Structure-property relationships in magnetism

Alexander Tsirlin

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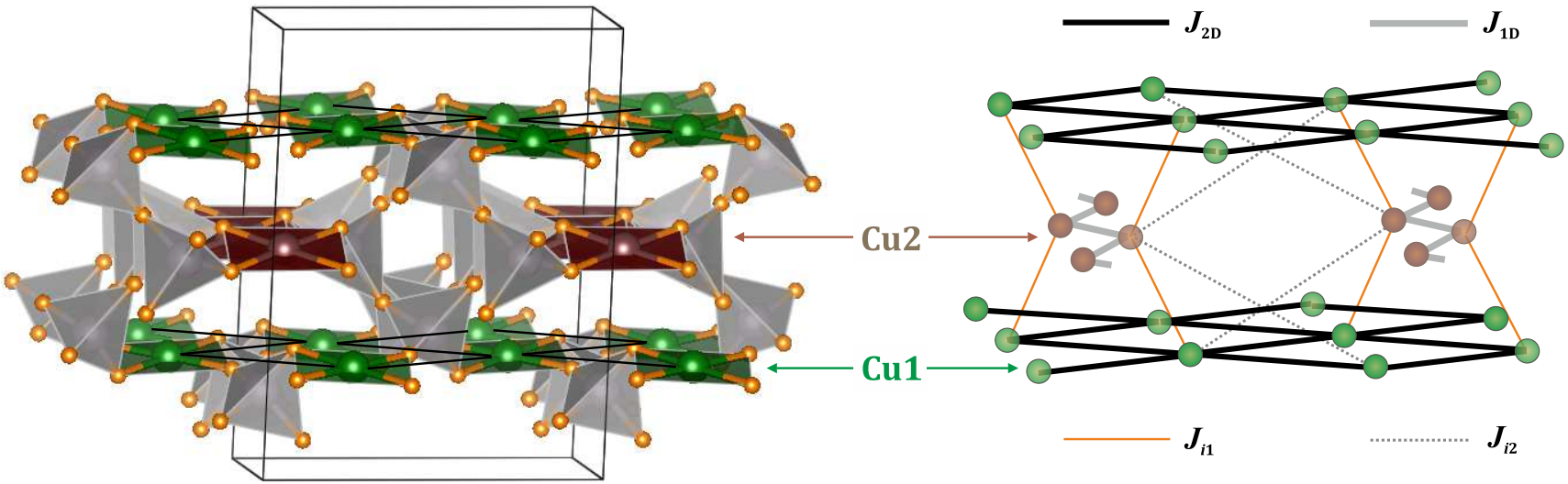
University of Augsburg, Germany

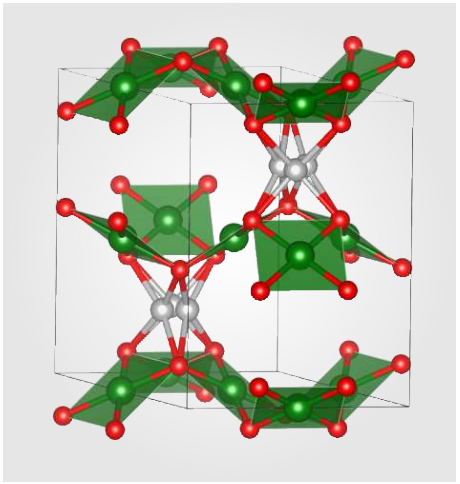


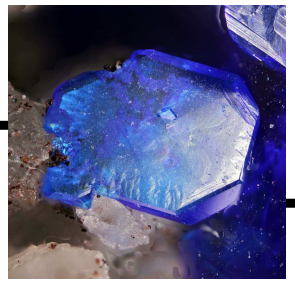
Alexander von Humboldt Stiftung/Foundation

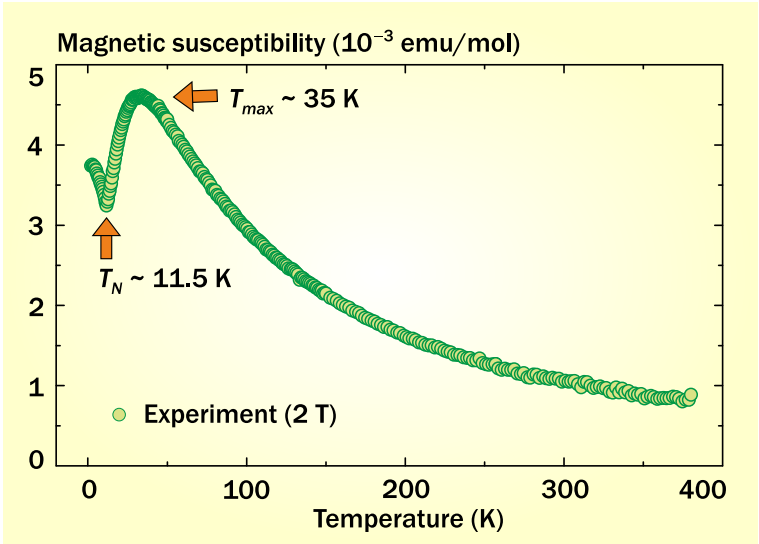
University of Lille, France
November 23, 2018

UNIA

General approach







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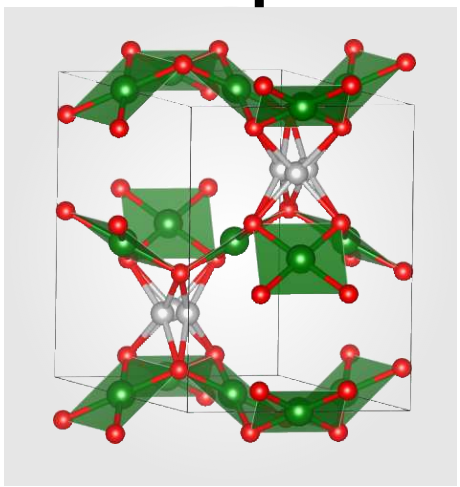

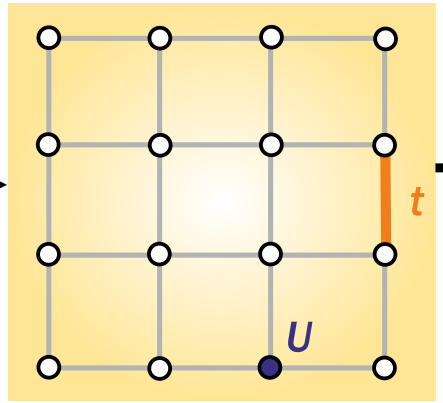

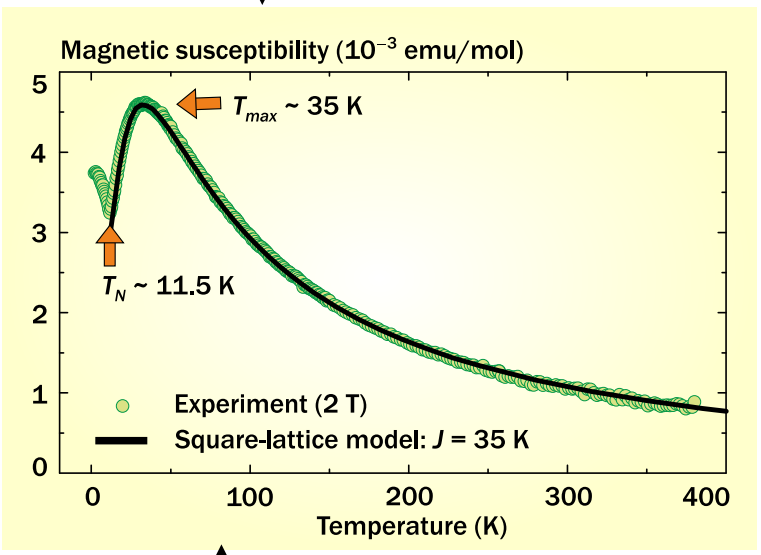

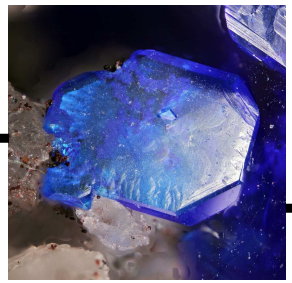

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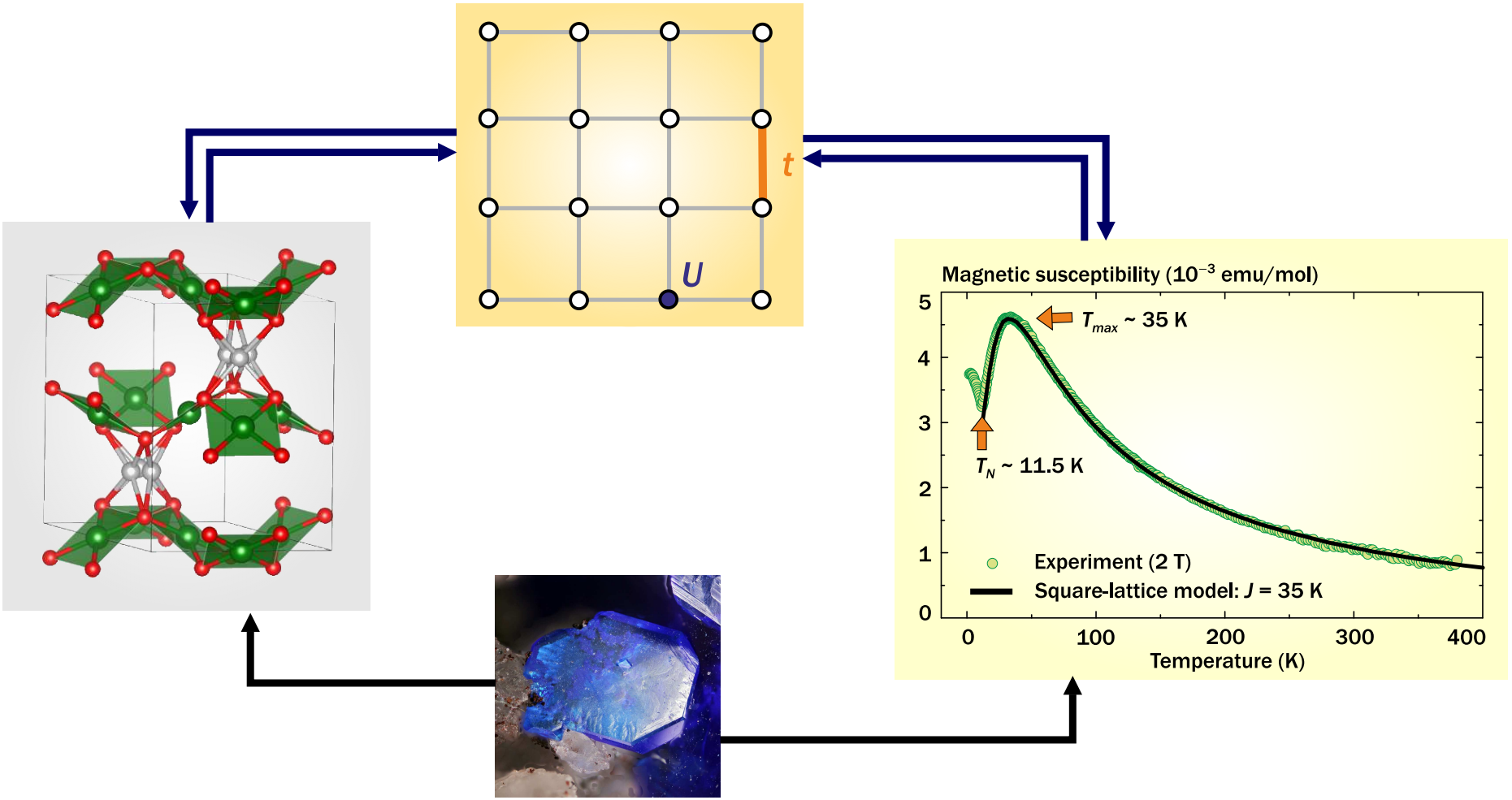
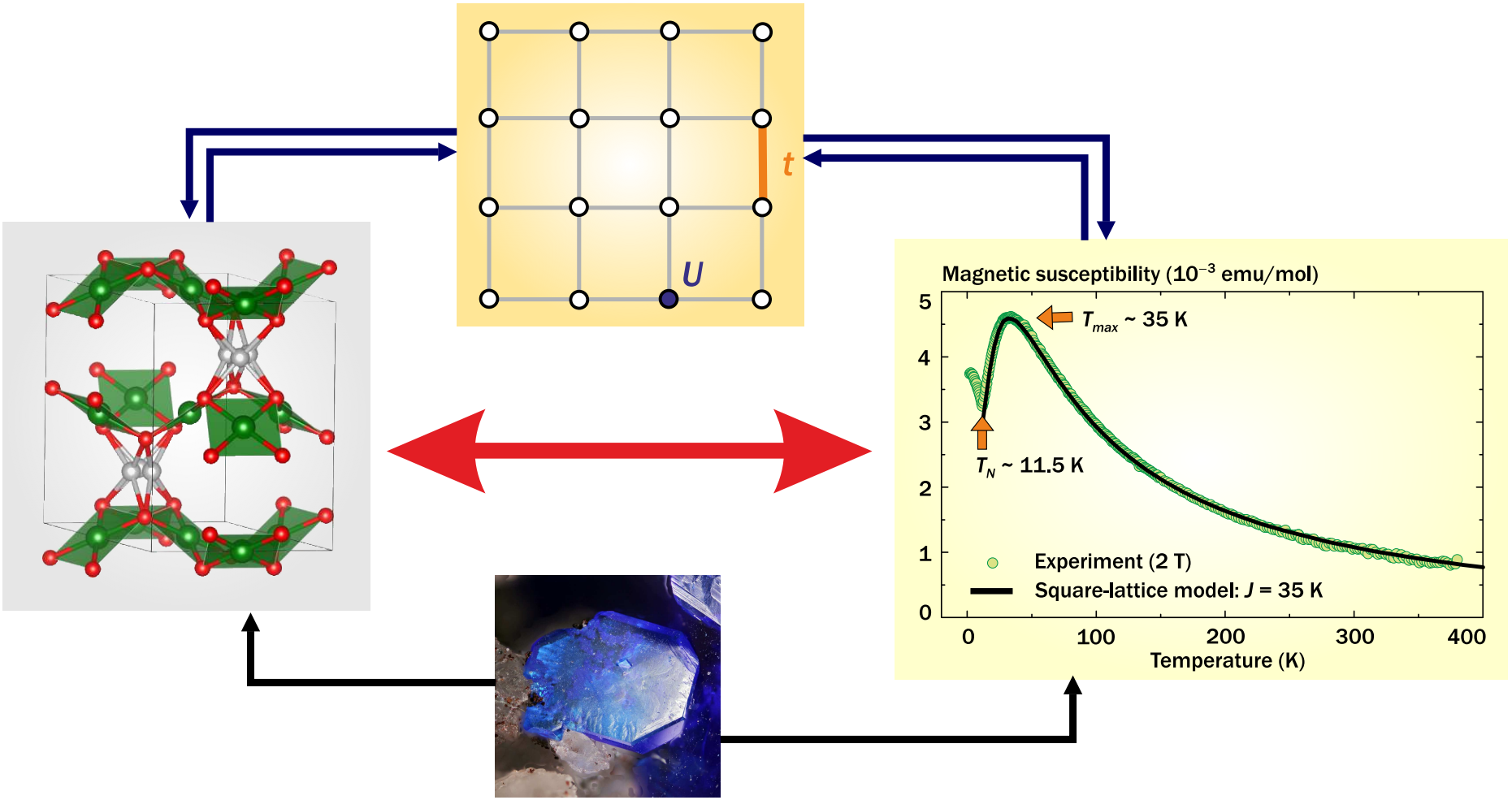


- Correlate experimental magnetic behavior with the microscopic (model) parameters
- Correlate the microscopic parameters with structural features

▶ Structure-properties relationship

General approach



- Correlate experimental magnetic behavior with the microscopic (model) parameters
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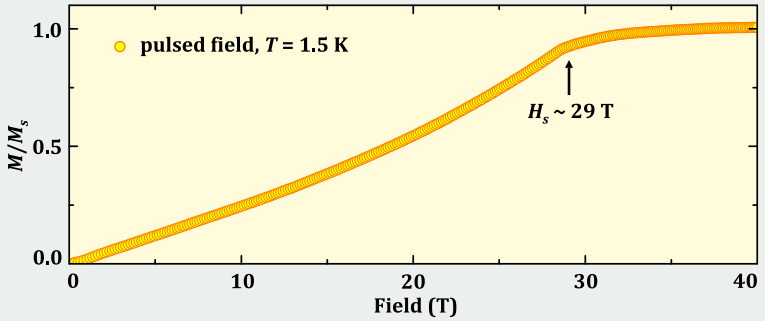
▶ **Structure-properties relationship**

Outline

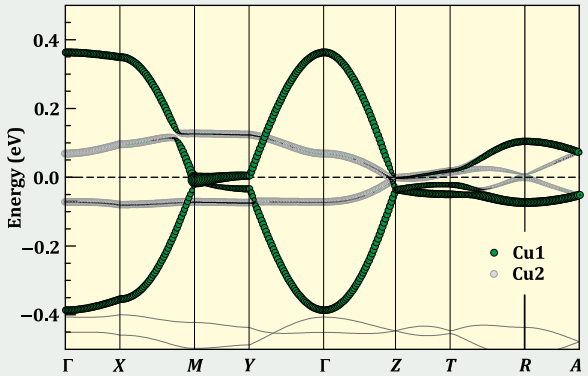
What can we measure?

- Magnetization (+susceptibility)
- Specific heat
- Neutron diffraction



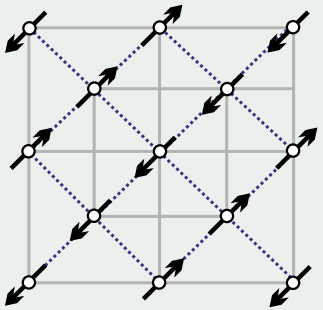
What can we calculate?

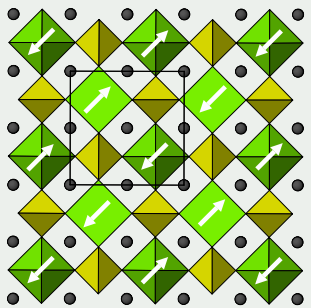
- Parameters of interest
- How to calculate?
- What to observe?



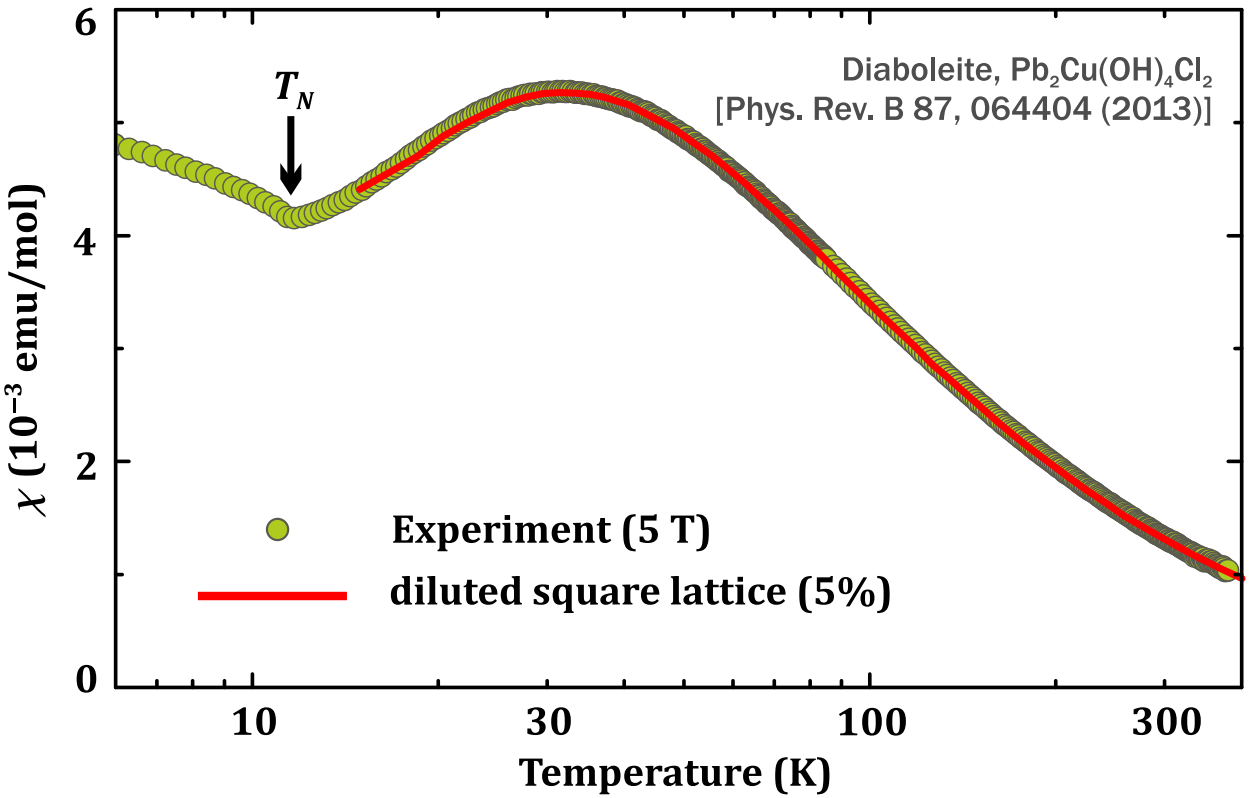
How to bring this together?

