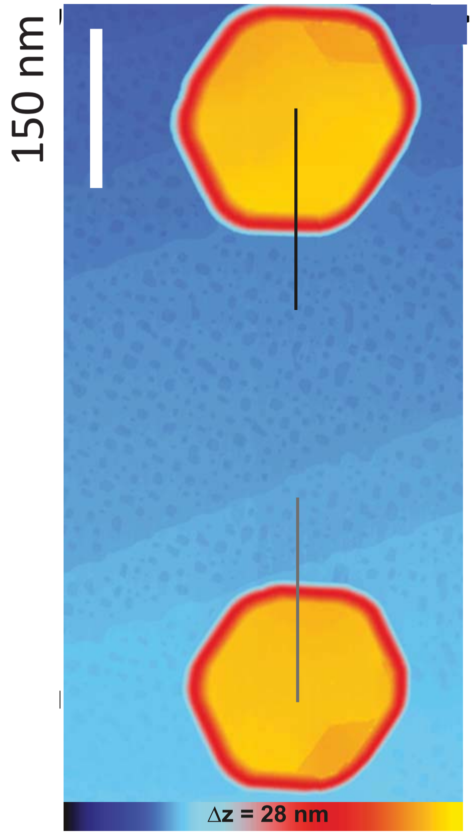
Spin polarised scanning tunneling microscopy (SP-STM)

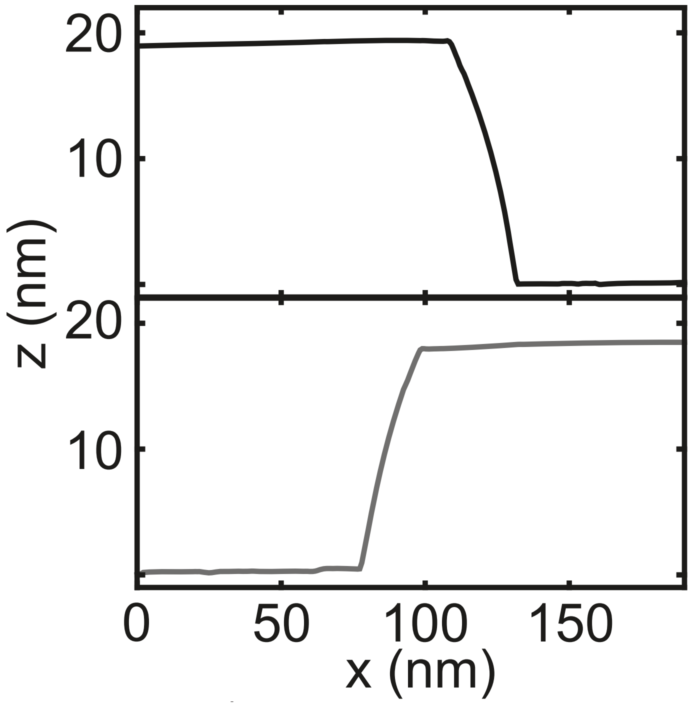
Temperatures from 30mK - 5K

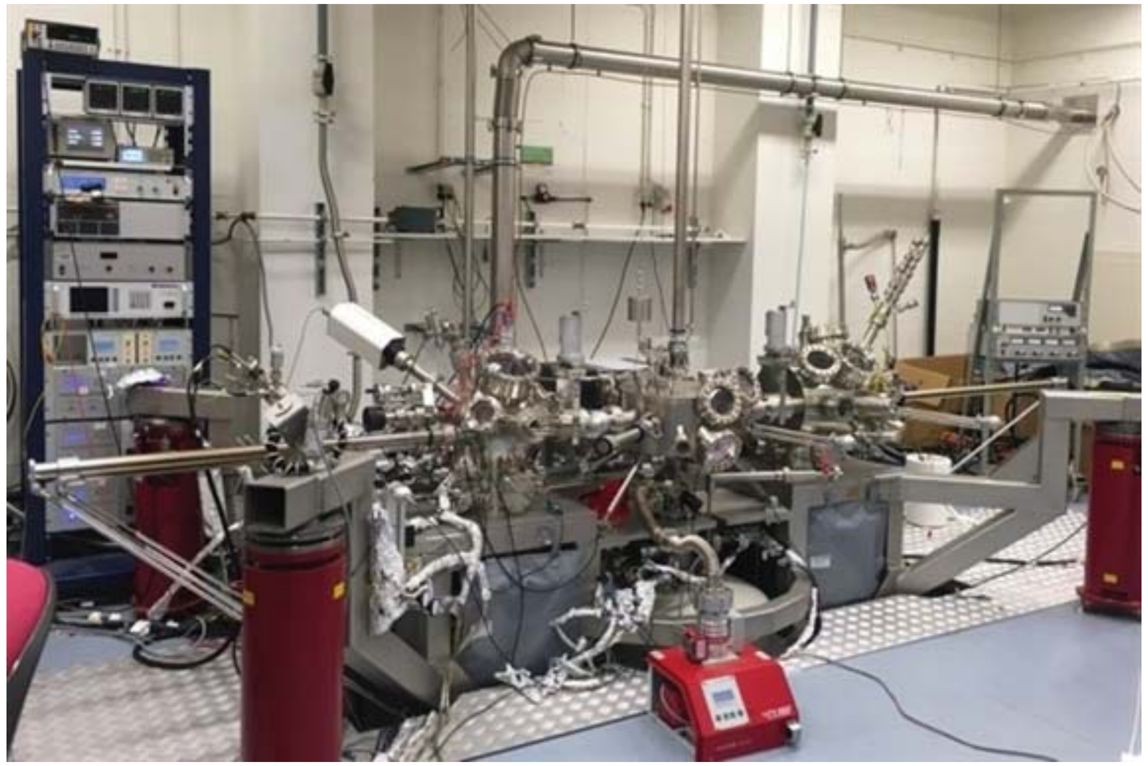
Island growth - well defined height profile

Low defect concentration - minimal disorder



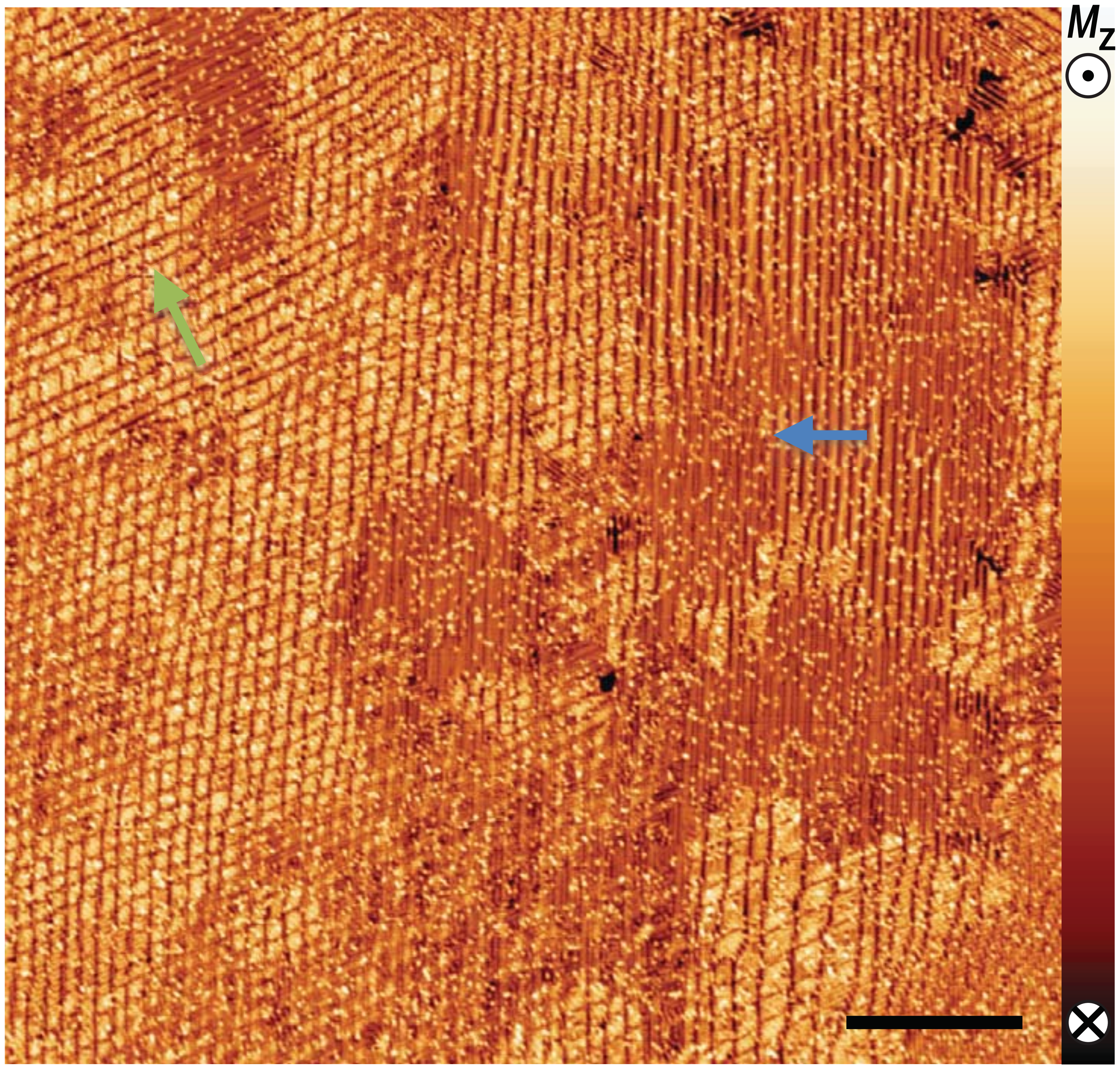






Von Allwörden et al. Rev. Sci. Instr. **89**, 033902 (2018)