- Analytical solutions
- Numerical simulations
- Classical approximation





Magnetic susceptibility



- Usually the easiest thing to measure
- Can be done on powder, polycrystalline pieces, single crystals, even thin films
- Used to determine nature of magnetism, characteristic temperatures, transitions...

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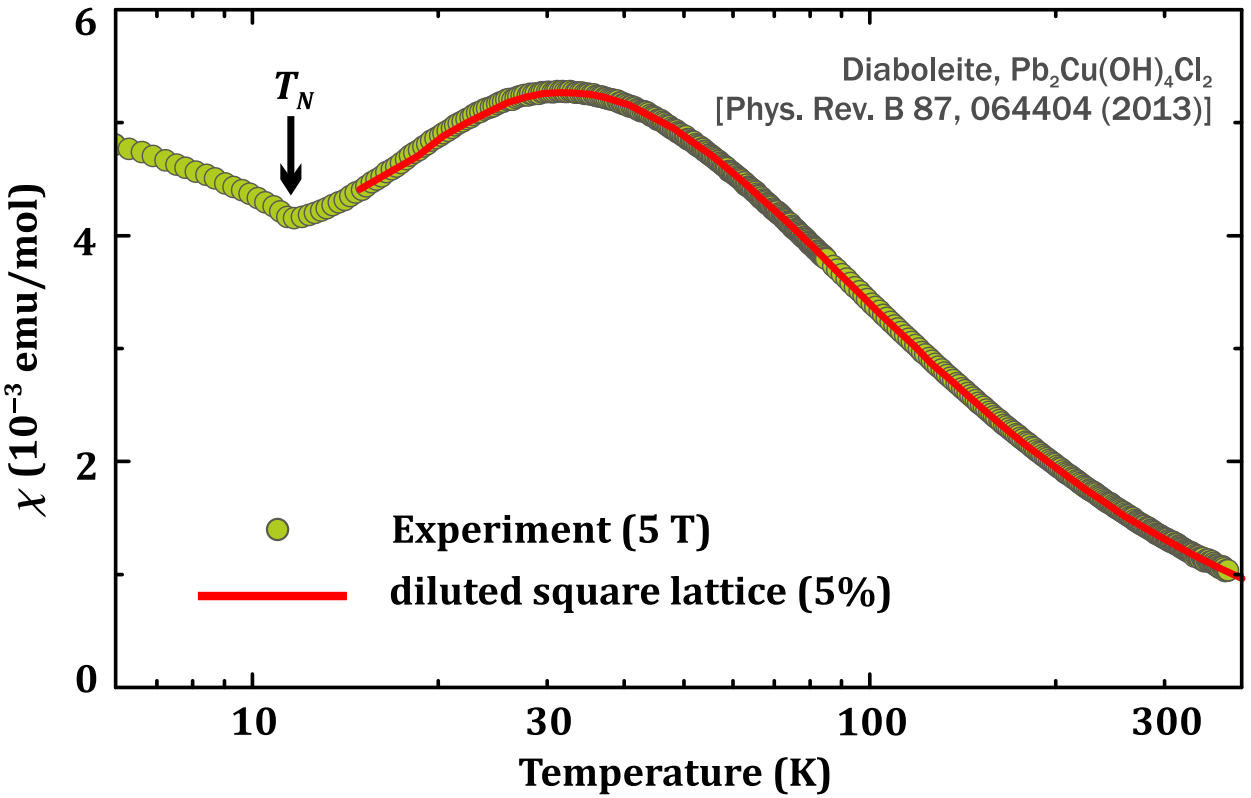

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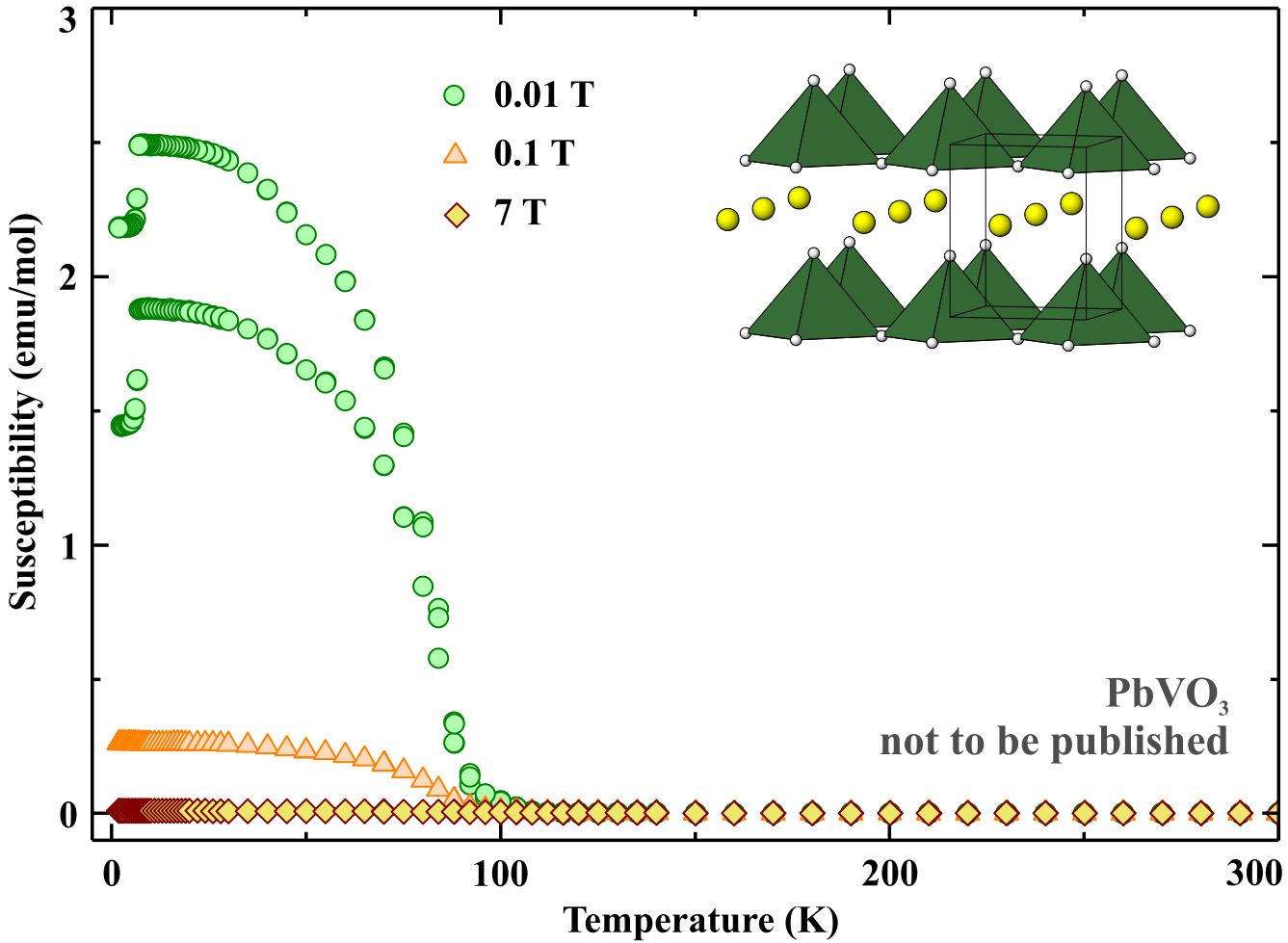
- **Problem: signal scales with the magnetic moment of the phase, not only with its volume fraction**

Magnetic susceptibility: caveats



- Ferromagnetic phases produce most of the signal, even if their amount is tiny
- Ferromagnetic contributions are suppressed by the field, but it does not always help

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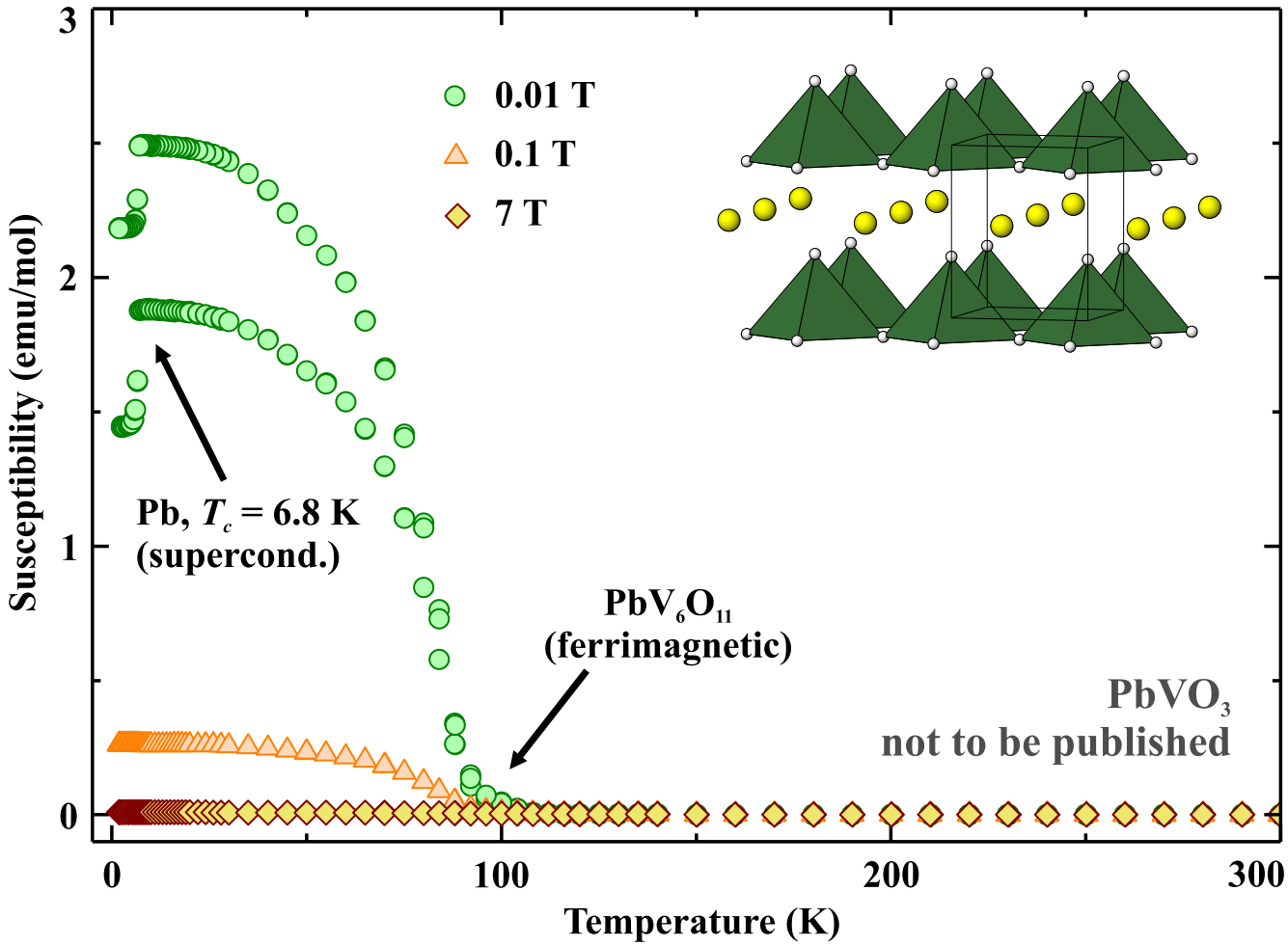

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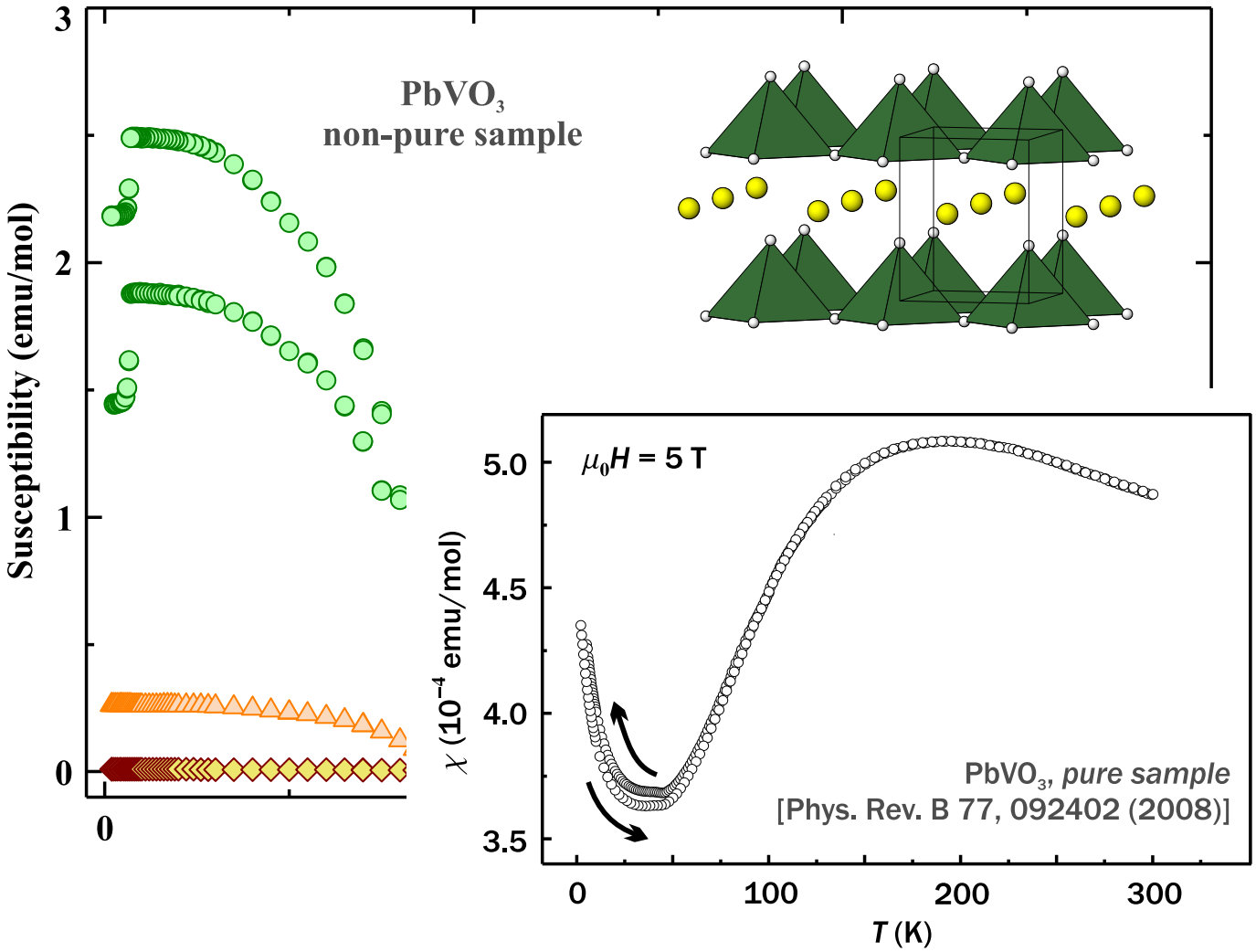

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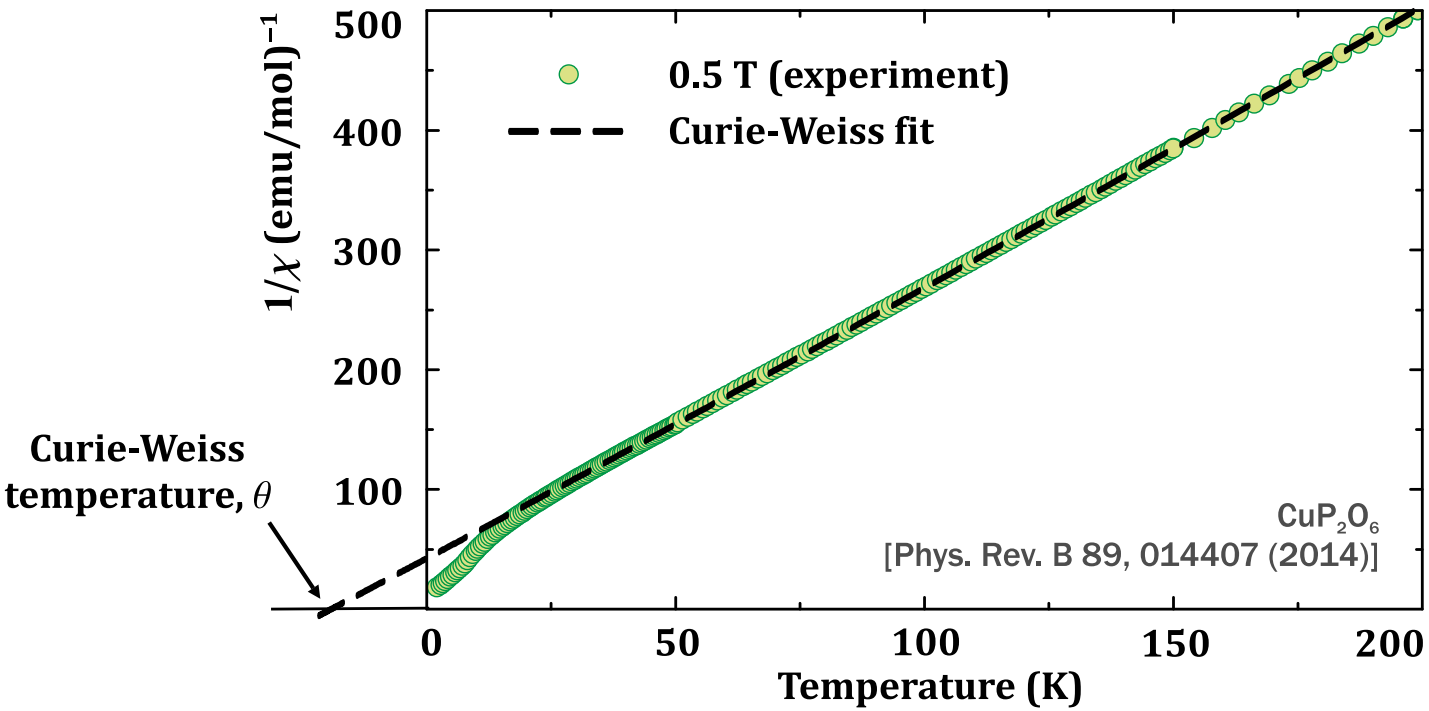
Magnetic susceptibility: local magnetic moment