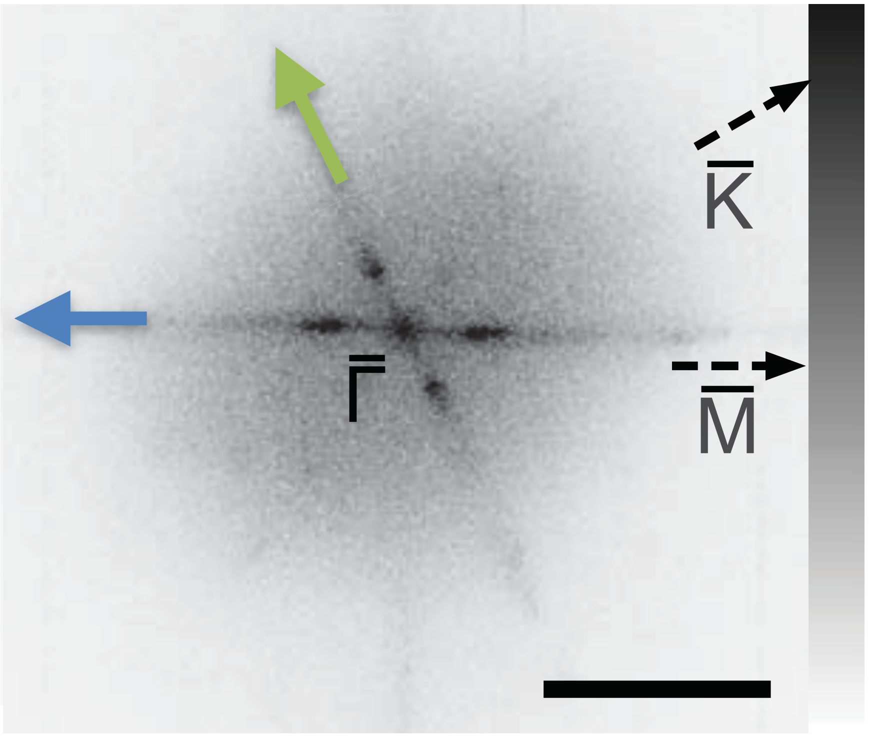
# Fourier space representation



50 nm

Striped phases:
Spin-spirals
Domains?
Multi-Q?

Distinct peaks in FFT
Noise from
lack of long range order
and numerical artefacts

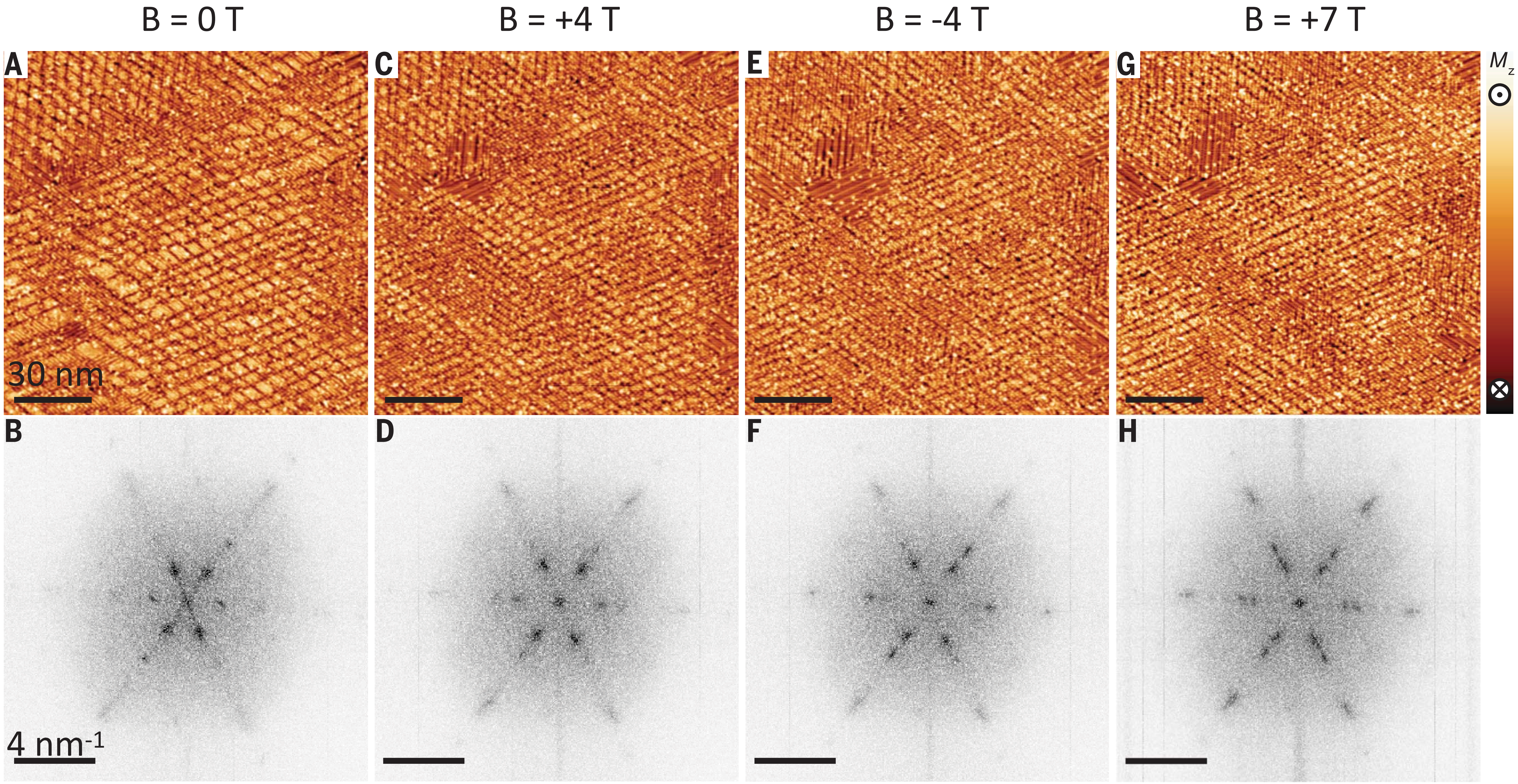


$5\ \text{nm}^{-1}$

# Applied field: Aging

Applying field for a duration of $10^5$ s at 1.3 K. No apparent relaxation after removal of field.