- Curie-Weiss fit $[\chi = C/(T - \theta)]$ at high temperatures returns:
  - **effective moment** μ_{eff} calculated from $C = N_A\, g^2 \mu_{\text{eff}}^2 / 3k_B$
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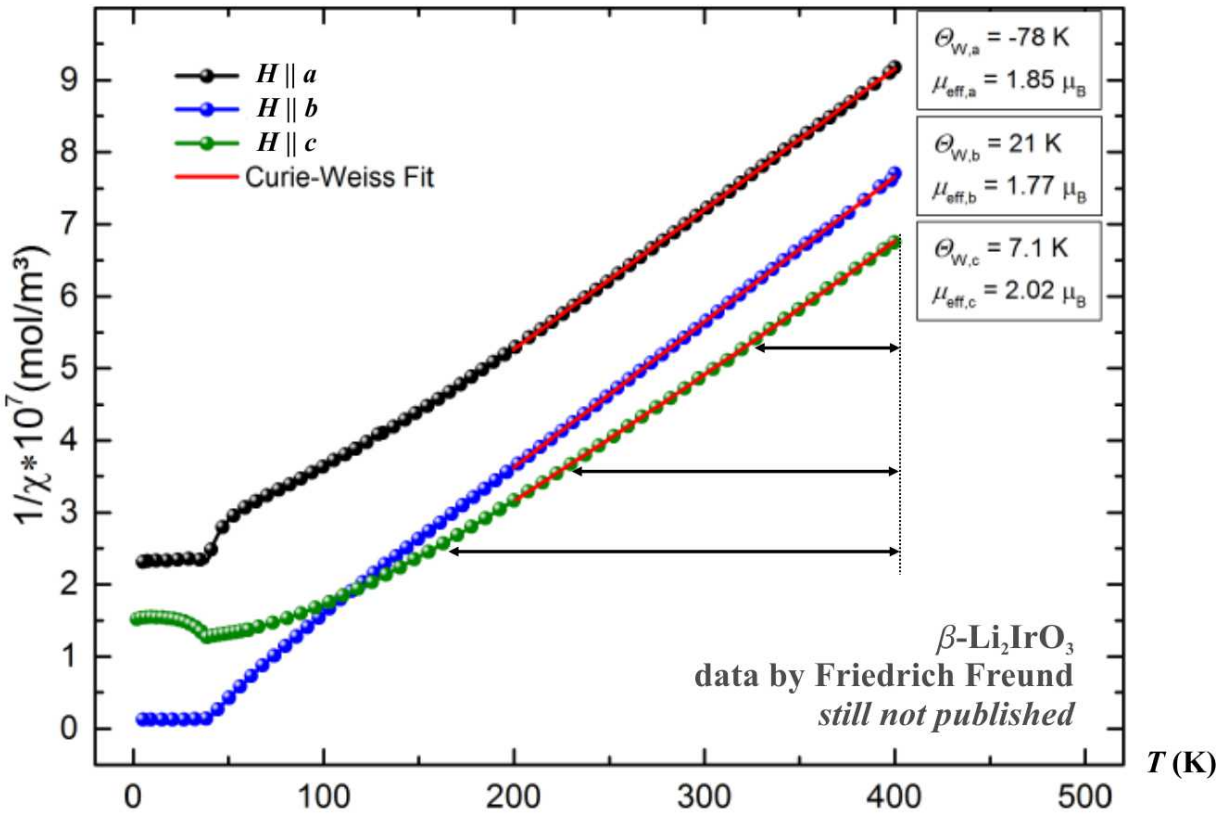

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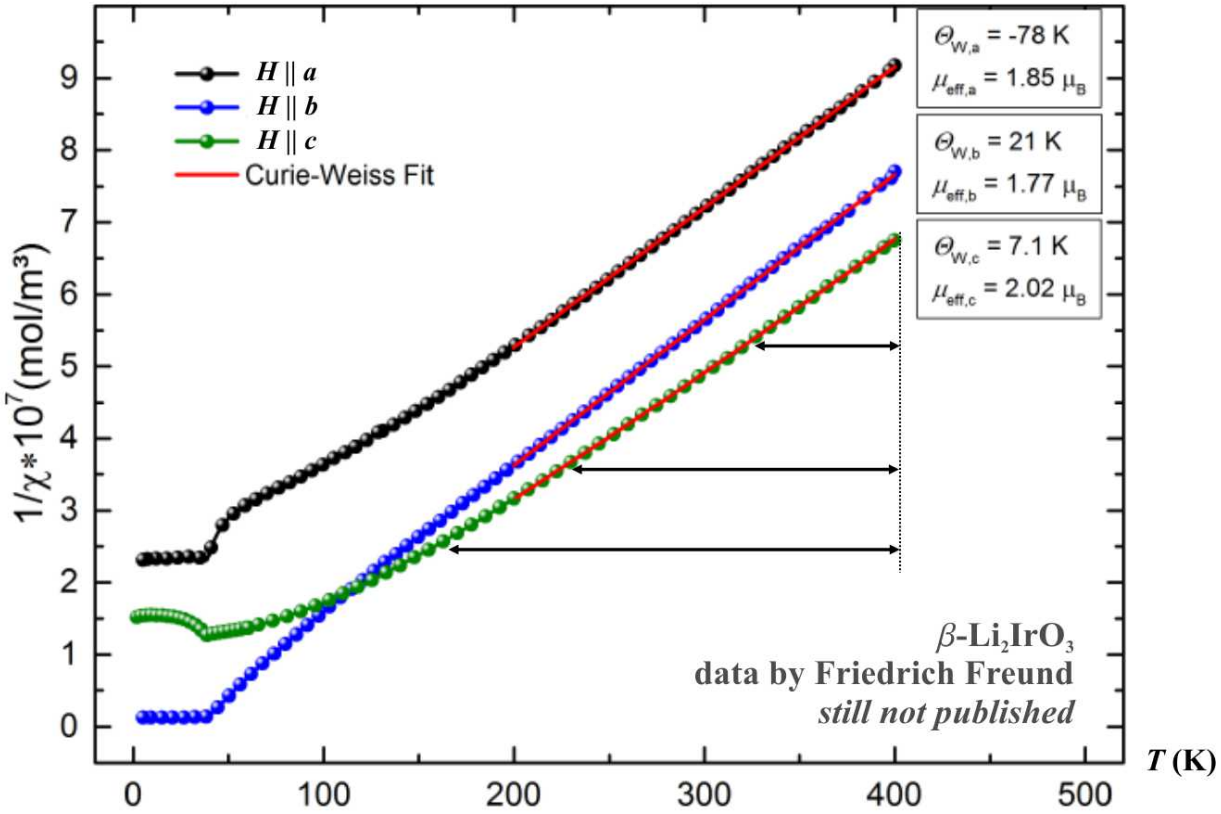

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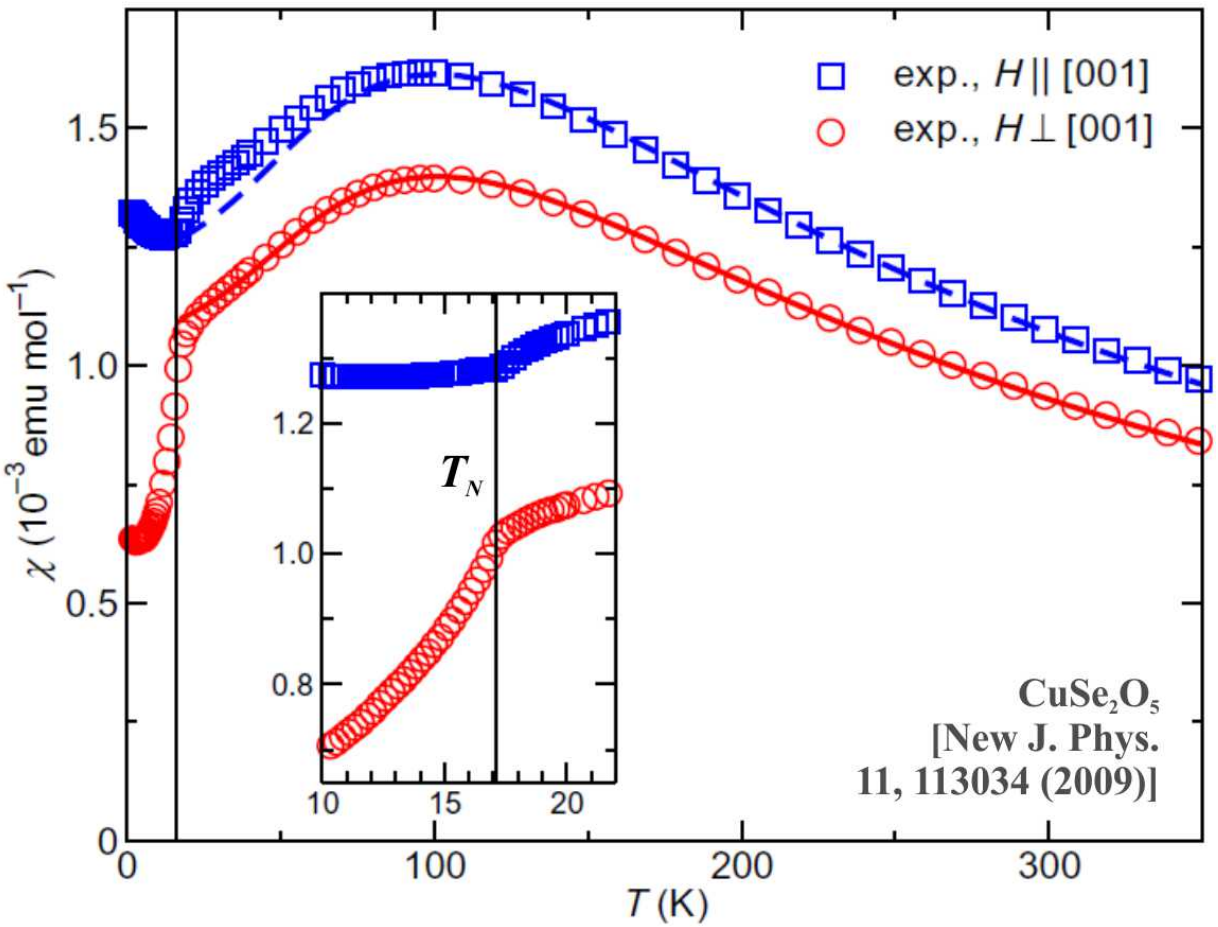
Magnetic susceptibility: identifying the transitions



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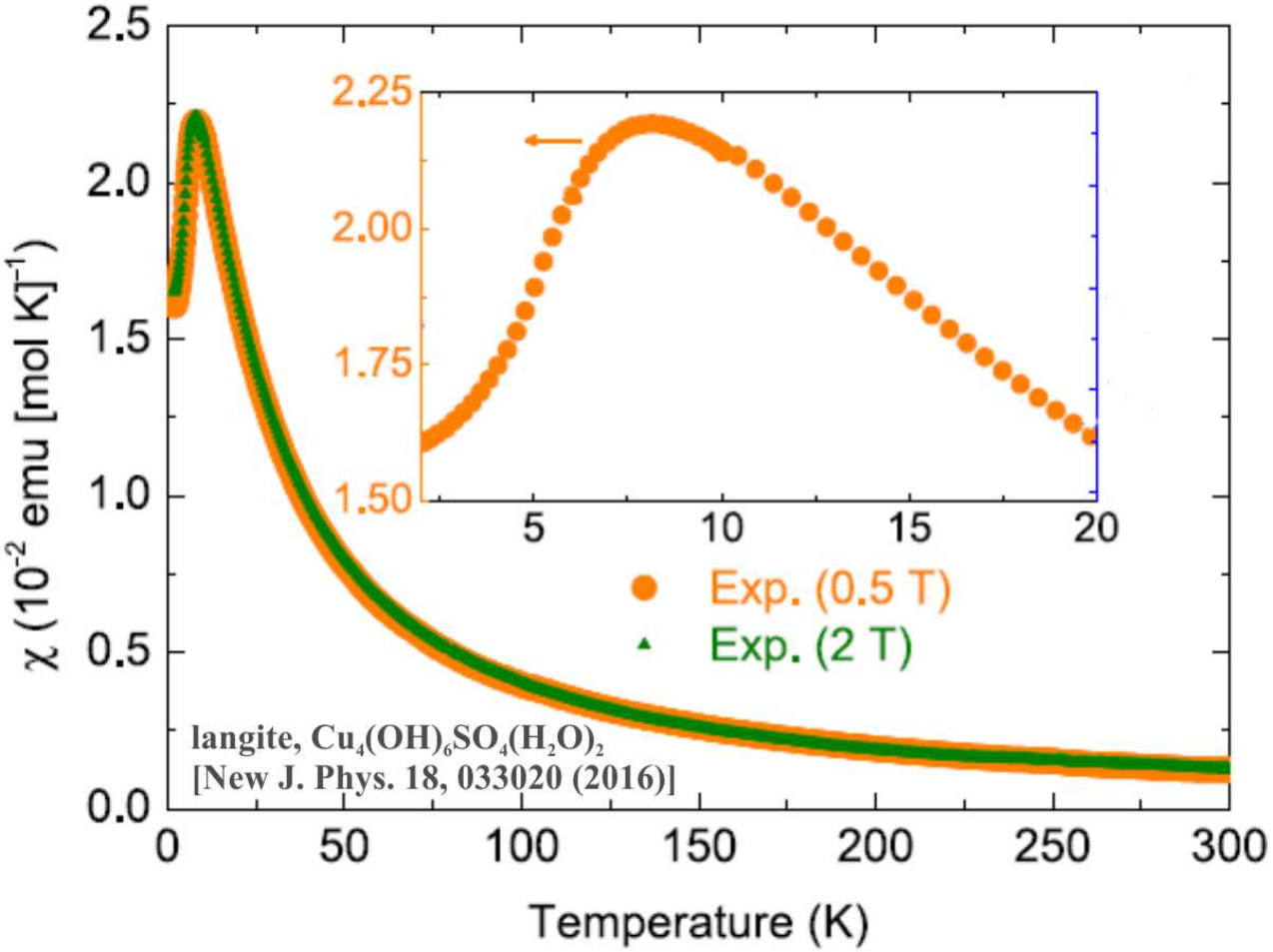
Magnetic susceptibility: identifying the transitions



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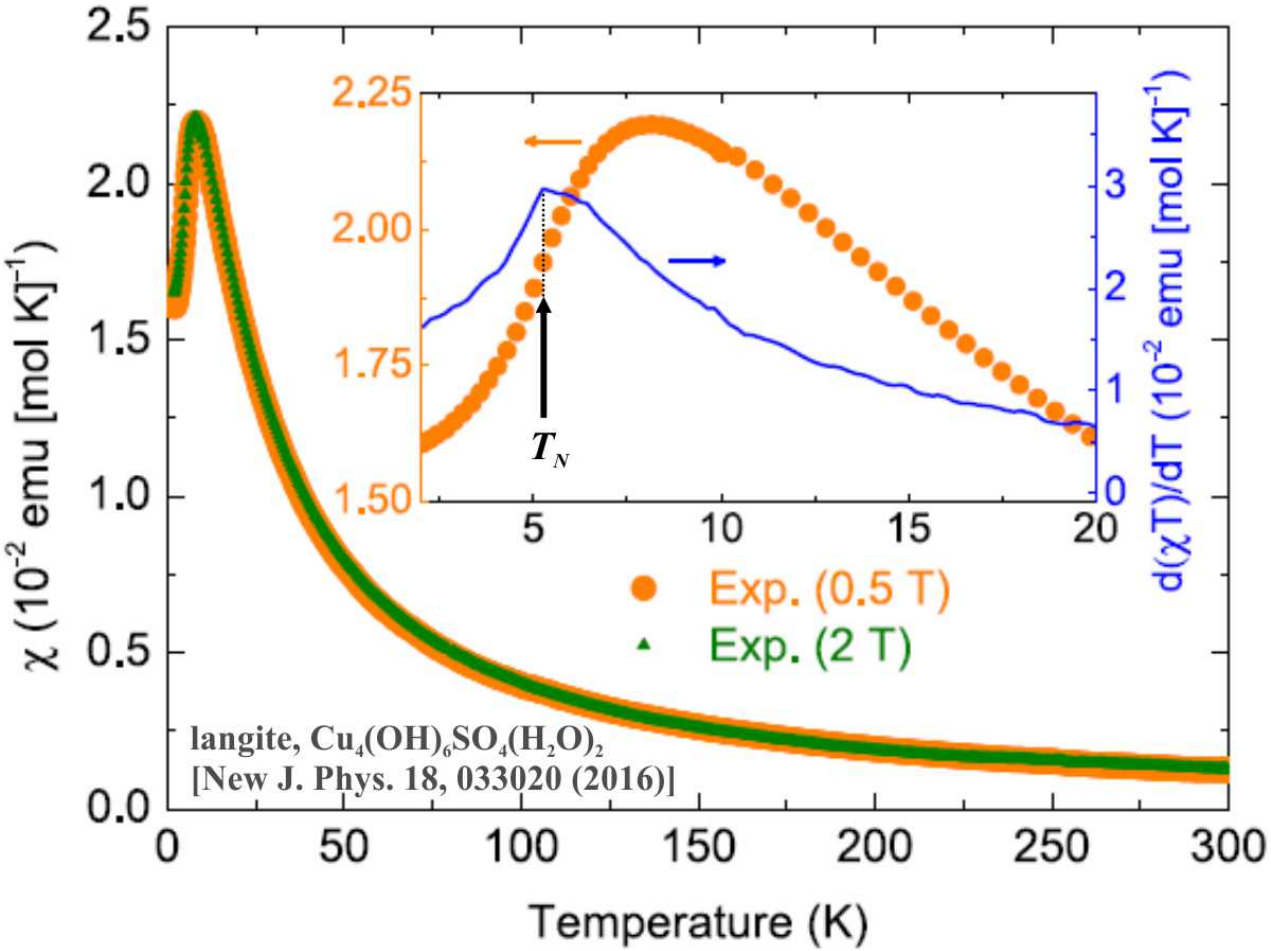

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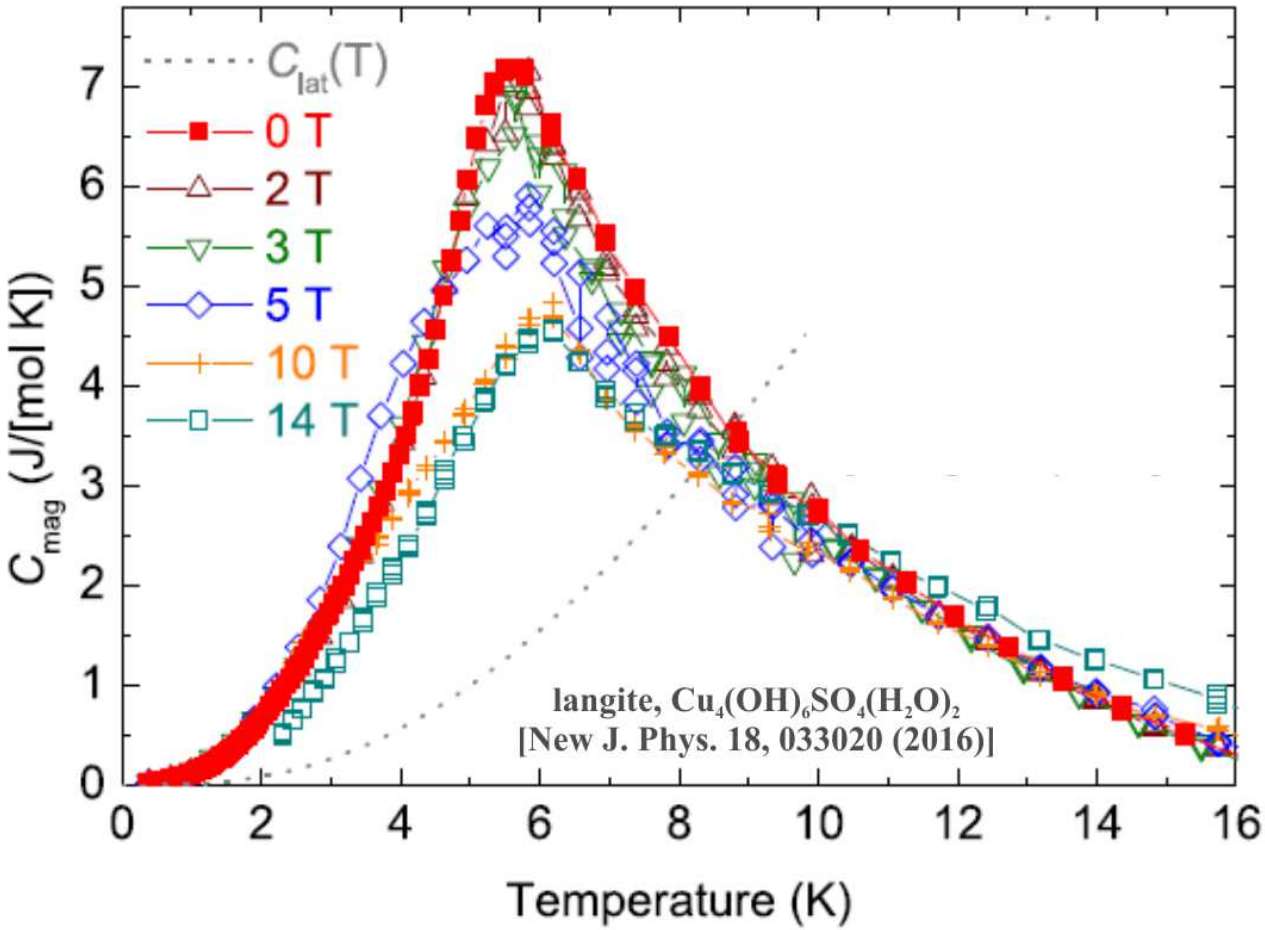

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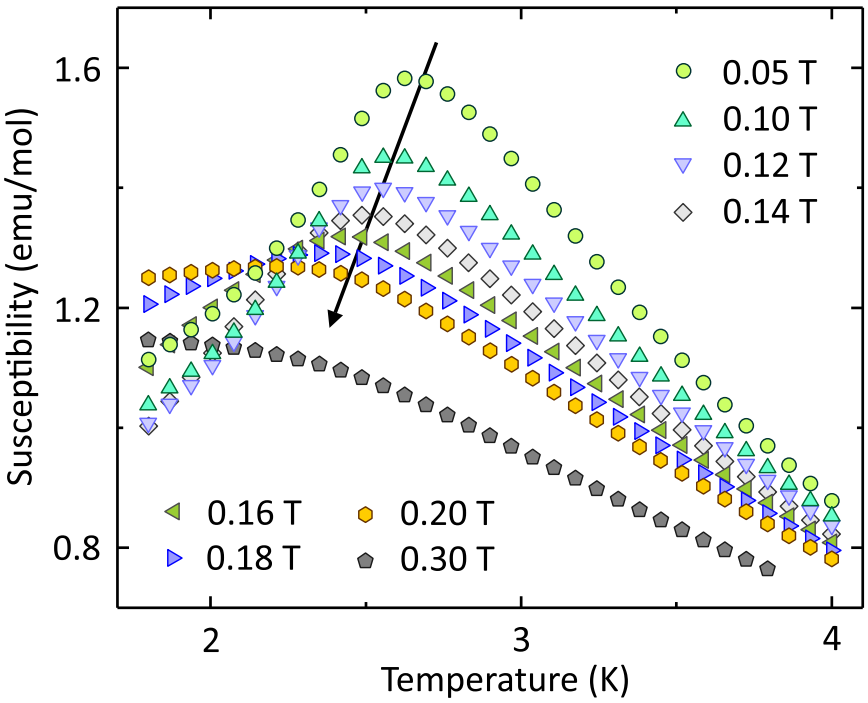
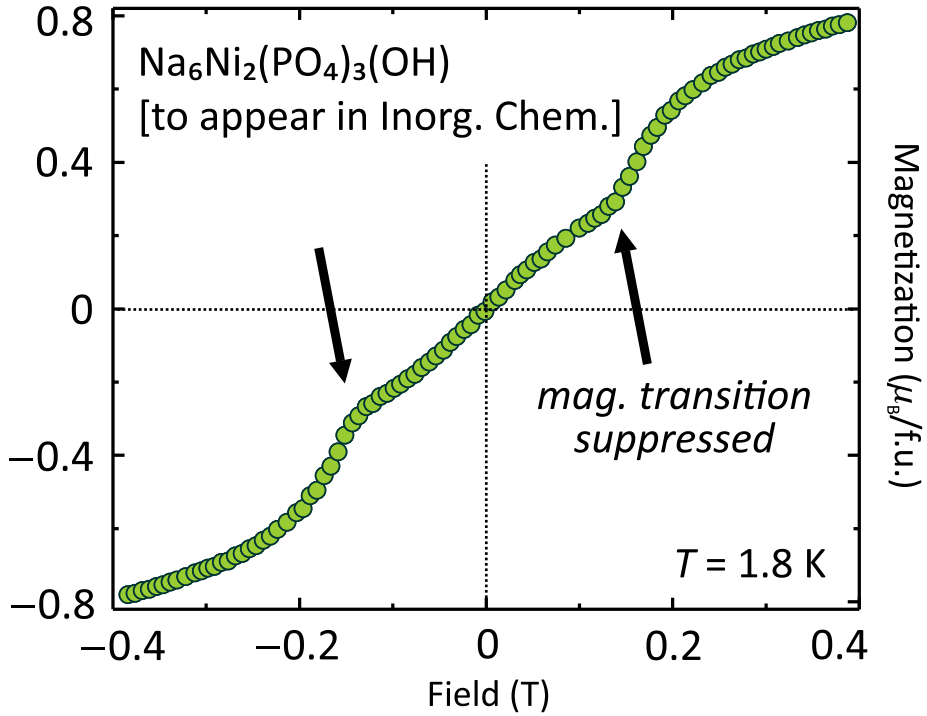
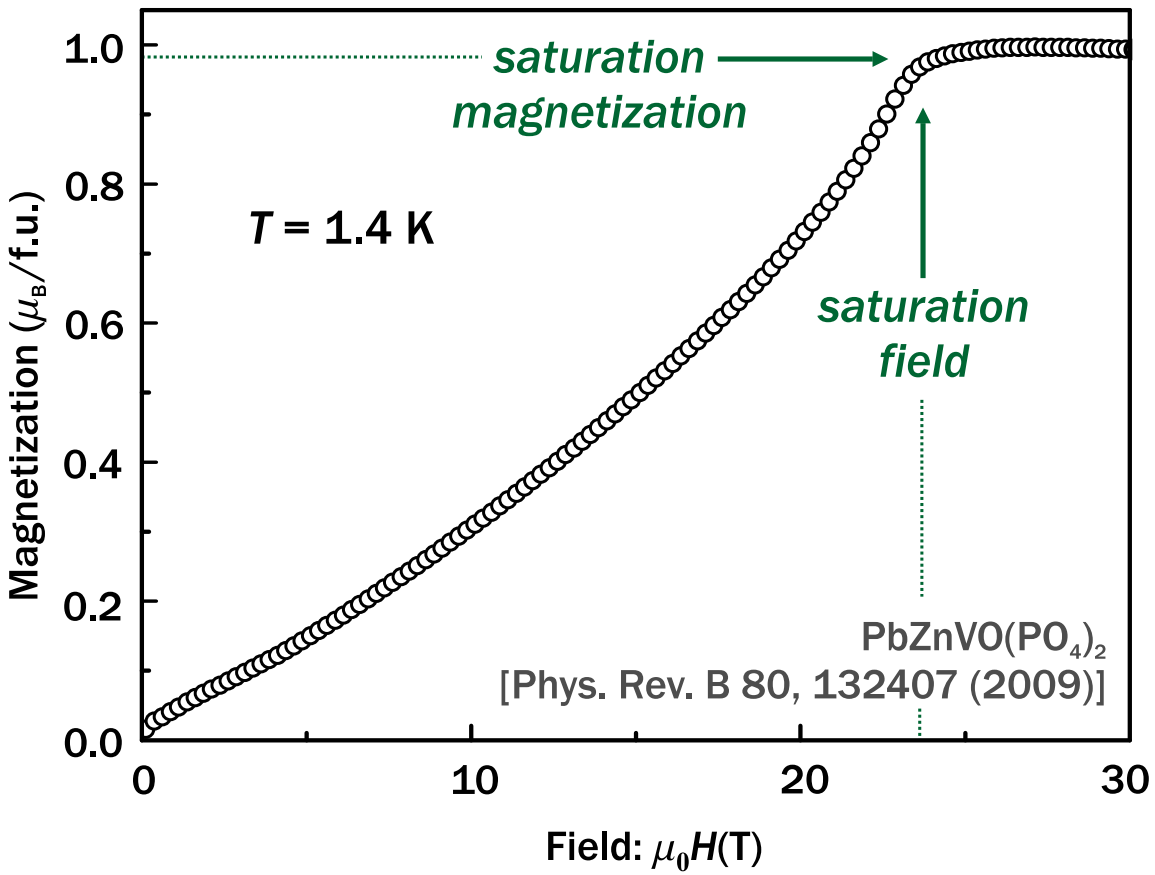
Magnetization vs. susceptibility





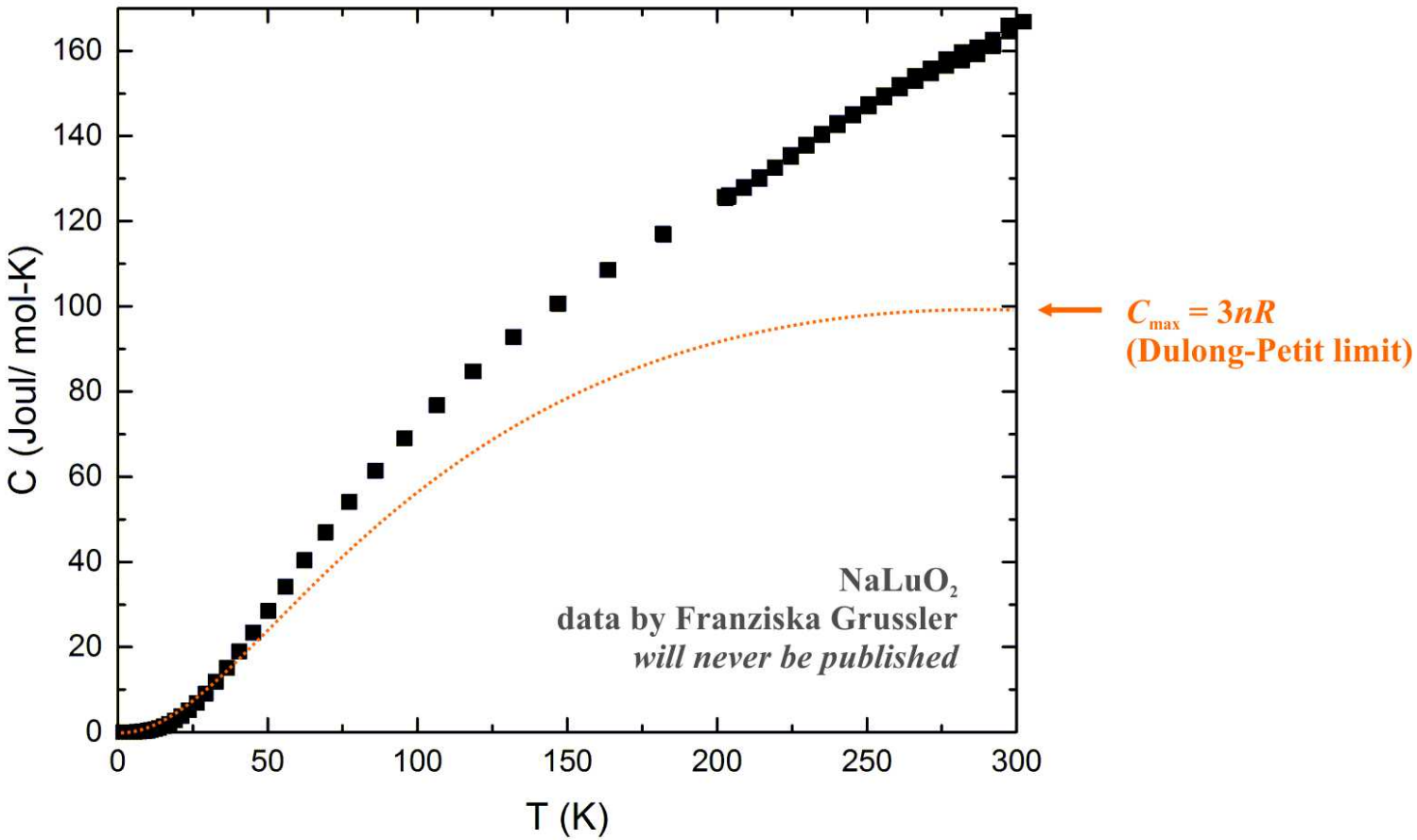
- MPMS/PPMS measure magnetic moment (magnetization) M that can be recalculated into magnetic susceptibility $\chi = dM/dH \sim M/H$
- $\chi(T)$ **and** $M(H)$ **are inextricably intertwined**

Magnetization: saturation



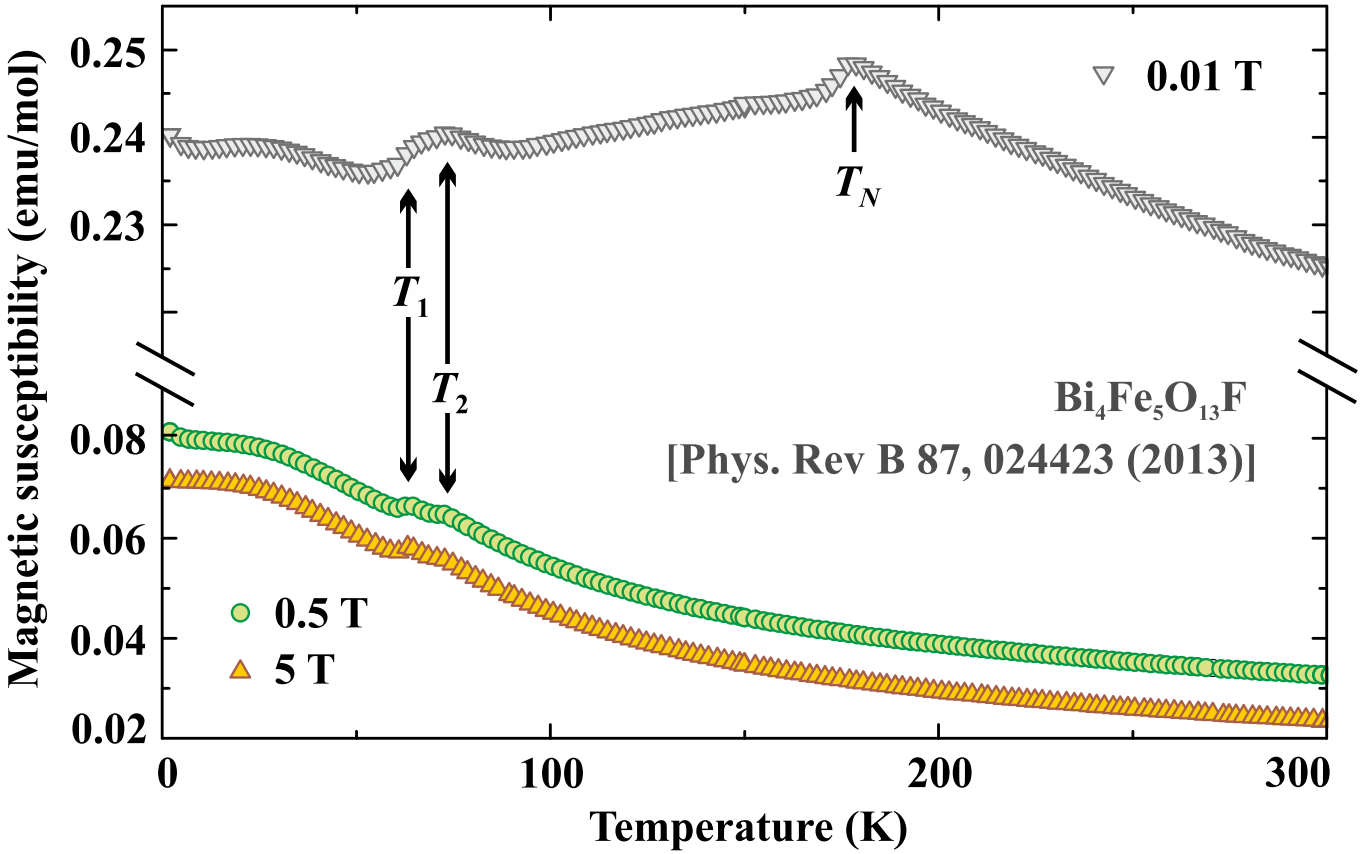
- **Saturation magnetization** gauges the local moment:
  - $\mu_{\text{eff}} = g\sqrt{S(S+1)}$ (effective moment, high-T)
  - $M_s = gS\mu_B$ (local moment, low-T)
- **Saturation field** is a measure of (antiferromagnetic) exchange couplings

Specific heat



- Not too difficult to measure, but **easy to make a mistake**
  (contributions of the platform and grease should be subtracted carefully)
- Solid piece of a material is required (powder is difficult)
- Signal scales with the volume fraction of the phase
  (minor impurities do not matter)

Specific heat: confirm phase transitions



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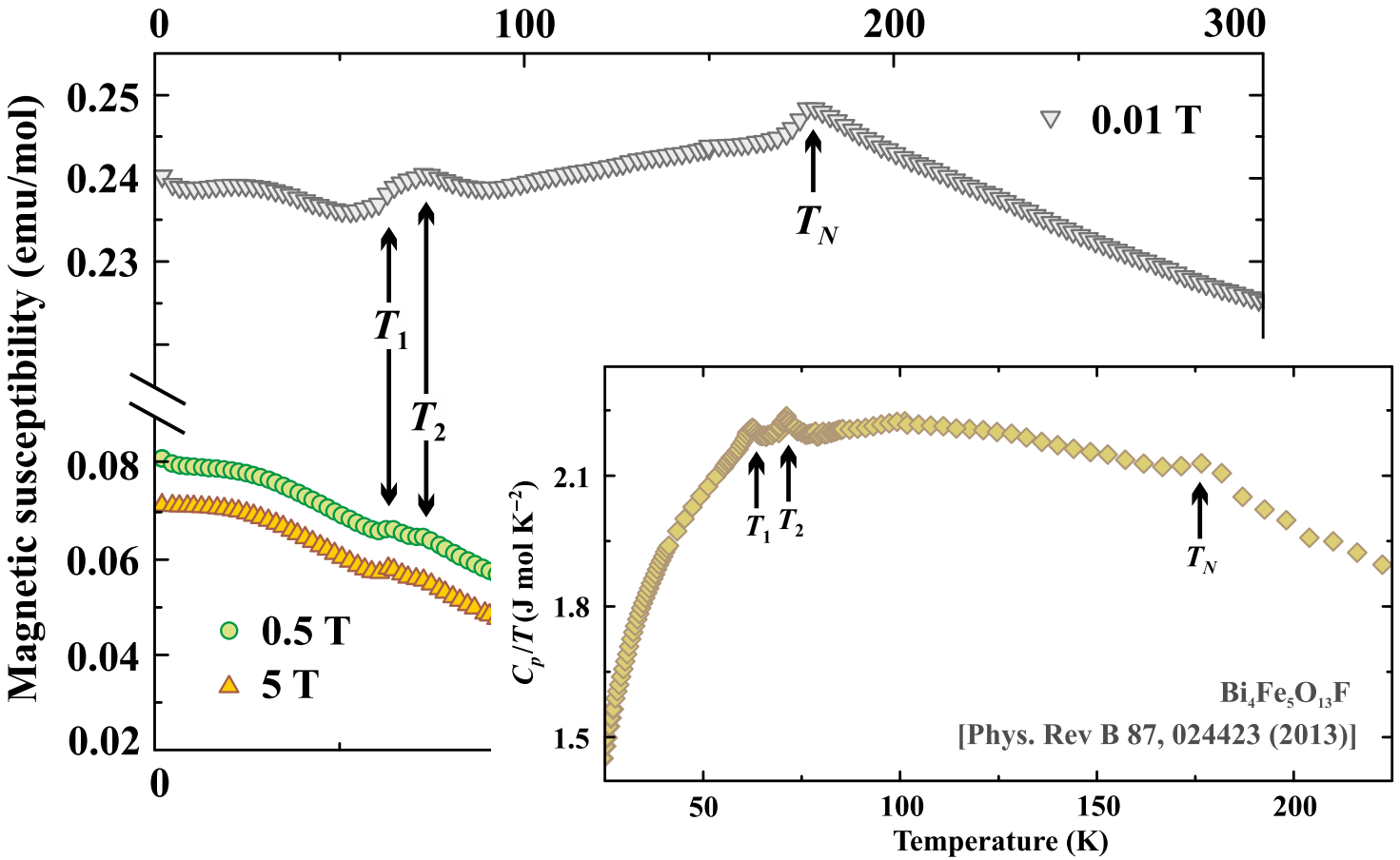