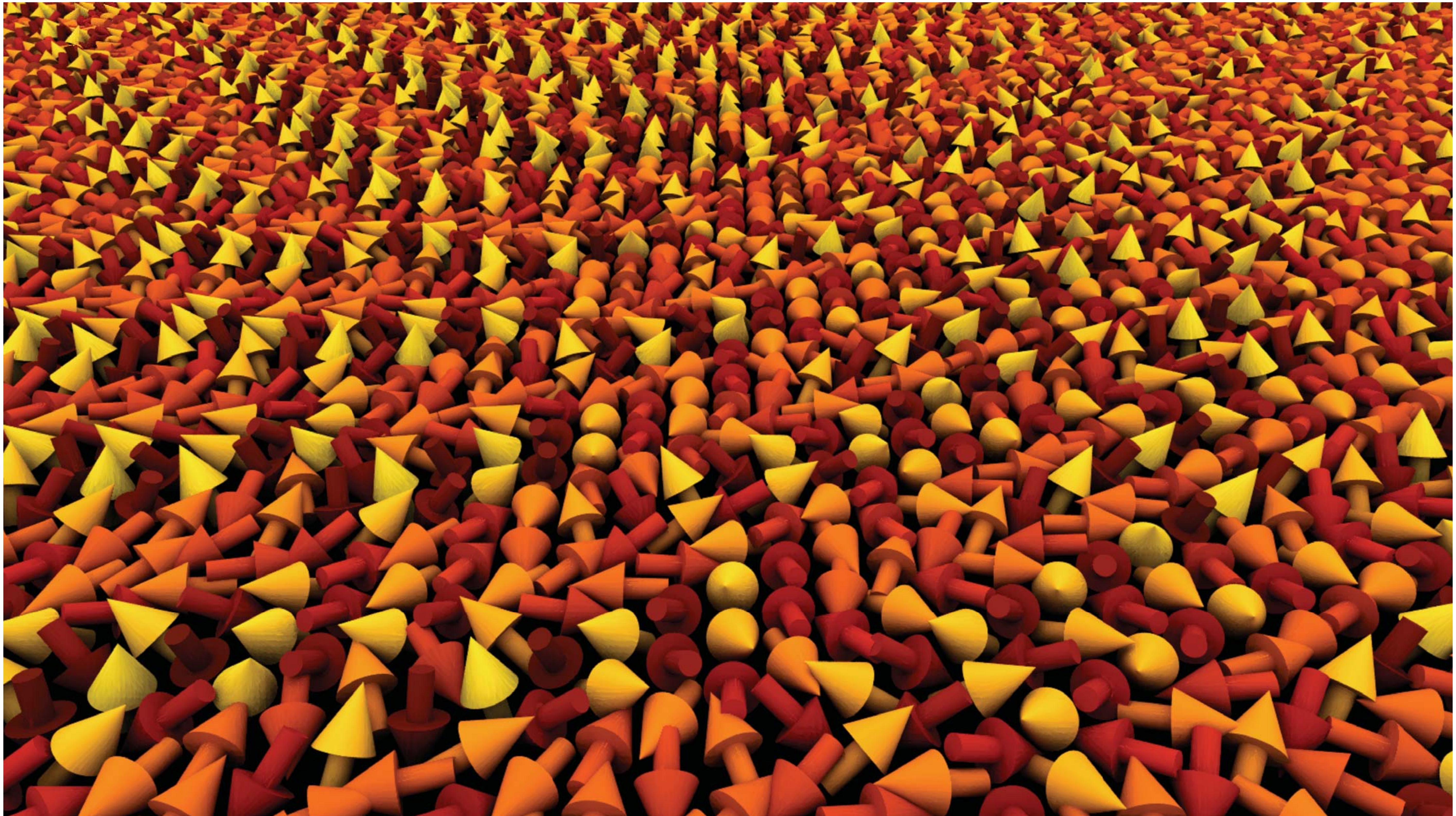
Continued dynamics: Aging



# Summary SP-STM experiments

- SP-STM imaging of clean thick films of dhcp Nd
- Magnetic contrast shows mixture of spin spirals
- Short range order
- Lack of long range order
- Field response do not cause single domain structures
- No clear relaxation after field cycling: Aging

# Simulations from ab initio exchange interactions



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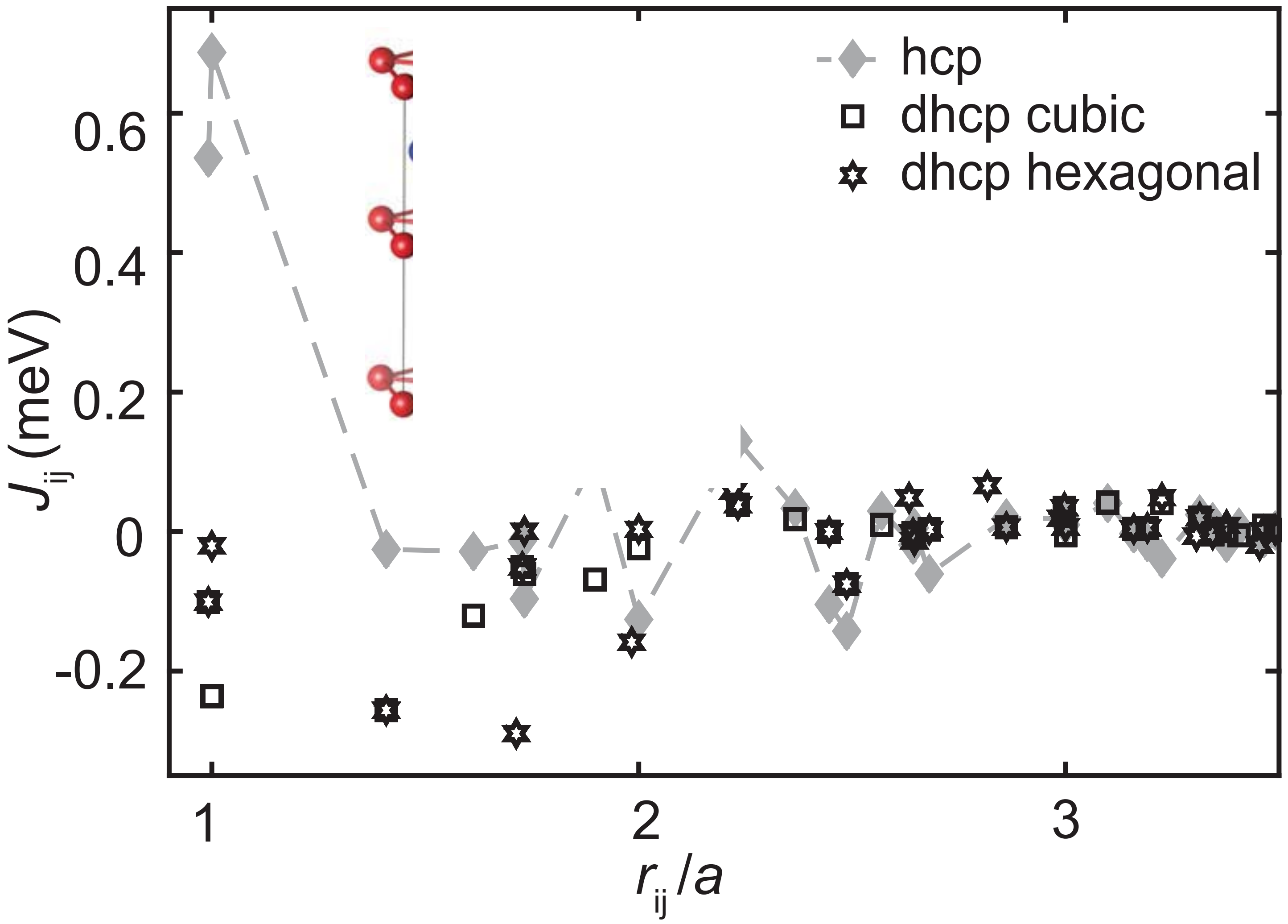
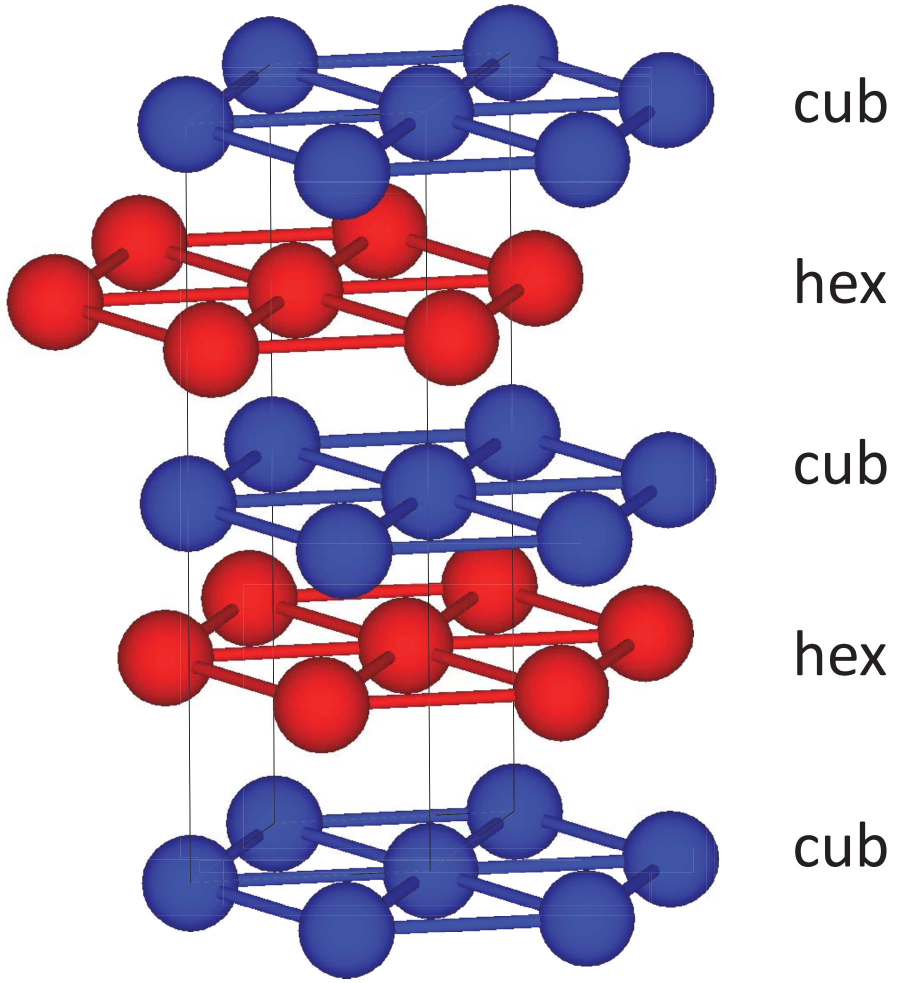
# Ab initio exchange interactions