- When you see signatures of a transition in both χ and C_p, you can be rather confident it is intrinsic
- **But:** low-D antiferromagnets may show very weak of absent transition anomalies

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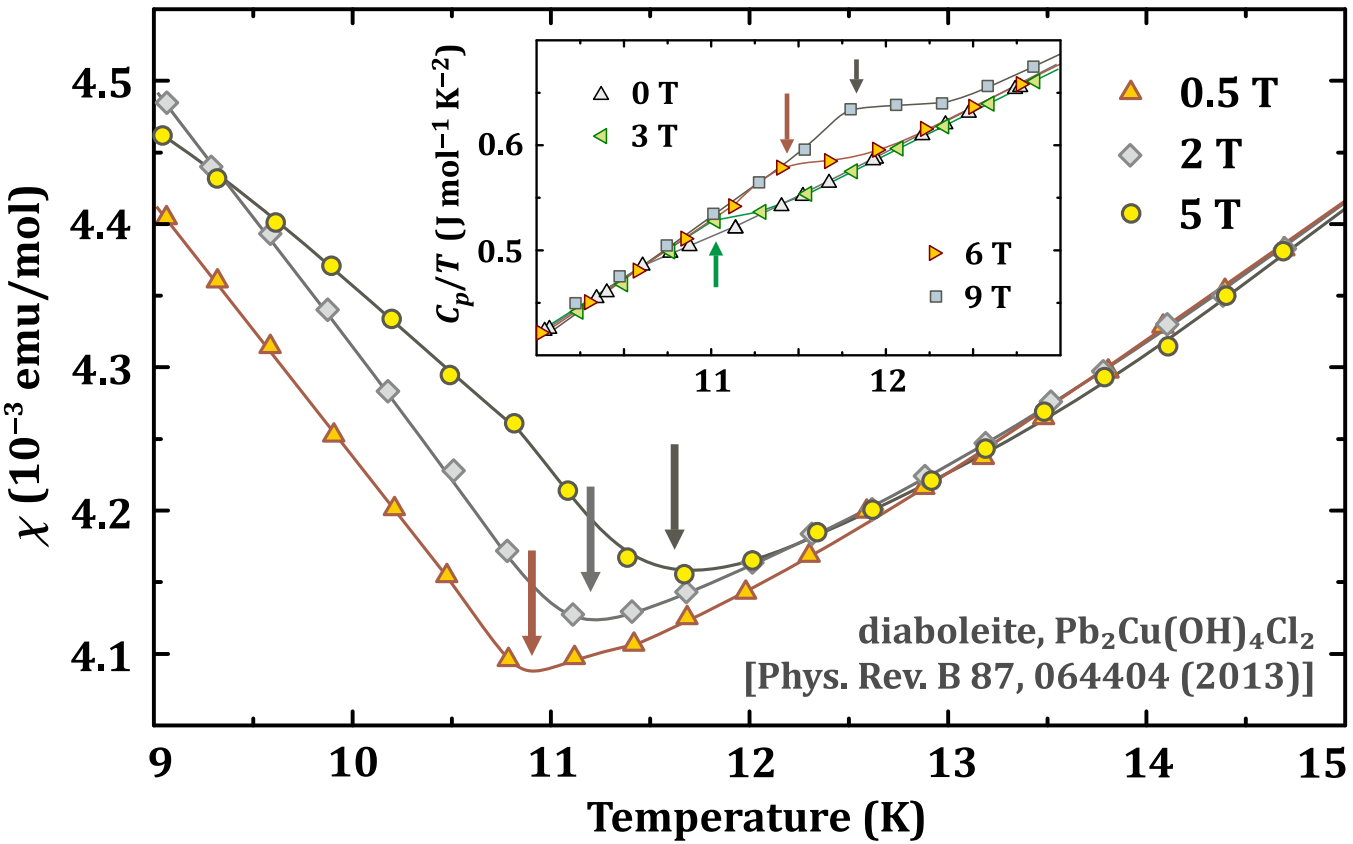

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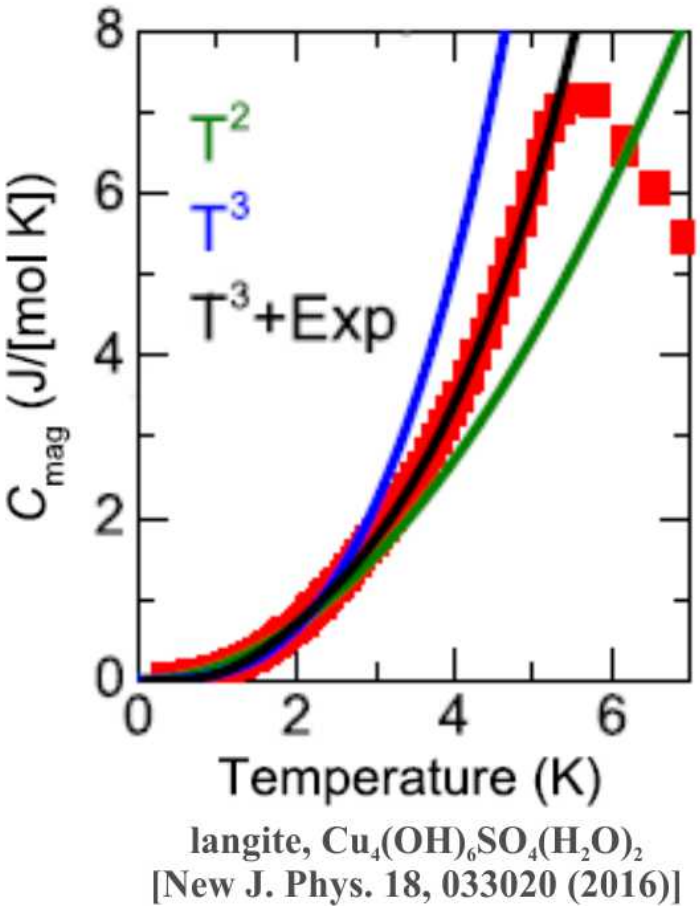
Specific heat: low-T contributions



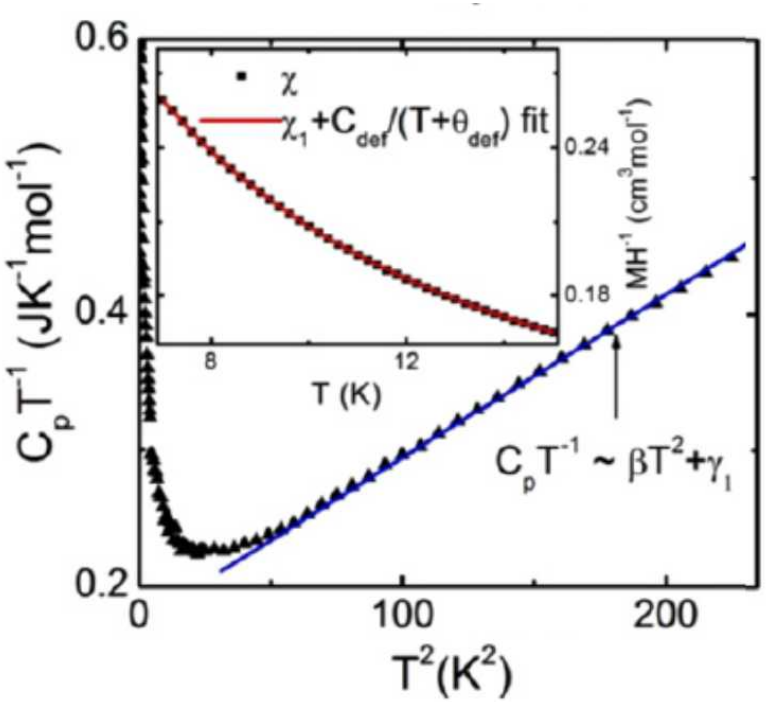
langite, $Cu_4(OH)_6SO_4(H_2O)_2$
[New J. Phys. 18, 033020 (2016)]

- **Phonons:** $C_p \sim T^3$ (always there!)

- **Heisenberg antiferromagnet:** $C_p \sim T^3$
- **Heisenberg ferromagnet:** $C_p \sim T^{\frac{3}{2}}$
- **Spin gap:** $C_p \sim \exp(-\Delta/T)$

- Low-temperature specific heat probes **characteristic magnetic excitations**
- The data below 1.8 K may be needed (PPMS with ^{3}He insert)
- Nevertheless, it helps to check C_p/T even above 1.8 K;

Specific heat: low-T contributions



$ZnCu_3(OH)_6SO_4$
[New J. Phys. 16, 093011 (2014)]

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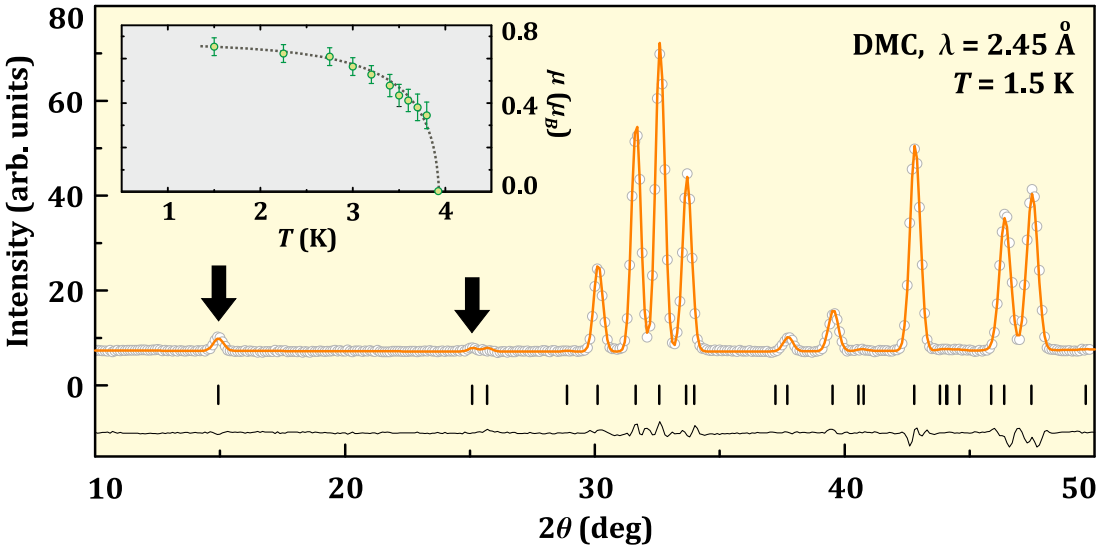
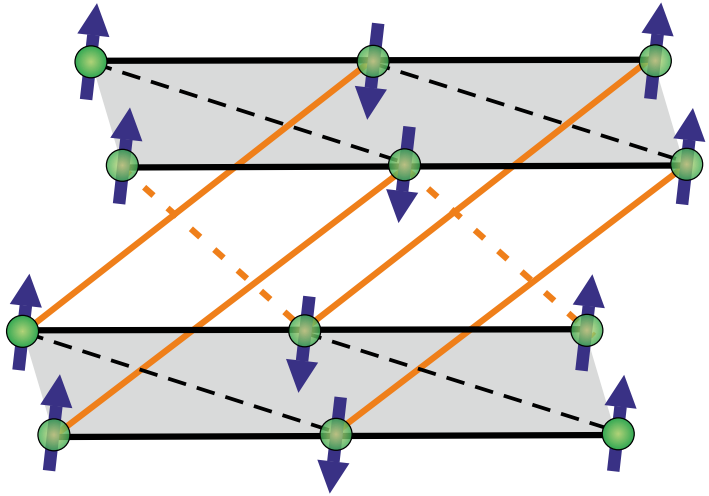
- **Other power laws:**
  you might have found something interesting!
  $C_p \sim T \quad \longrightarrow$ gapless spin liquid

- Low-temperature specific heat probes **characteristic magnetic excitations**
- The data below 1.8 K may be needed (PPMS with ^{3}He insert)
- Nevertheless, it helps to check C_p/T even above 1.8 K; finite zero-temperature value means you have an unusual magnet, or simply a metal...

Neutron diffraction

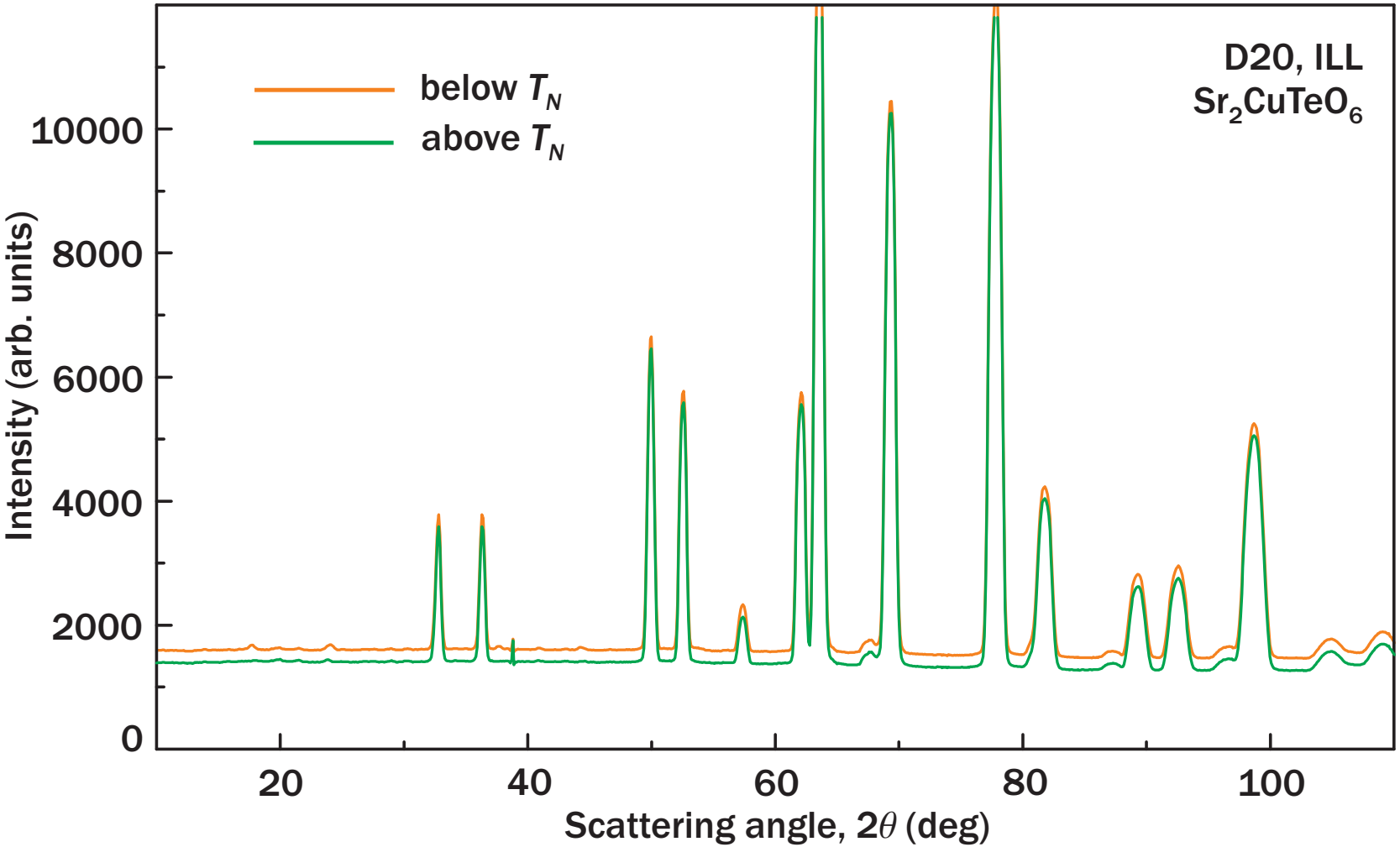




$Li_2CuW_2O_8$ [Phys. Rev. B 92, 094426 (2015)]

- **Type of magnetic order** (you get from the experiment)
- **Size of the ordered moment** (need an idea in advance)

Ordered moment is important



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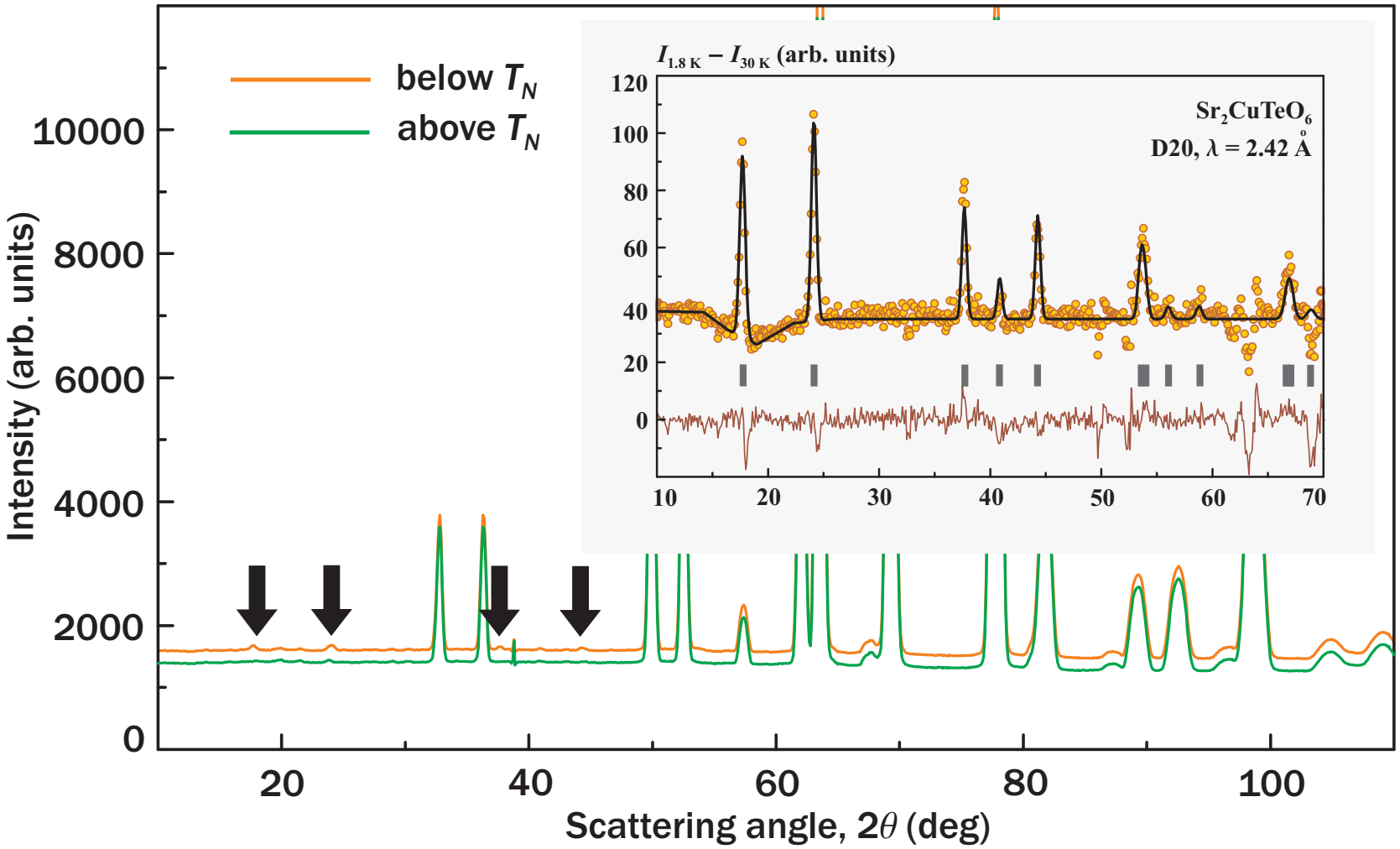
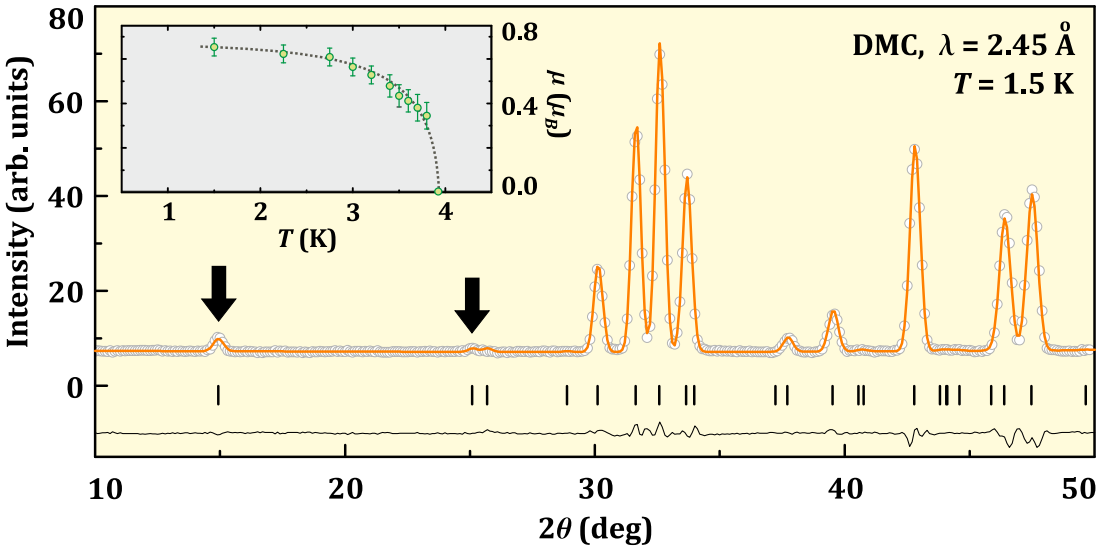
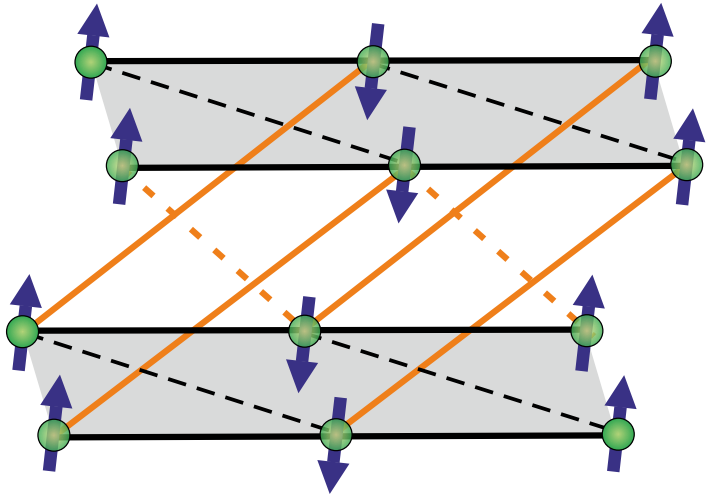


- $I_{\mathrm{mag}} \sim \mu^2$ and can be very low, especially for spin-$\frac{1}{2}$
- **Always choose the right diffractometer** (long wavelength, high flux)

Neutron diffraction





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Successful beamtime proposal should include:

- *Transition temperatures* confirmed by thermodynamic measurements (susceptibility, specific heat)
- *Estimate of the ordered moment* (Curie-Weiss effective moment, saturation magnetization)

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- Magnetization (+susceptibility)
- Specific heat
- Neutron diffraction

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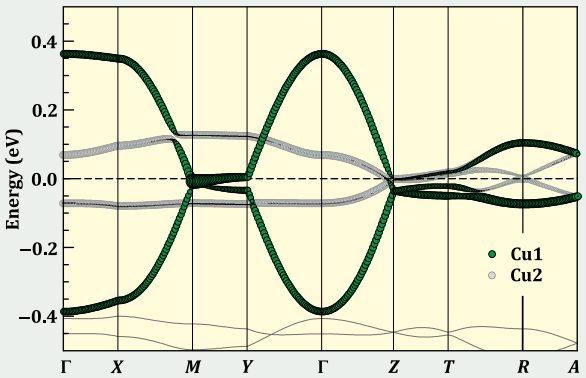

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$$\hat{H} = \sum_{\langle ij \rangle} J_{ij}\, \hat{\mathbf{S}}_i\, \hat{\mathbf{S}}_j + \sum_{\langle ij \rangle} \mathbf{D}_{ij} [\hat{\mathbf{S}}_i \times \hat{\mathbf{S}}_j] + \sum_{\langle ij \rangle} \hat{\mathbf{S}}_i\, \Gamma_{ij}\, \hat{\mathbf{S}}_j + \sum_i A_i \hat{S}_{iz}^2$$

- J_{ij} – isotropic (Heisenberg) exchange; normally, this is the leading term
- $\mathbf{D}_{ij}$ – Dzyaloshinsky-Moriya interactions (3 components)
- Γ_{ij} – symmetric part of the anisotropy (5 components)
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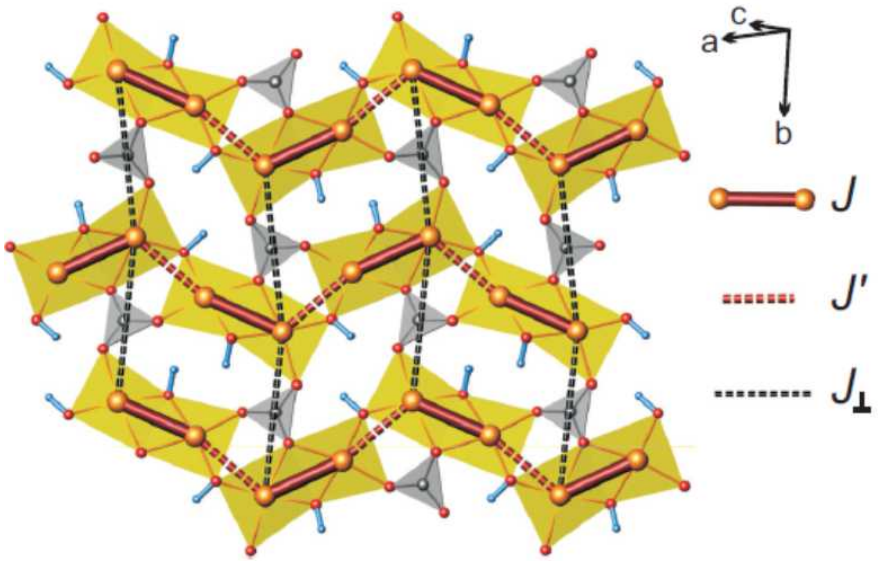
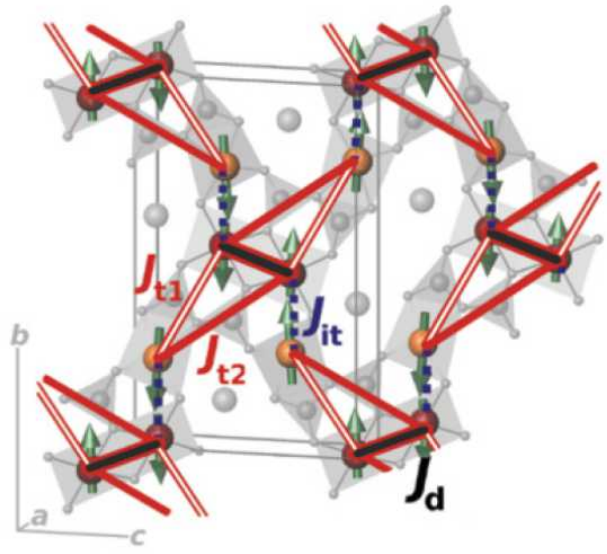
- Use **only the first term** unless you are interested in the magnetic moment direction, or observe anisotropic effects experimentally
  (very different behavior for different field directions, spin canting...)



malachite, $Cu_2(OH)_2CO_3$ [Phys. Rev. B 88, 224406 (2013)]

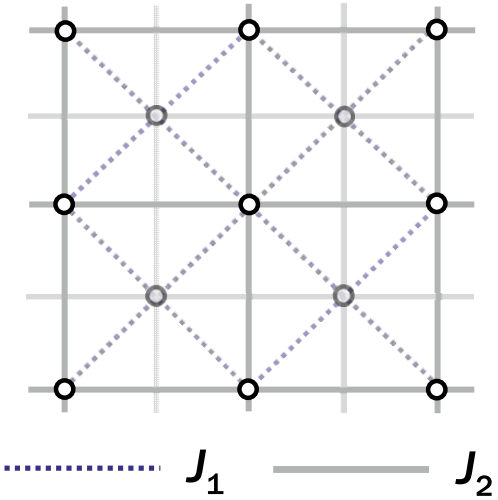


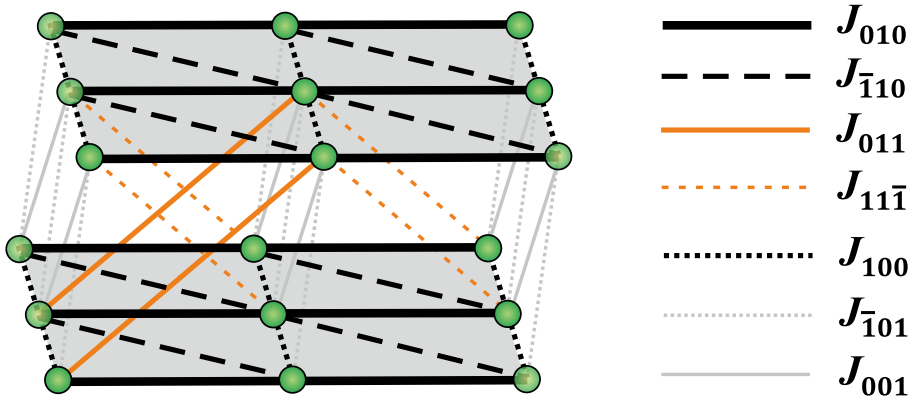
$CdCu_2(BO_3)_2$ [Phys. Rev. B 85, 064404 (2012)]

$$\hat{H} = \sum_{\langle ij \rangle} J_{ij}\, \hat{\mathbf{S}}_i\, \hat{\mathbf{S}}_j$$

J_{ij} are **exchange integrals** = magnetic interaction energies denoted by bonds of a **spin lattice**

Heisenberg model





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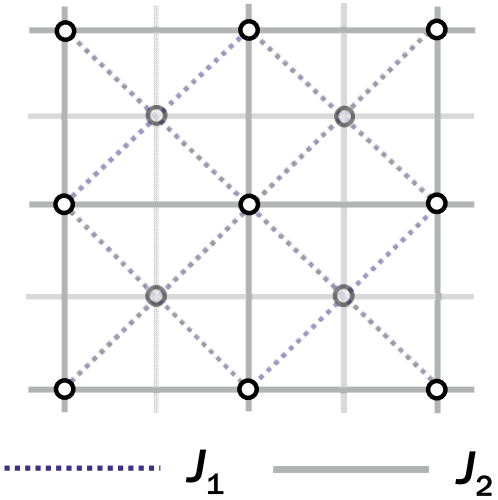

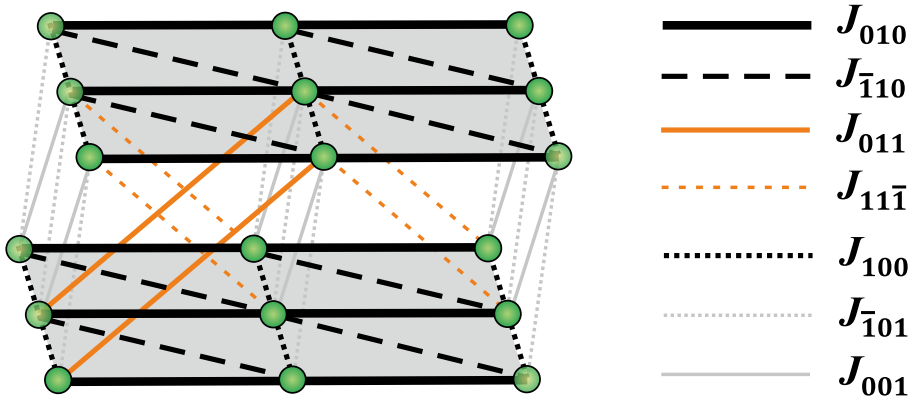

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- **The model is quantum, i.e., it contains spin operators, not simply spin vectors**
- Quantum features are important when we consider the magnetic behavior
- However, we usually disregard them when calculating J_{ij}'s from DFT

Two ways to extract the exchange parameters

- We usually do **DFT**
- It is also possible to use *quantum chemistry* (at least the MRCI level required), but then you are restricted to small clusters (long-range interactions are hard to get)

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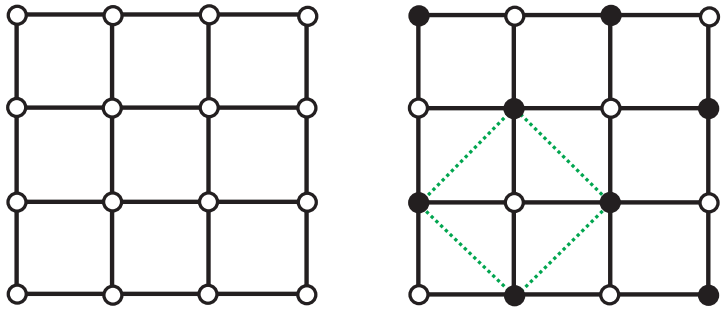
- Empirical corrections (DFT+U) or hybrid functionals required
- Can be applied to a wide range of materials
- "Shut up and calculate" type of approach



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- Take only free-electron part from DFT
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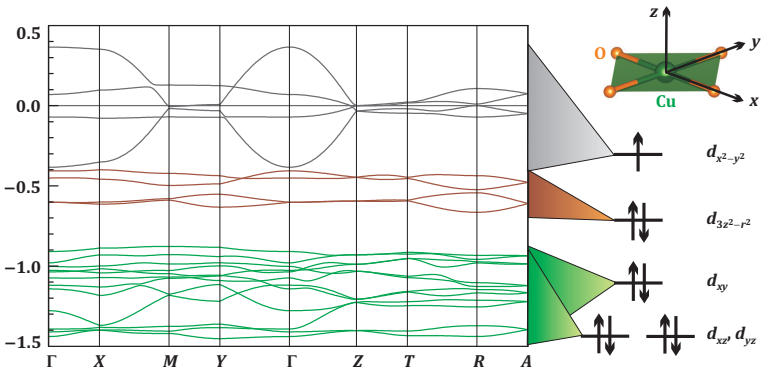
- More reliable and gives better insight



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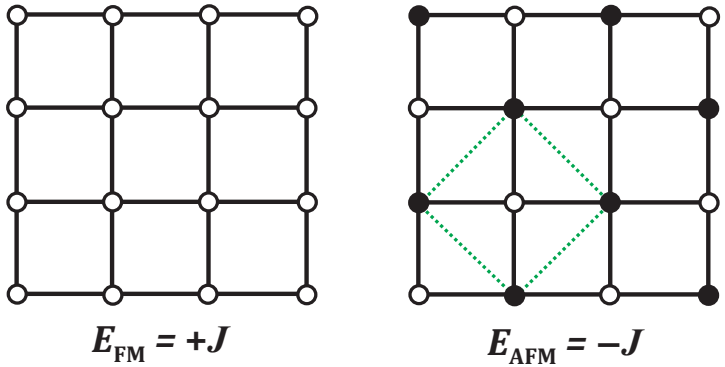

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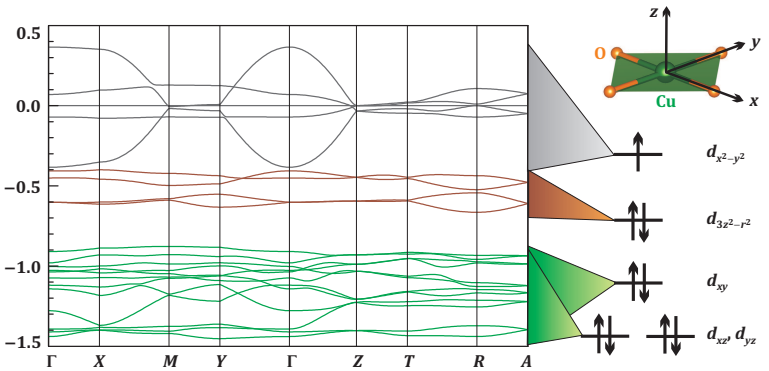
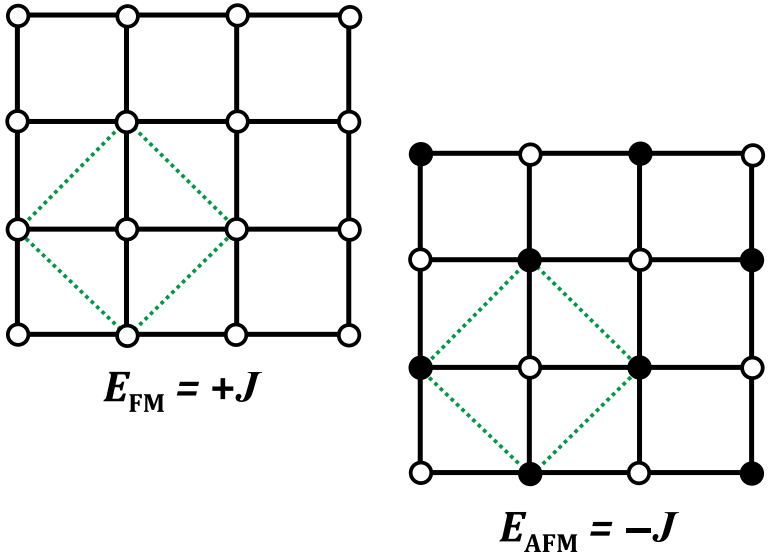


$$E = \sum_{\langle ij \rangle} J_{ij} S_i S_j$$

In a nutshell, $J \propto J_{\mathrm{FM}} - J_{\mathrm{AFM}}$



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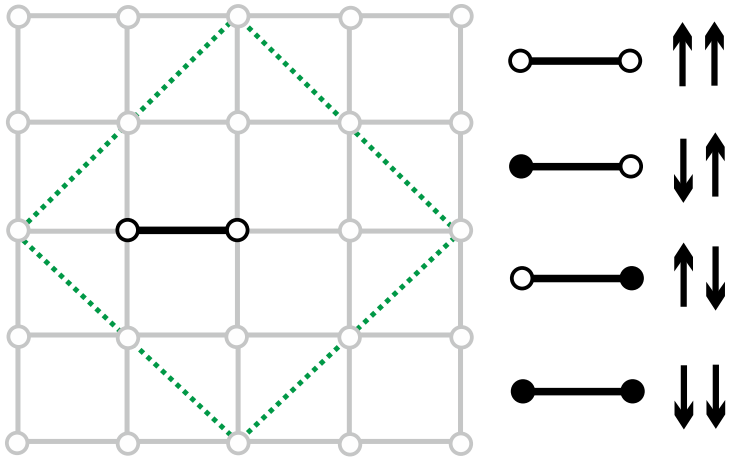
Advanced version:

$$J = \frac{E_{\uparrow\uparrow} + E_{\downarrow\downarrow} - E_{\uparrow\downarrow} - E_{\downarrow\uparrow}}{4S^2}$$



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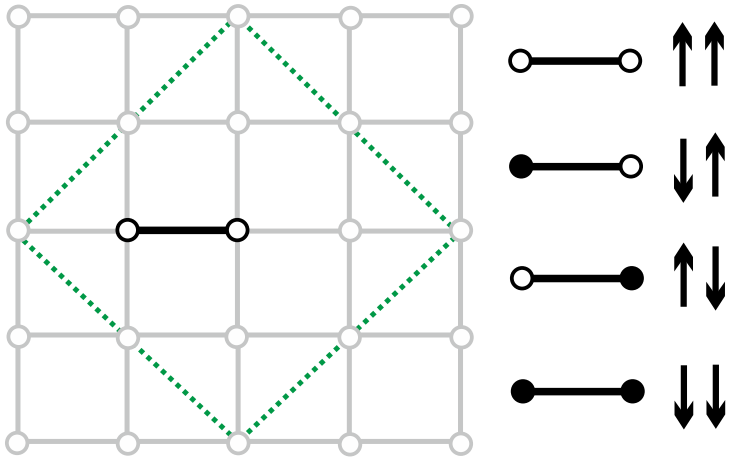