The interactions $J_{ij}$ are calculated using DFT for bulk dhcp Nd

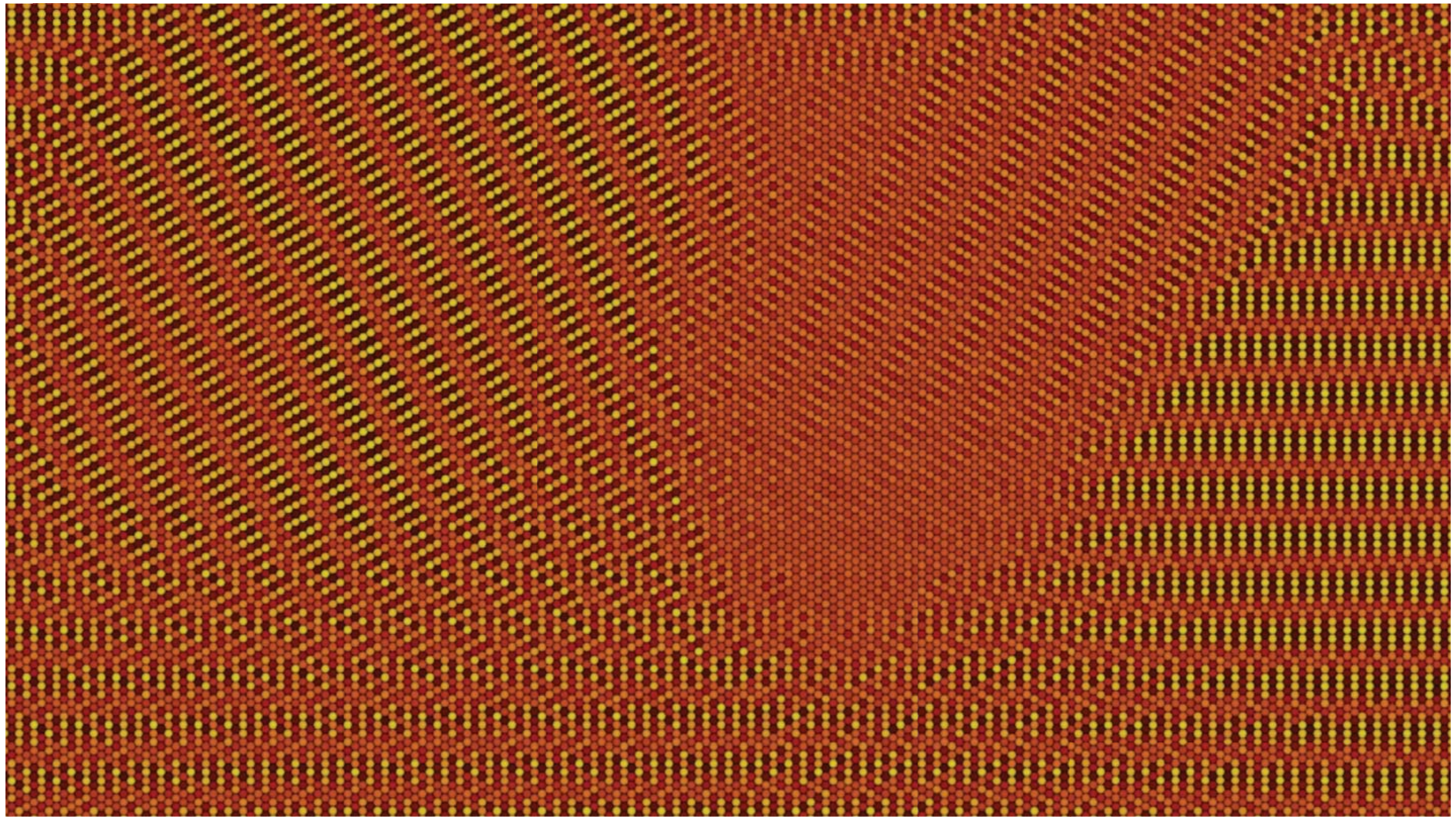
Nd was modelled using the standard model of the Lanthanides,
i.e. 4f electrons are treated as local and unhybridized core-like states

Mostly negative interactions: Tendencies towards AF/spiral ordering or frustration

*The full-potential LMTO code RSPt: J. M. Wills et al., "Full-Potential Electronic Structure Method" (Springer, 2010).*

# Comparison with experiment

MC quench from T=7K to 5 mK



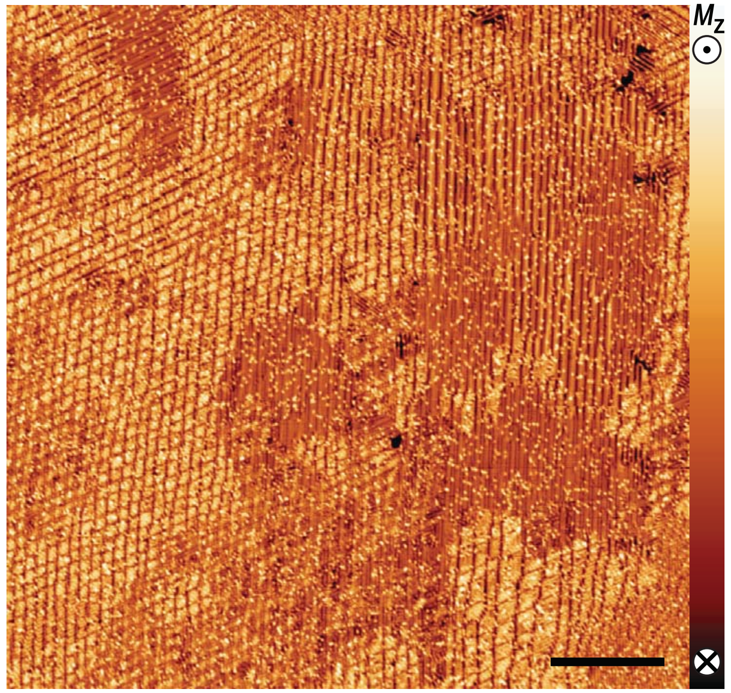
Intertwined spirals with several wave vectors.

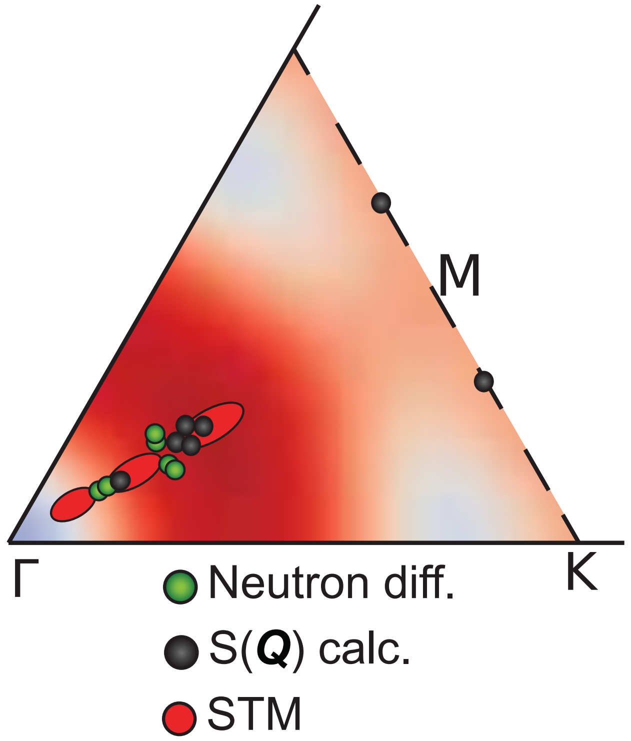
The system is very sensitive to the relaxation protocol.

Simulated annealing can give more homogeneous patterns.

Static correlation function S(q) obtainable from the simulations.