- Very easy and straight-forward, but you need accurate total energies
- **Hybrid functionals** may be OK, but you'll have to calculate large supercells (50+ atoms), so you may not like hybrid functionals for this particular problem
- **DFT+U** is faster and comparable in accuracy, especially if you choose the right U
  - Remember to use $J_H \neq 0$ (**Hund's exchange** is there and may be important) [Phys. Rev. B 79, 035103 (2009)]
  - Don't underestimate the (acute) problem of the **double-counting correction** [`LDAUTYPE` in VASP], see also [Phys. Rev. B 84, 144429 (2011)]

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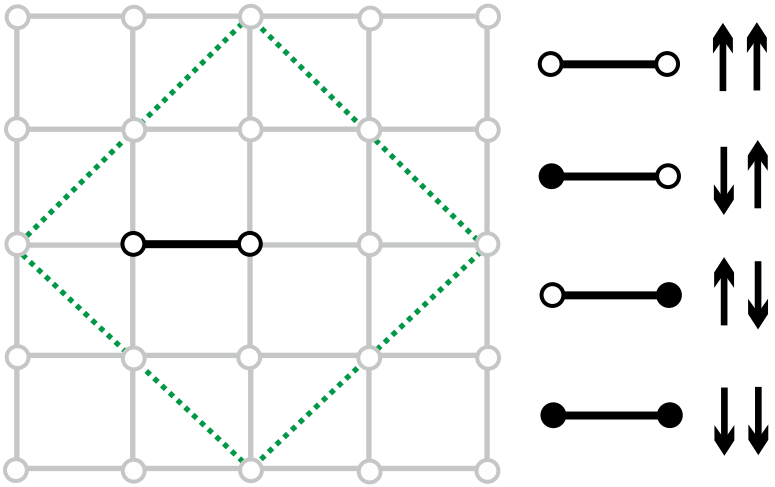

Choice of Hubbard U in DFT+U:

- Ask Olivier
- Ask recent literature
- Use several U values and choose the one that better fits (your) experiment

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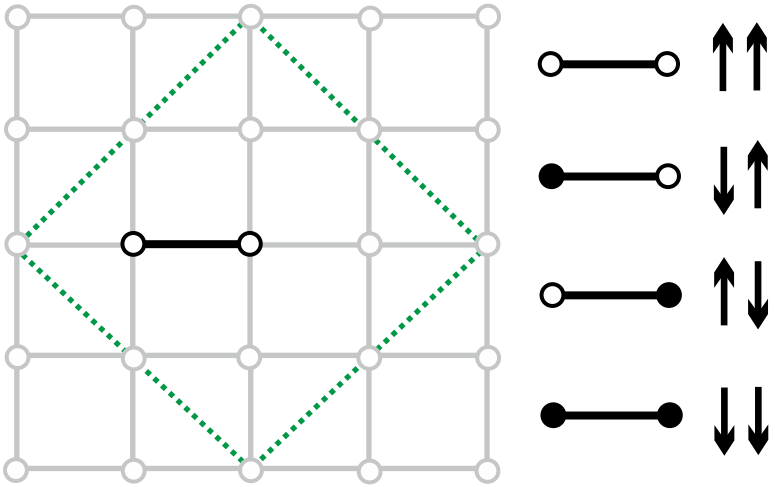

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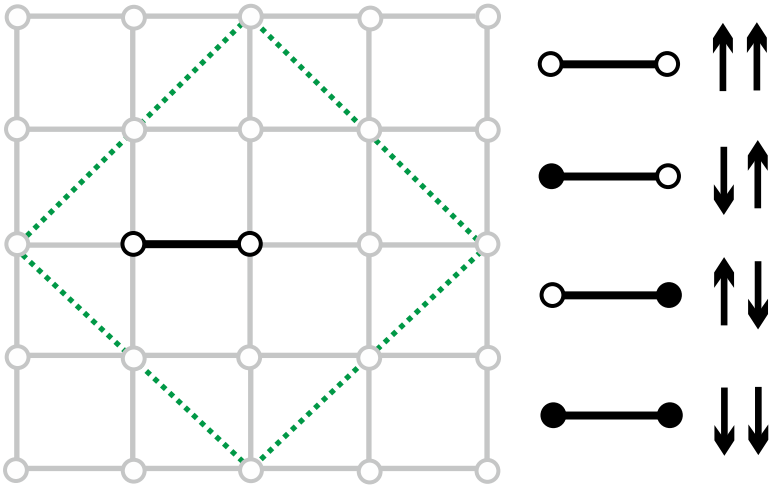

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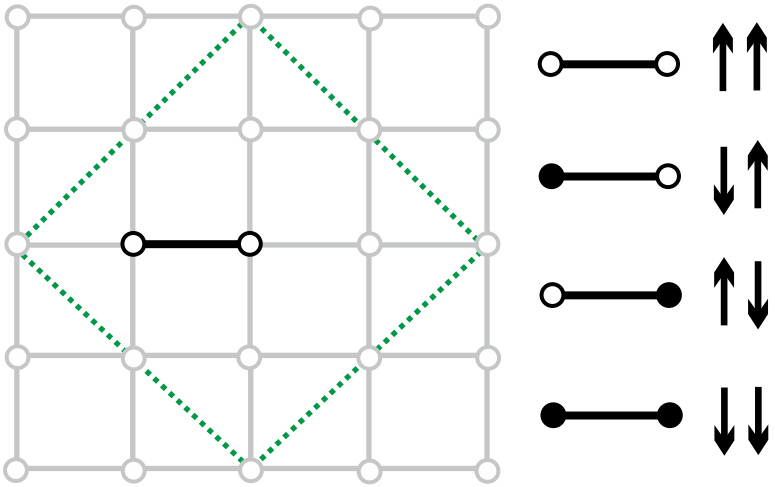

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- Use several U values and choose the one that better fits (your) experiment

- **Everyone has his/her own U value. That's normal. Take it easy!**
- *Philosophical remark*: We are not doing true *ab initio* here. One may be more *ab initio* with quantum chemistry, but you will also find junctures, where you have to look up some experimental data before you can really "predict" anything

$$\hat{H}_{\text{electronic}} = \sum_{i,j,\sigma} t_{ij}\, \hat{C}^{+}_{i\sigma} \hat{C}_{j\sigma} + \sum_{i} U_{\text{eff}}\, \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}$$

i and j label sites

$$\hat{H}_{\text{spin}} = \sum_{i,j} J^{\text{AFM}}_{ij}\, \hat{\mathbf{S}}_i\, \hat{\mathbf{S}}_j$$

One-orbital model

J^{AFM}

at $t \ll U_{\text{eff}}$

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$\Downarrow$

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$$+ \sum_{i,\sigma,\alpha} (\varepsilon_0 + \Delta_\alpha)\hat{n}^{\alpha}_{i\sigma} - \sum_{\substack{i,\sigma,\sigma' \\ \alpha\neq\beta}} \frac{J_H}{2} (\hat{C}^{+}_{i\alpha\sigma}\, \hat{C}_{i\alpha\sigma'}\, \hat{C}^{+}_{i\beta\sigma'}\, \hat{C}_{i\beta\sigma} + \text{H.c.})$$

Multi-orbital model

$\Downarrow$

i and j label sites, α and β label orbitals

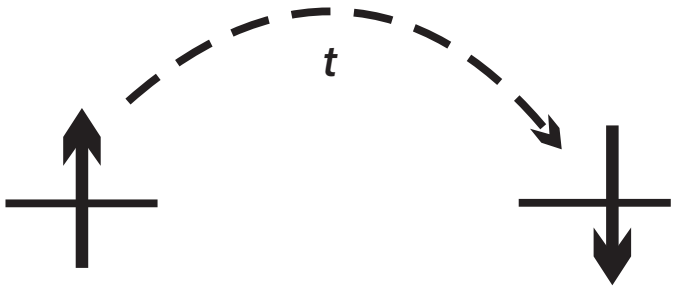
Δ_α are energy splittings, J_H is the Hund's coupling

$$\hat{H}_{\text{spin}} = \sum_{i,j} J_{ij}\, \hat{\mathbf{S}}_i\, \hat{\mathbf{S}}_j$$

$J = J^{\text{AFM}} + J^{\text{FM}}$

at $t \ll U_{\text{eff}}$

Kugel-Khomskii model



Electron hops to the half-filled orbital

$$J^{\mathbf{AFM}} = 4t^2/U$$

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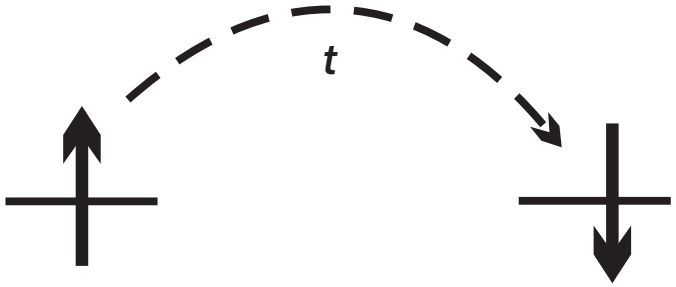

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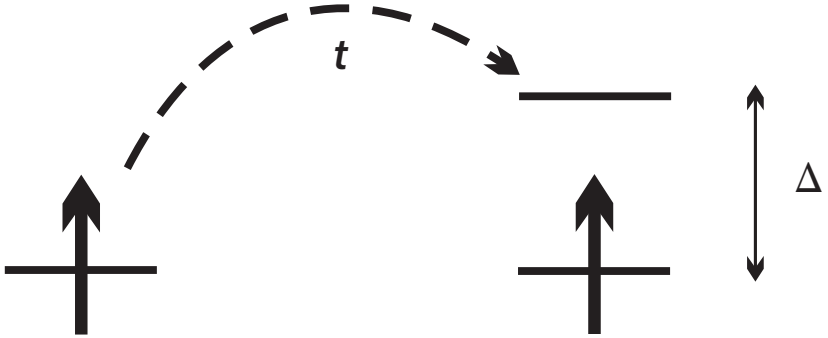
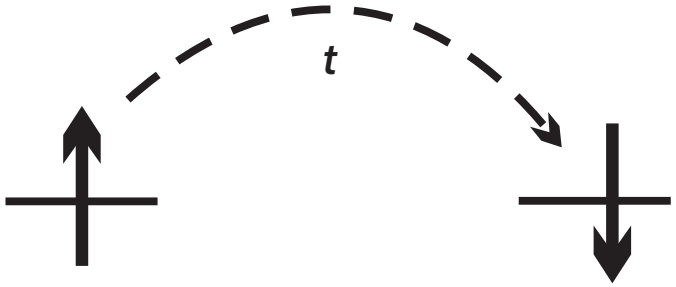


Electron hops to an empty orbital

$$J^{\mathbf{FM}} = -\frac{4t^2}{(U+\Delta)(U+\Delta-J_H)}$$

J_H is the *on-site Hund's coupling*
Δ is the *crystal-field splitting*



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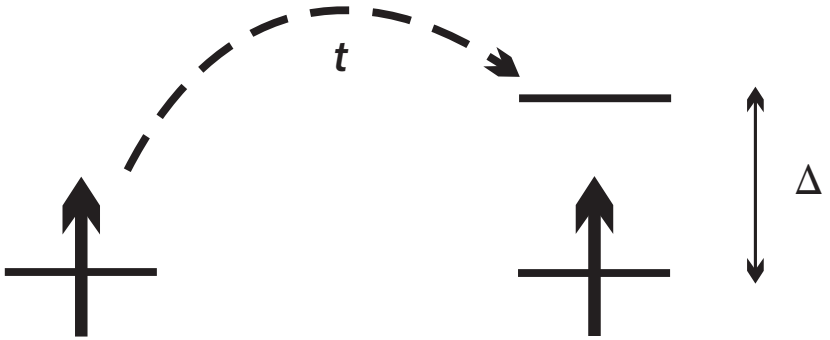

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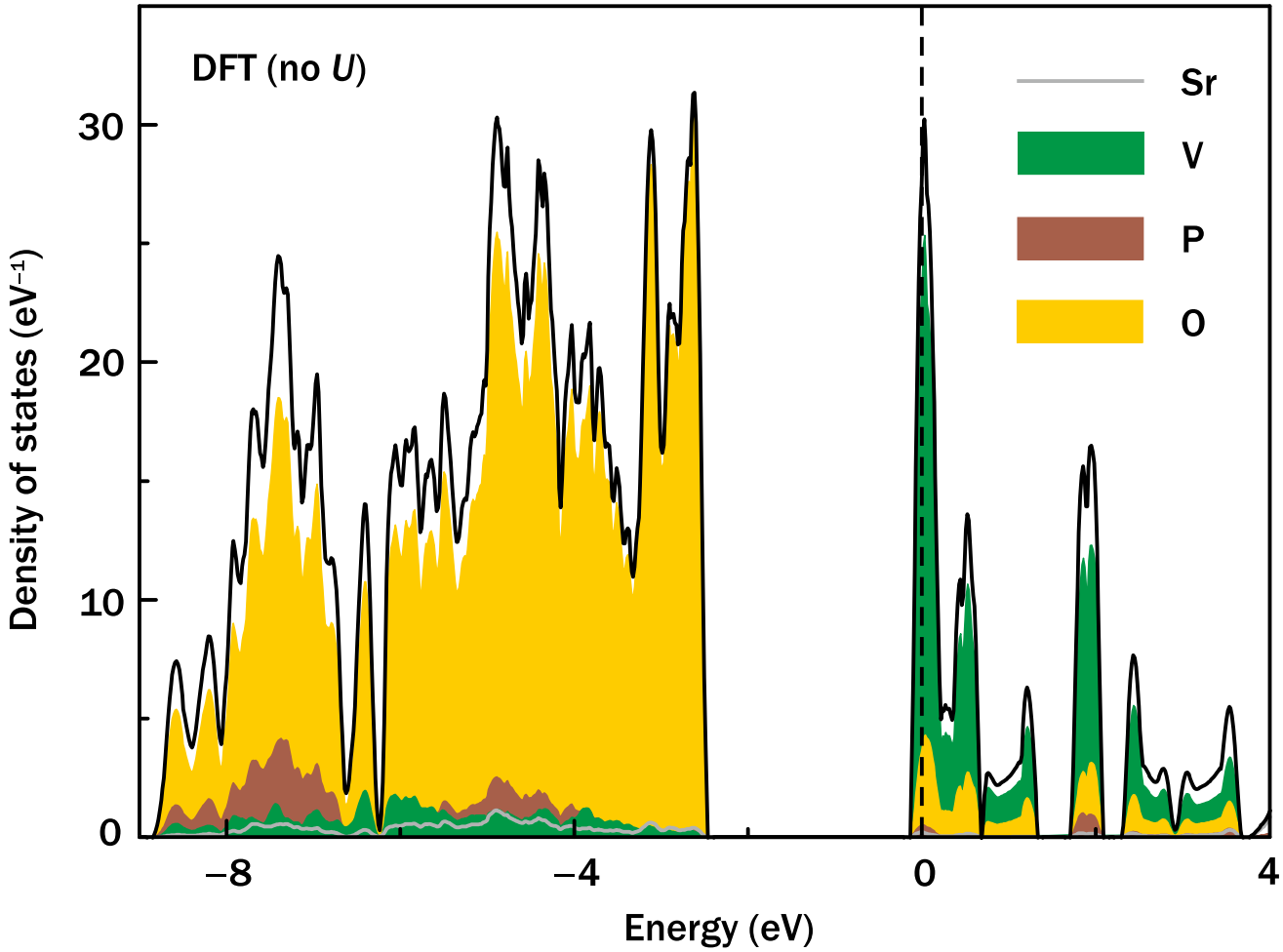
- Use the *uncorrelated* band structure (no need to mess around with DFT+U)
- The results still depend on U, but this dependence is explicit now, and, in some cases, just unimportant: $J_2/J_1 \sim t_2/t_1$

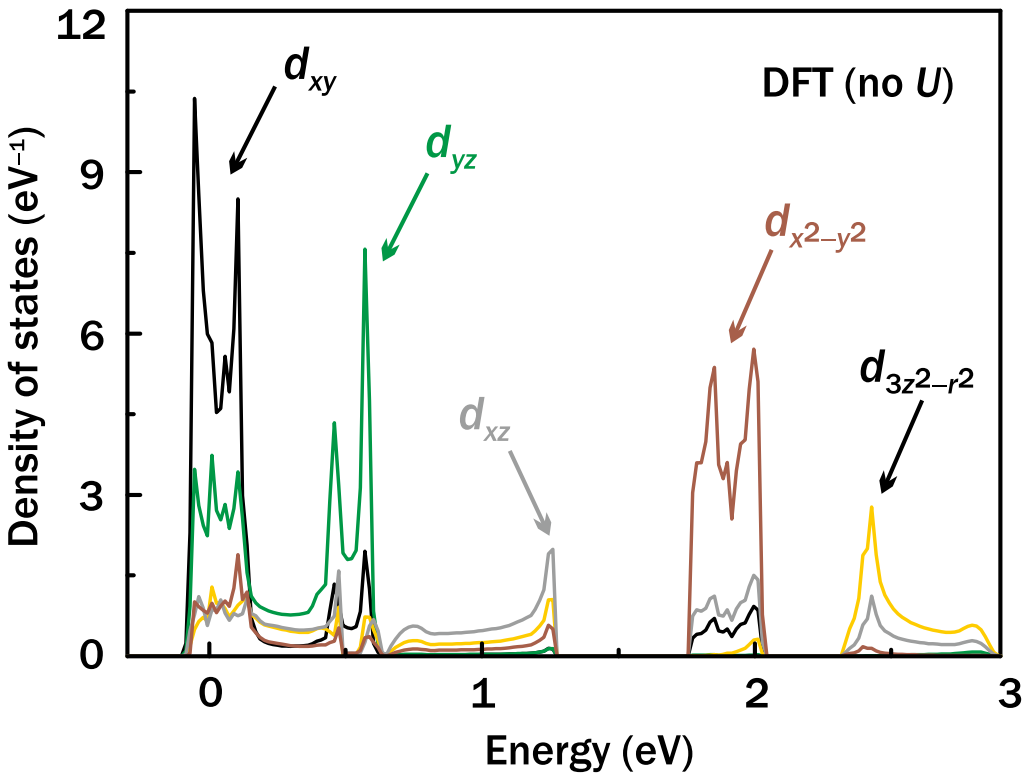
▶ **Clear microscopic picture behind the magnetic interactions**

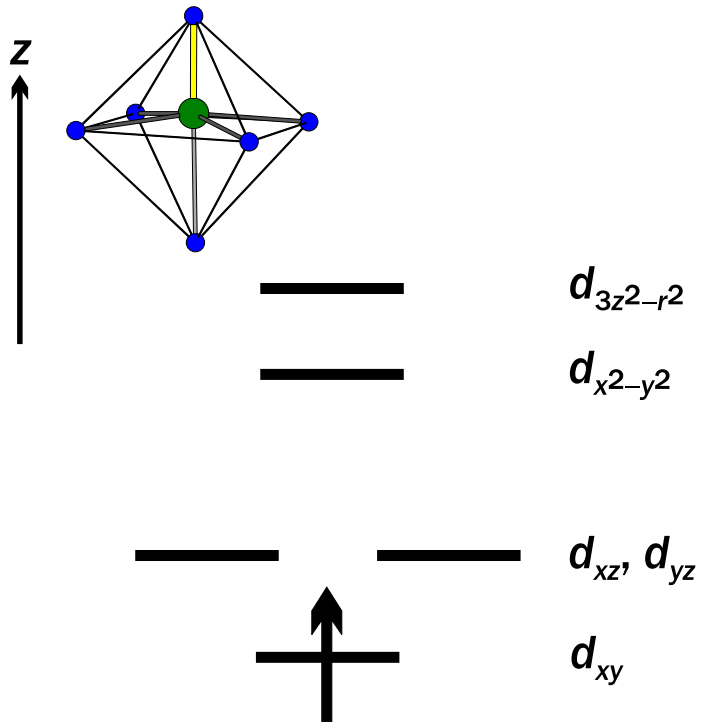
Example: $Sr_2VO(PO_4)_2$



- $Sr_2VO(PO_4)_2$ is magnetic **insulator**, $V^{4+} = d^1$
- We obtained metallic band structure because we have not used U
  That was intentional!