SP-STM image





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# Dynamics: Autocorrelation

ASD gives access to spatial and temporal correlation functions from moment trajectories

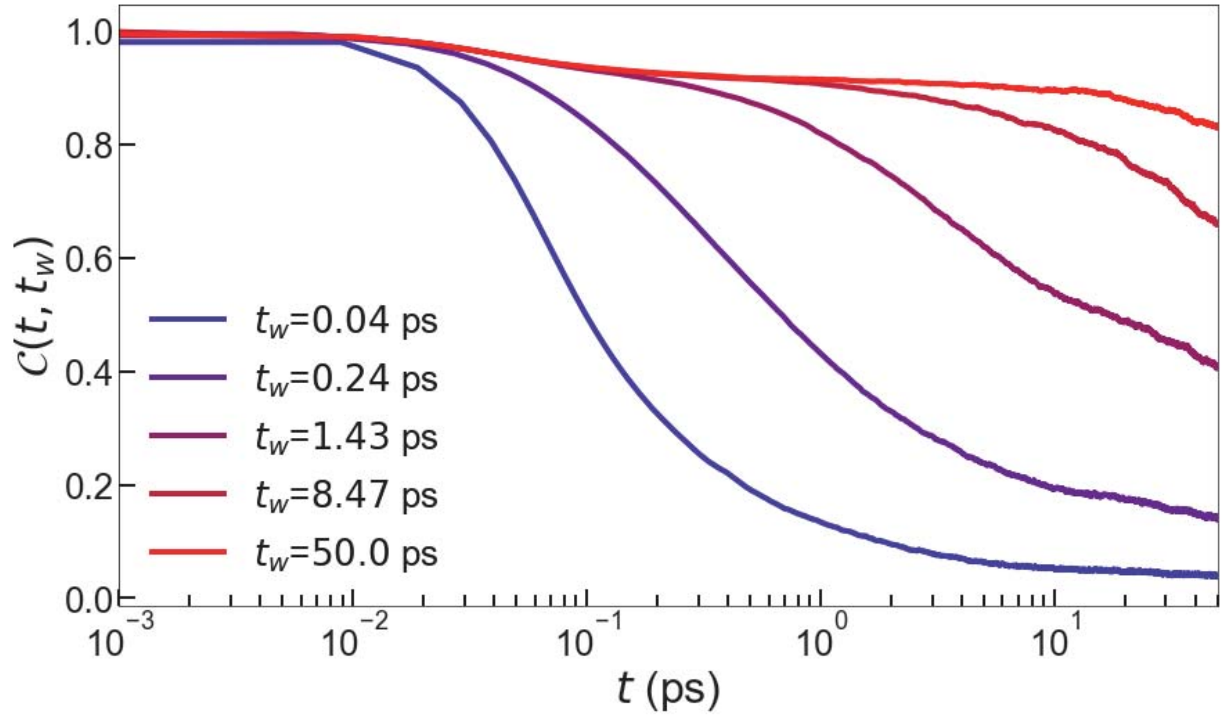
Of particular interest here is the two-time autocorrelation function

$$C(t_w, t) = \langle \mathbf{m}_i(t + t_w) \cdot \mathbf{m}_i(t_w) \rangle$$

Which typically shows a logarithmic decay for spin glass systems.

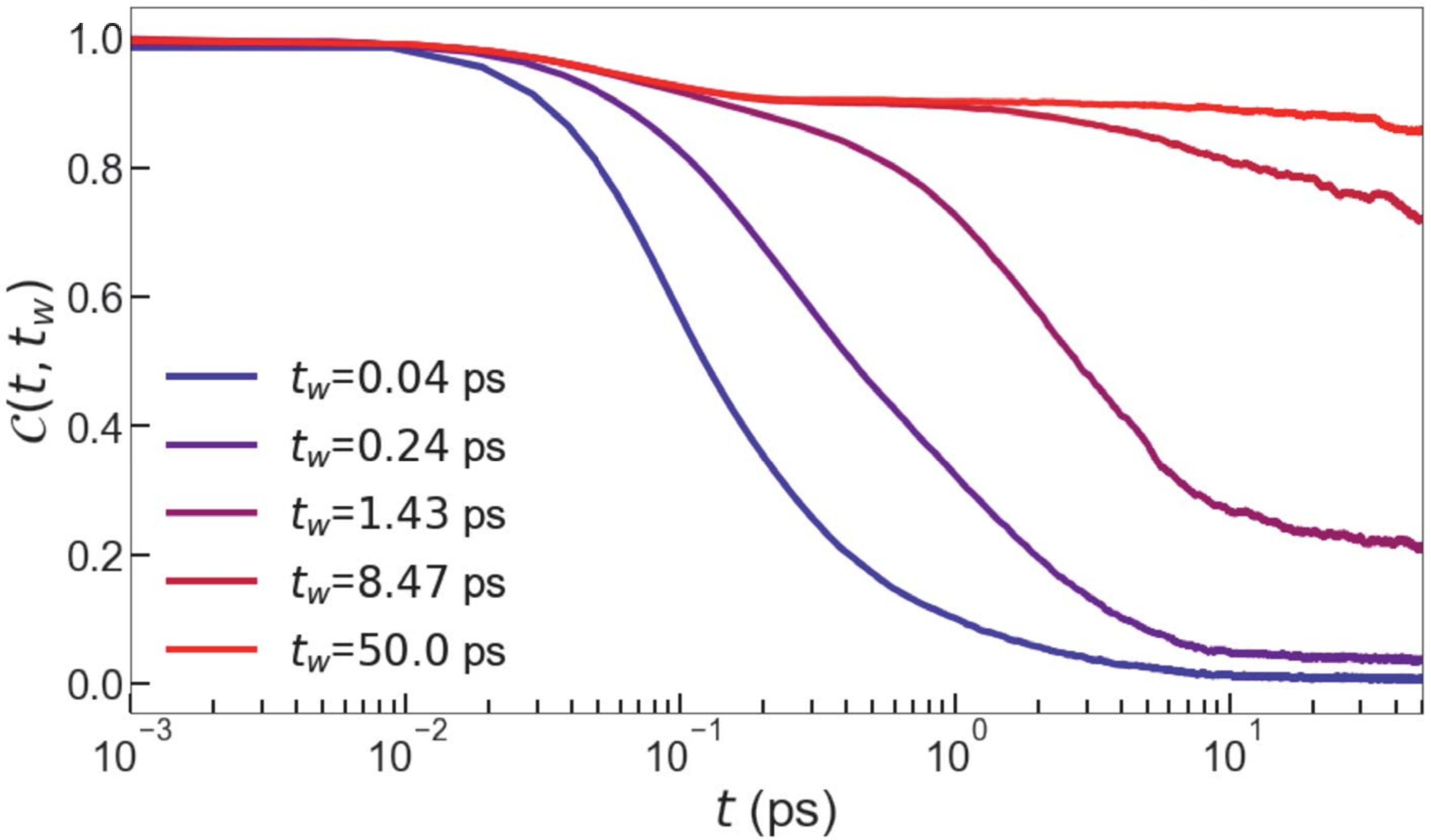
<u>Model example:</u>

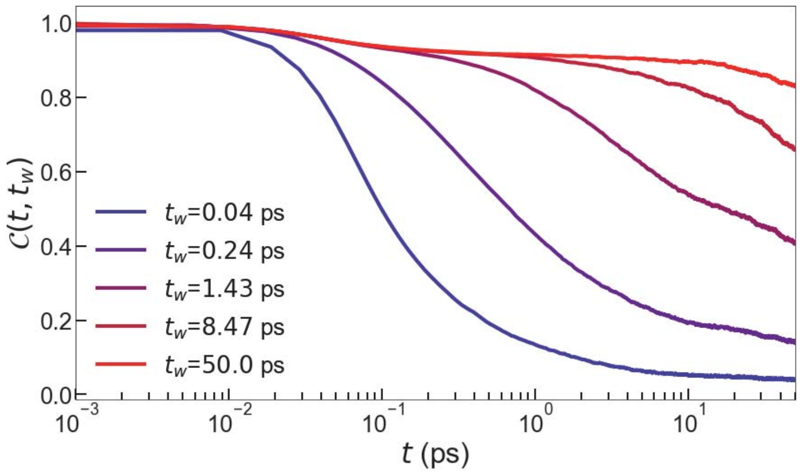
Edwards-Anderson exchange (random) on the dhcp lattice



# Dynamics: Autocorrelation

Nd with ab initio exchange interactions. T=1.0 K





Reference:
Edwards-Anderson exchange (random) on the dhcp lattice

Similar relaxation behaviour with respect to waiting times as the EA model

Ongoing dynamics across several time scales: **glassy behaviour**!

Remember: Experiments showed similar behaviour over $10^5$ s.

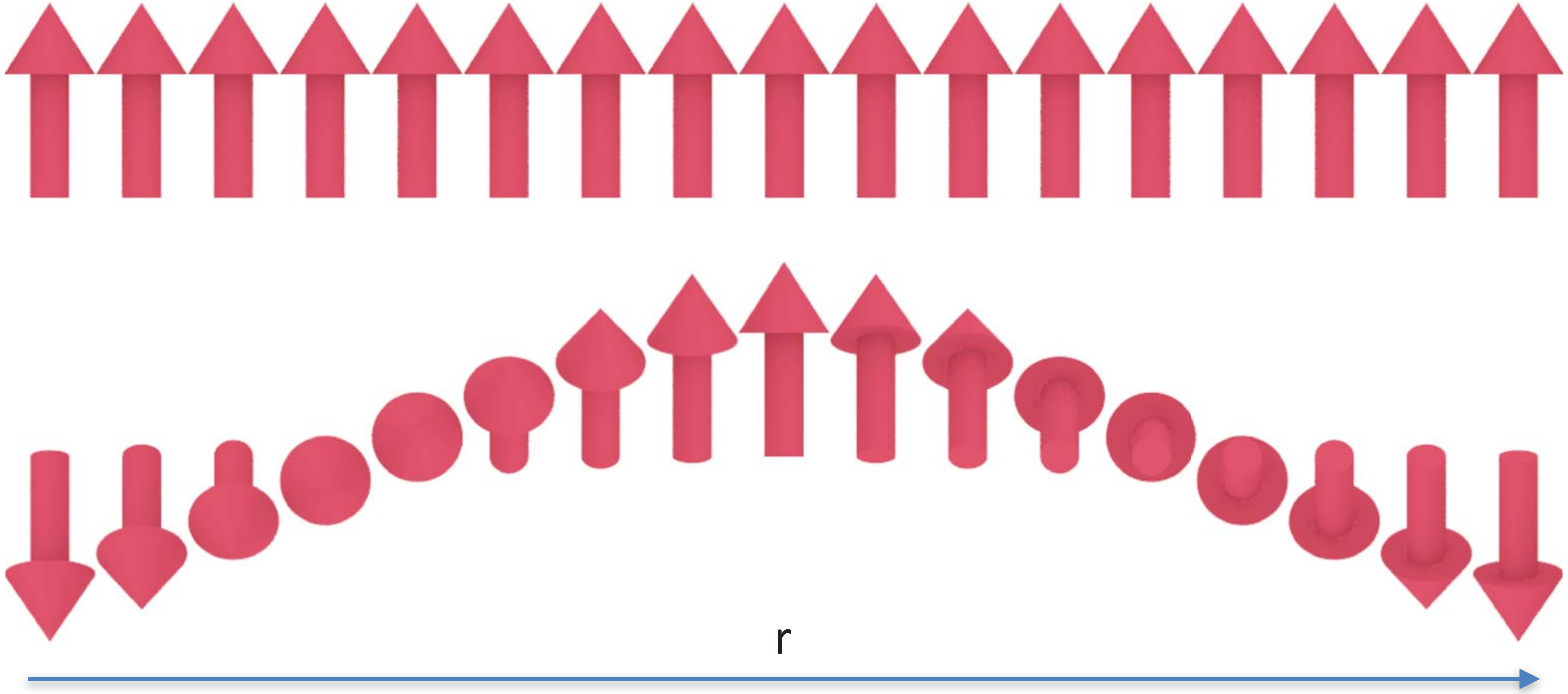
# Analysis: Energy landscape

Bulk dhcp Nd - minimal disorder : What is the cause of the glassy dynamics?

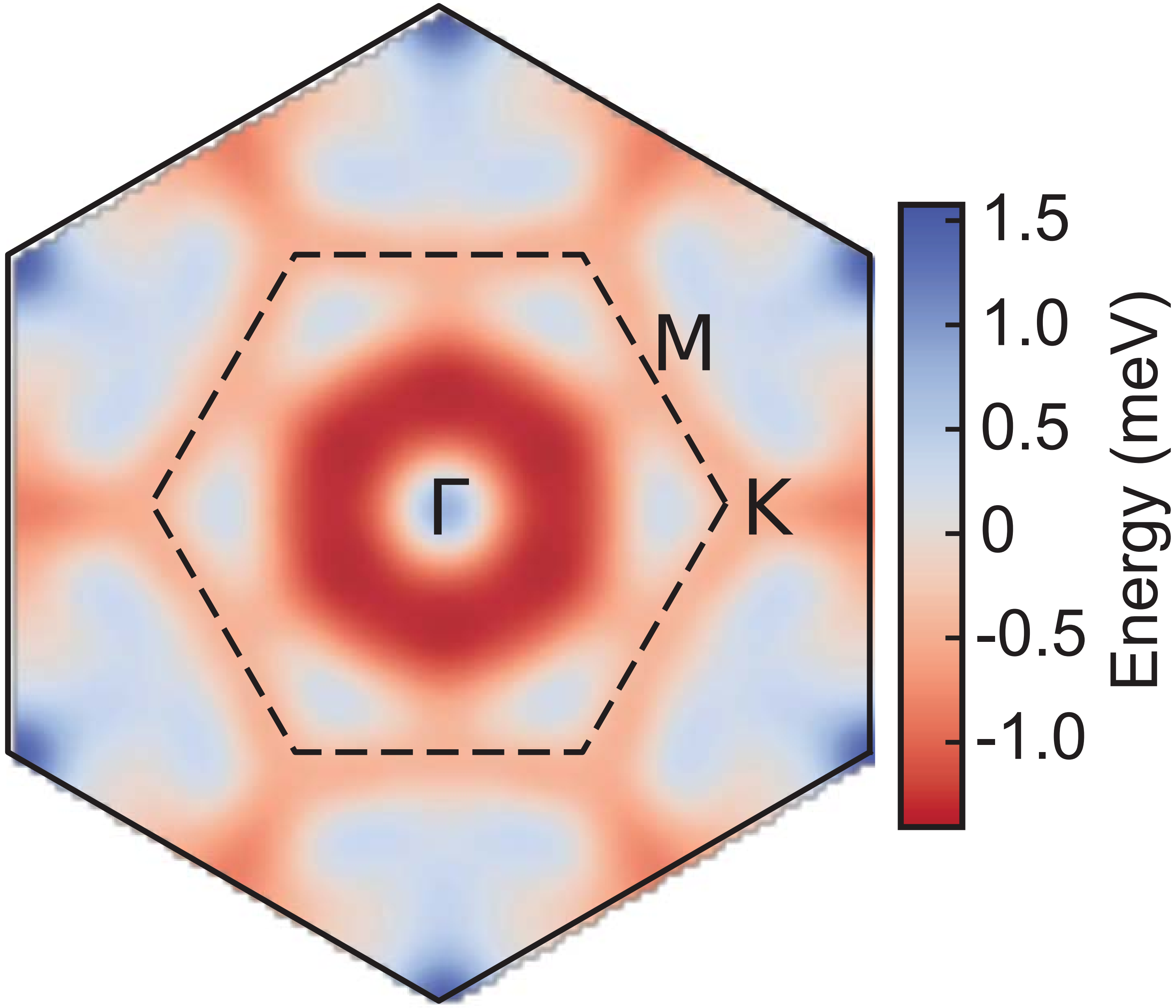
Map the energy landscape of our atomistic model for single-q spin spirals

Simple modelling of spin spiral: Rotate magnetic moments

$$\mathbf{m}(\mathbf{r}_i, \mathbf{q}) = \mathbf{R}(\theta = \mathbf{r}_i \cdot \mathbf{q}, \hat{\mathbf{n}})\mathbf{m}_i^0$$



# Analysis: Energy landscape

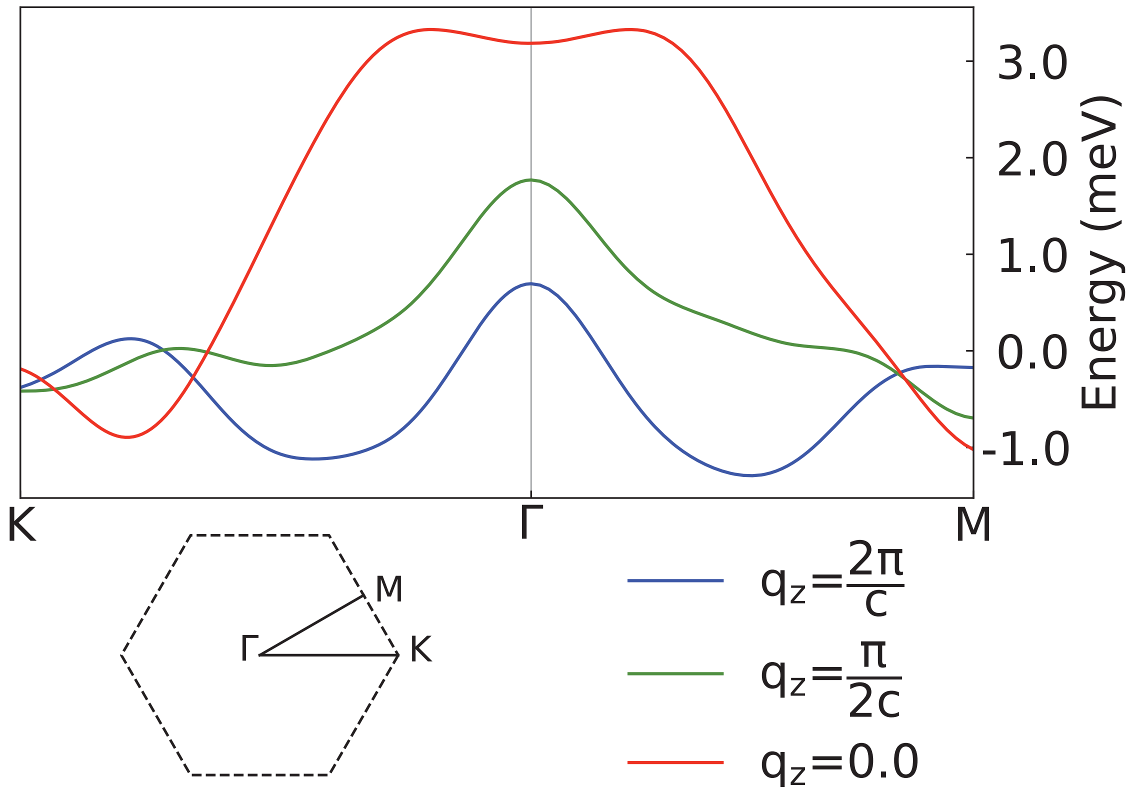


Dark red: Energy minimum

Constant color: Flat energy landscape

Here: Circular flat region

Resembles mexican hat potential



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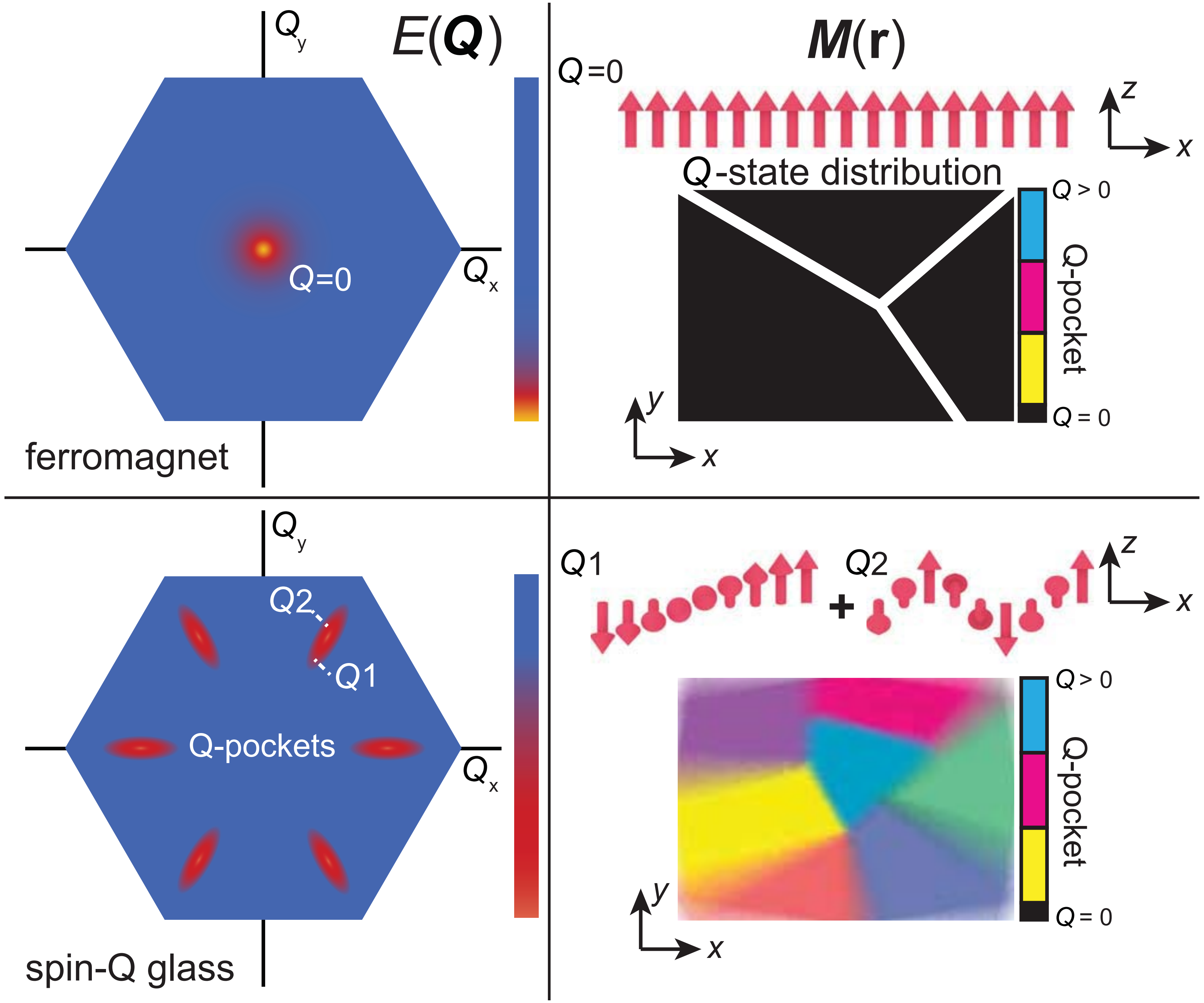
# New magnetic state: Spin-Q glass



Ferromagnet:
Well defined, deep minimum for Q=0.
Domains and domain walls

Spin-Q glass:
Flat regions (pockets) for a distribution of q-vectors
Superposition of spin spirals
No clear domain walls
Lack of long range order

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# Summary: Experiment and Theory

- Bulk/Thick film Nd has **glassy dynamics** at low temperatures (< 4K)
- Here we use ”local” probes. Still consistent with earlier scattering studies on larger samples
- Negligible disorder effects: **Self-induced spin glass**
- Spin-spiral, not paramagnetic ”background”. Local short-range order
- Energy pockets from competing interactions between sub-lattices
- Novel magnetic state: Spin-Q glass

U. Kamber, AB et al., Science **368**, 966 (2020)

# Summary

# Correlated basis

$$\hat{\boldsymbol{A}}_R \equiv \sum_{\xi,\xi'} |R,\xi\rangle\langle R,\xi| \sum_{\mathbf{k}} \hat{\boldsymbol{A}}_{\mathbf{k}} |R,\xi'\rangle\langle R,\xi'|$$

Two choices of $|R,\xi\rangle$, muffin-tin based and orthogonal:

i) MT

$$\chi_{lm} = i^l Y_{lm}(a\phi_{l\nu} + b\phi'_{l\nu})$$

$$\chi_{lm} = i^l Y_{lm} n_l$$

ii) ORT

$$(\mathbf{H} - \epsilon\mathbf{O})\mathbf{x} = 0$$

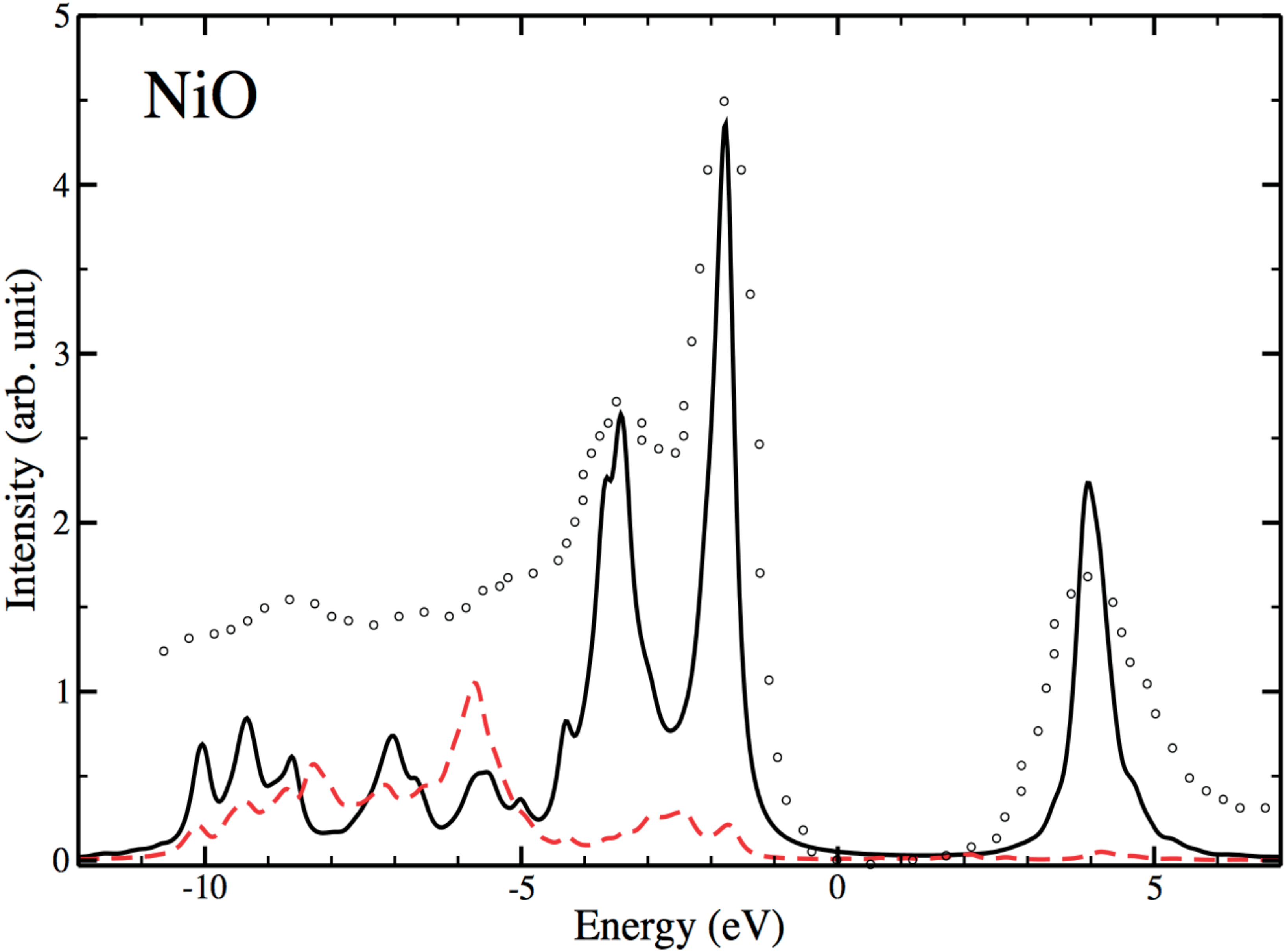
$$\mathbf{O} = \mathbf{L}\mathbf{L}^h$$

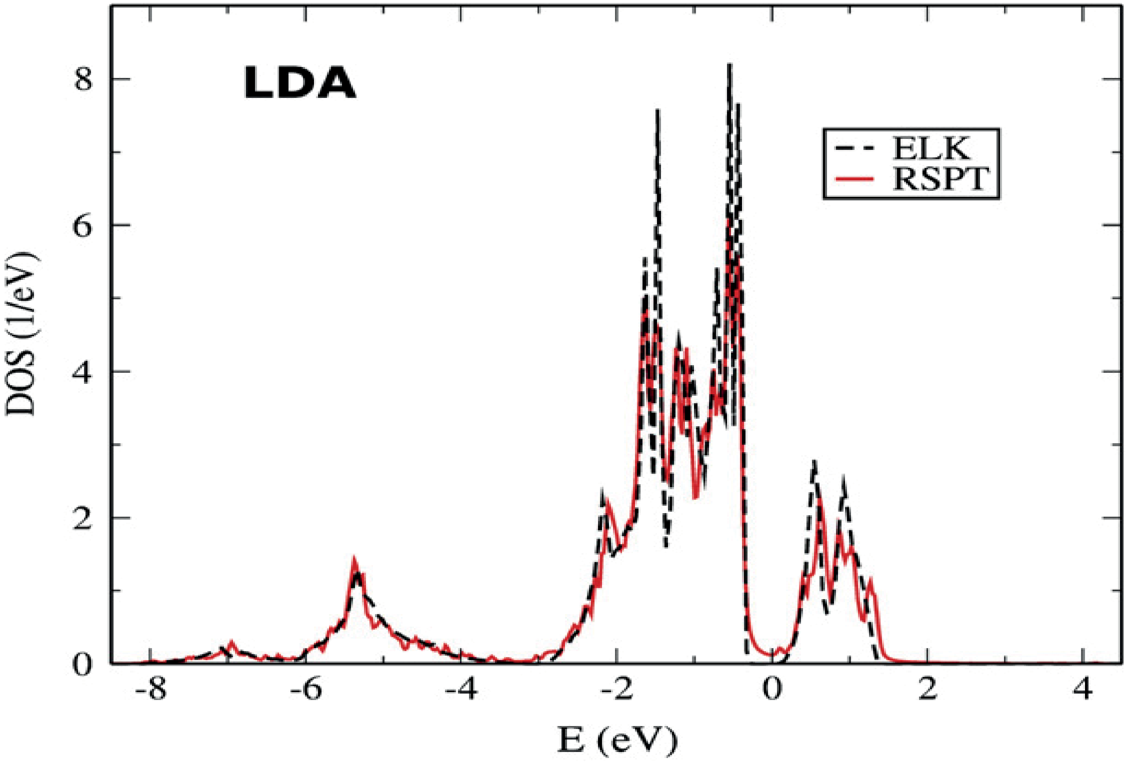
Cholesky decomposition gives

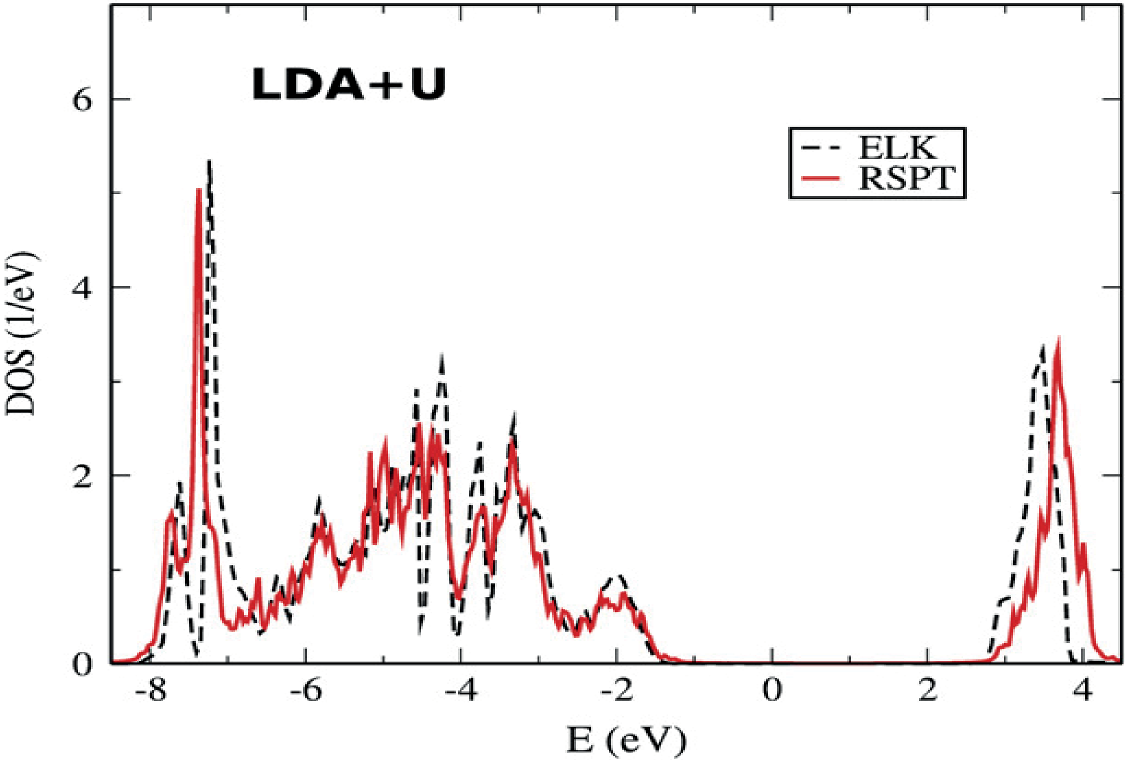
$$(\mathbf{L}^{-1}\mathbf{H}\mathbf{L}^{-h} - \epsilon\mathbf{1})\mathbf{y} = 0$$

$$\mathbf{y} = \mathbf{L}^h\mathbf{x}$$

# Valence band spectra




LDA
ELK
RSPT
DOS (1/eV)
0
2
4
6
8
-8
-6
-4
-2
0
2
4
E (eV)


LDA+U
ELK
RSPT
DOS (1/eV)
0
2
4
6
-8
-6
-4
-2
0
2
4
E (eV)