Example: $Sr_2VO(PO_4)_2$, V^{4+} is magnetic





- Identify the magnetic orbital(s) [those lying close to the Fermi level]
- Check that crystal-field levels make sense
- Use **Wannier functions** to extract orbital energies (ε) and electron hoppings (t)
- Introduce t's into the Kugel-Khomskii or similar formulas

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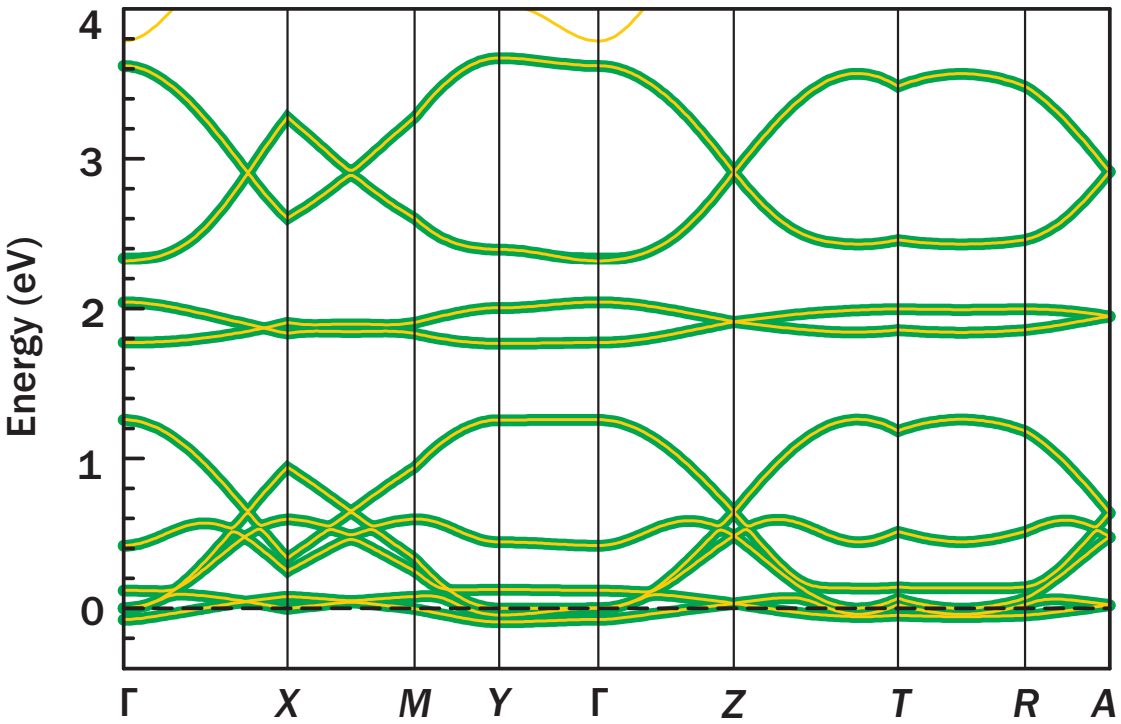

	ε_0
$3z^2-r^2$	2.94 eV
x^2-y^2	1.91 eV
xz	0.64 eV
yz	0.32 eV
xy	0.06 eV

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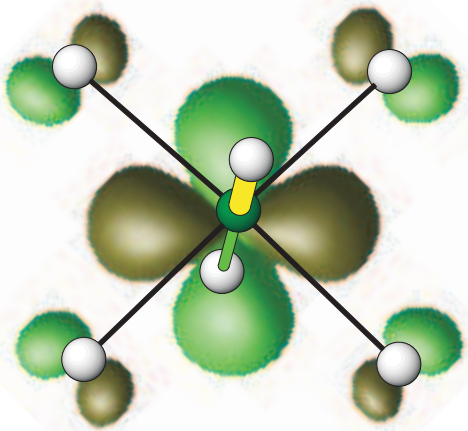
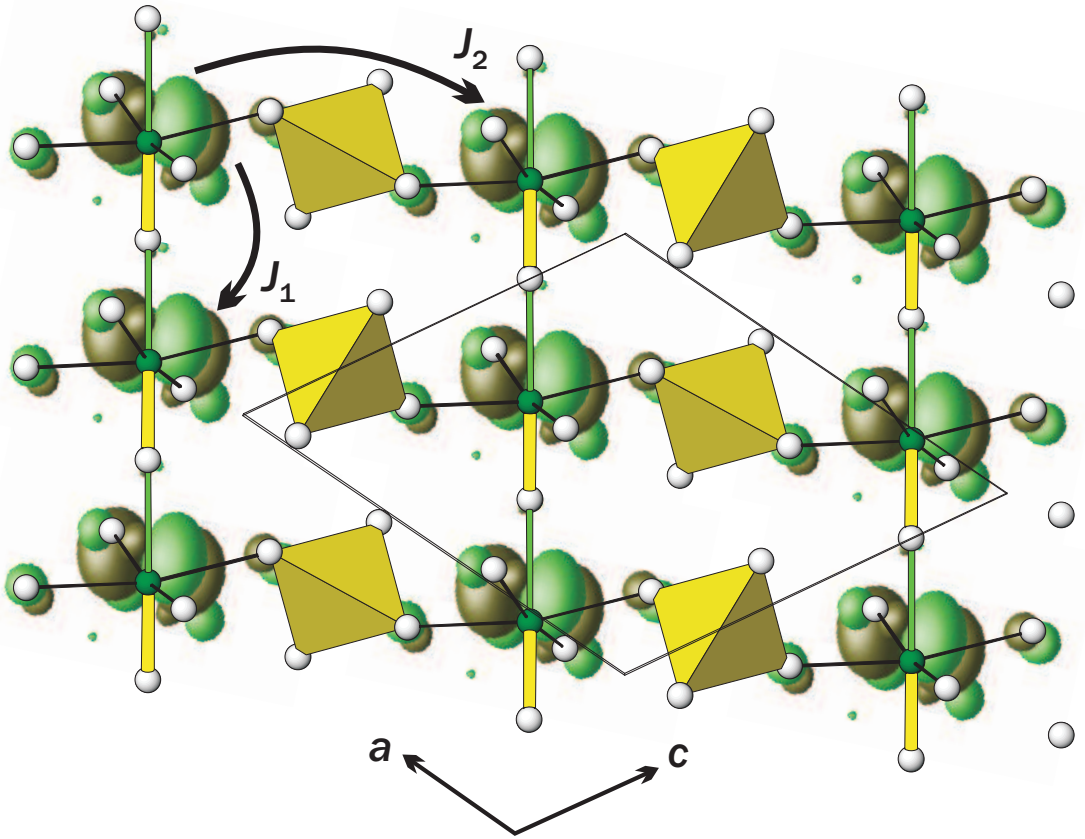
Example: $Sr_2VO(PO_4)_2$, orbital picture



VO_6 octahedron



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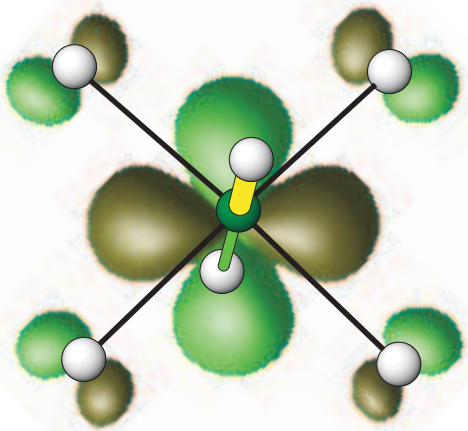

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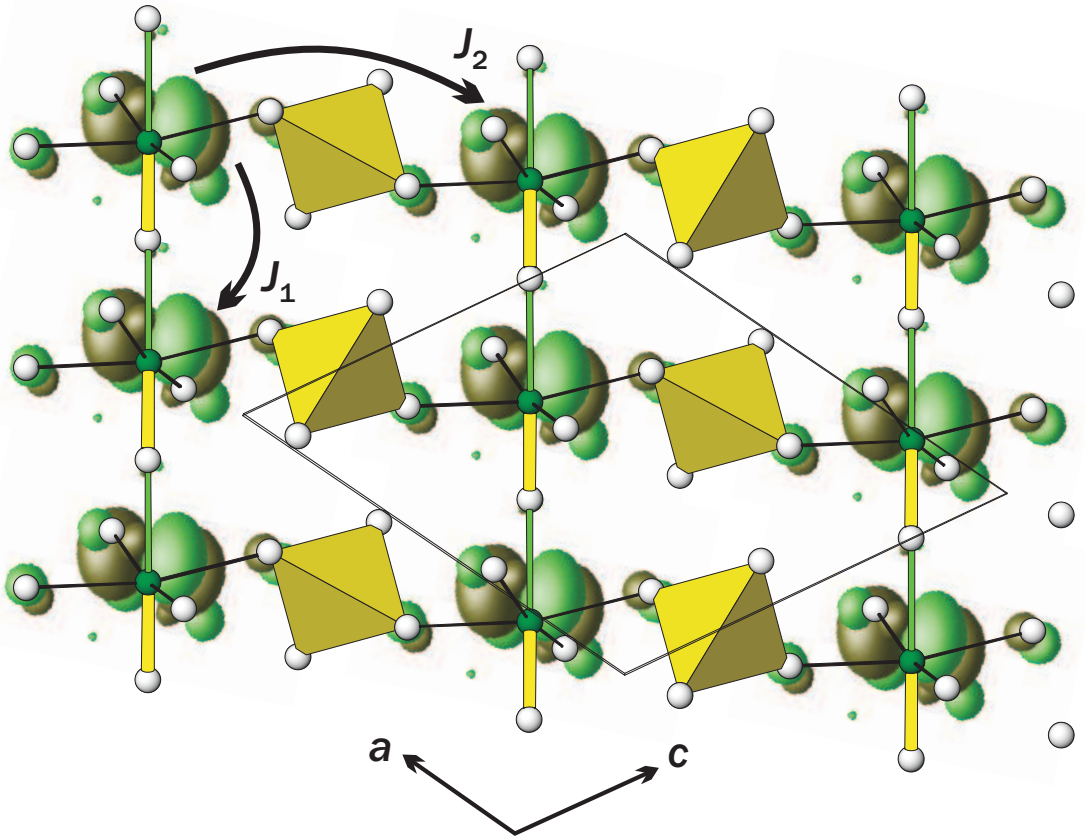

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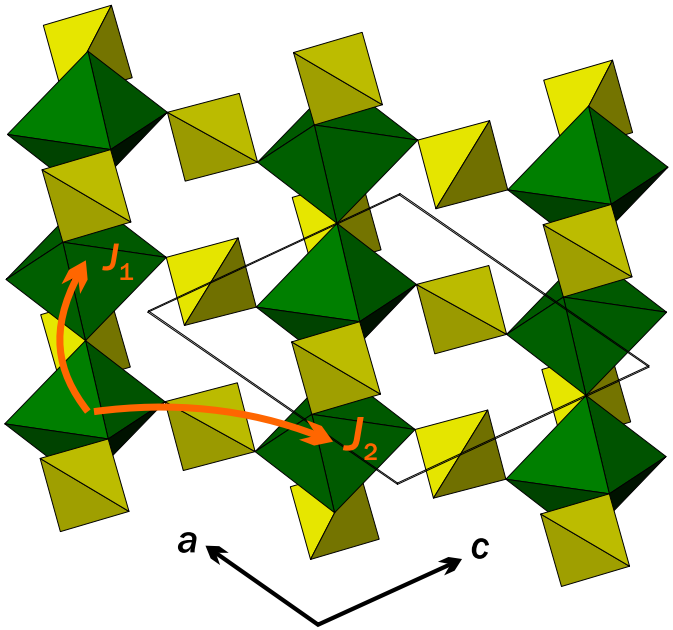
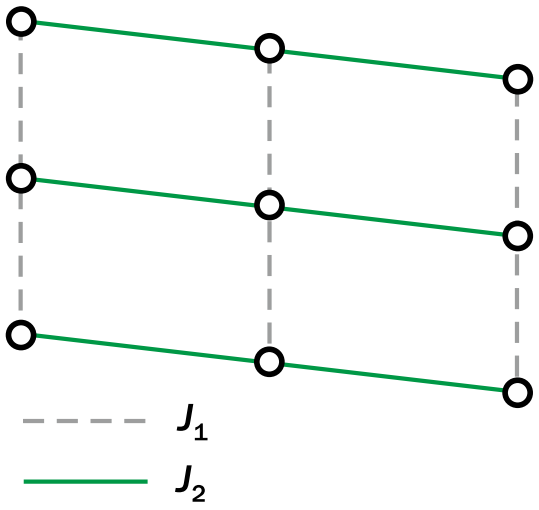
Magnetic orbital is perpendicular to the –V–V–V– chain

$Sr_2VO(PO_4)_2$: model vs. mapping approaches





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Model approach	−4.7	9.7
DFT+U, $U_d = 4$ eV	2.5	15.7
DFT+U, $U_d = 6$ eV	−8.1	13.2
Experiment	−8.3	5.9

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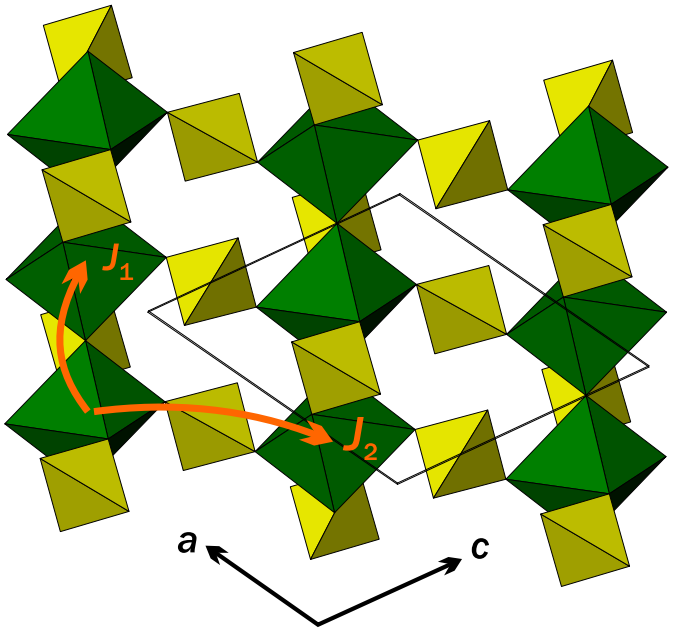

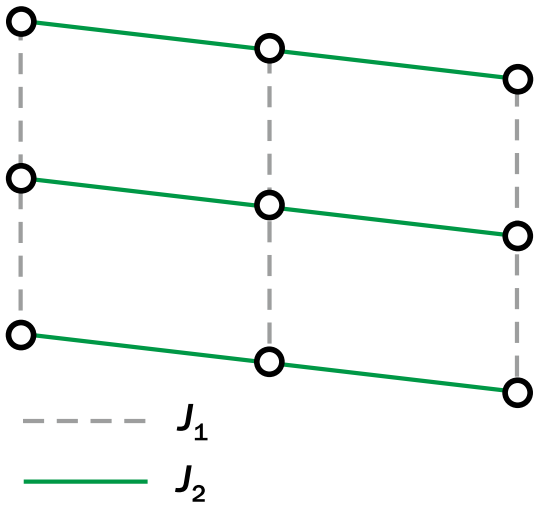

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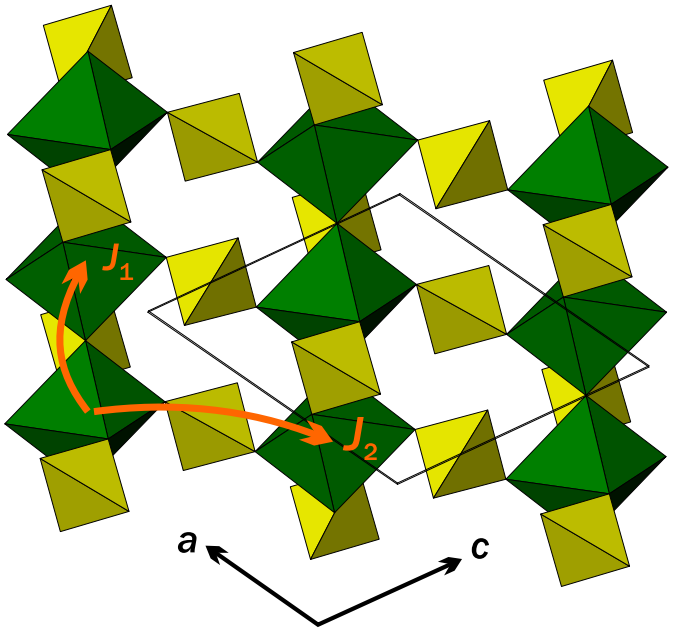

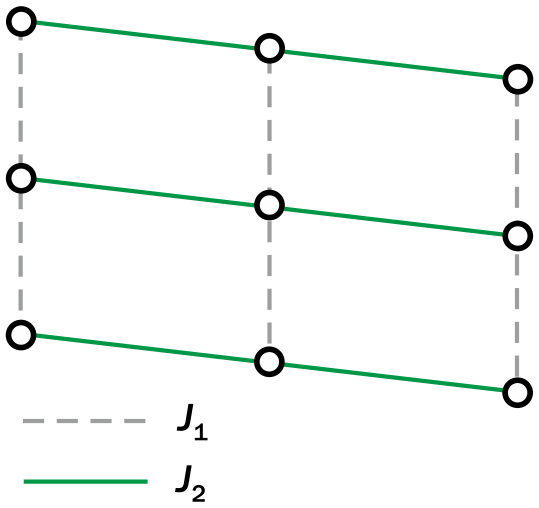

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Model vs. mapping approaches

- **Model approach** is most convenient when you have only one magnetic orbital
  viz. spin-$\frac{1}{2}$: Cu^{2+}, V^{4+}, Ti^{3+}, etc.
- **Mapping approach** can be used for any magnetic ion
  without thinking how many orbitals it has
- **But:** orbitally degenerate scenarios are difficult in DFT+U (Ti^{3+}, Cr^{2+}, etc.),
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Before you use DFT+U, especially for magnetic parameters:

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- know what the **charge-transfer insulators** are, and where they appear
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- **Good news:** in most of the problematic cases, DFT+U will simply not converge
- **Bad news:** some non properly converged or otherwise flawed DFT+U results have
  been published, see [J. Phys. Chem. A 114, 12345 (2010)] vs. [arXiv:1106.3665]

Sanity checks

- There is a chance your DFT($+U$+whatever) results will be wrong. **What to do?**
  - Calculate J's in **different supercells**, make sure that the results are consistent
  - **Use model approach:** look at the electron hoppings and make sure that there are relevant hoppings for all strong J's
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  - $J \simeq 100\,\mathrm{K}$ for the Cu–Cu distance of 6 Å is quite possible,
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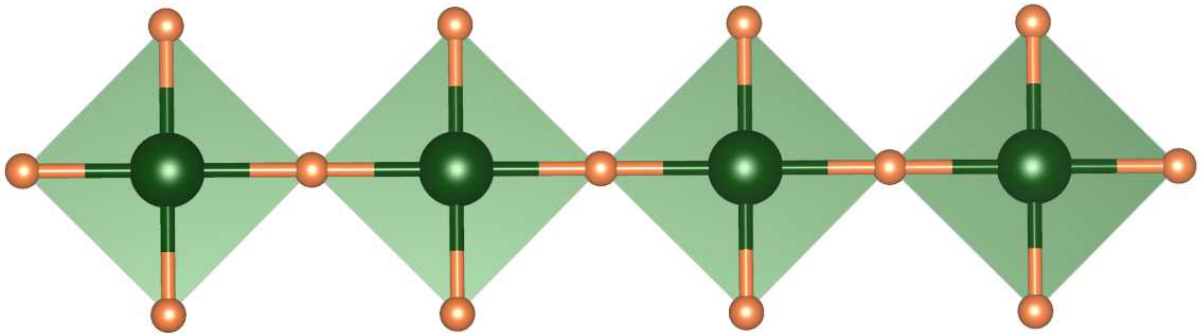
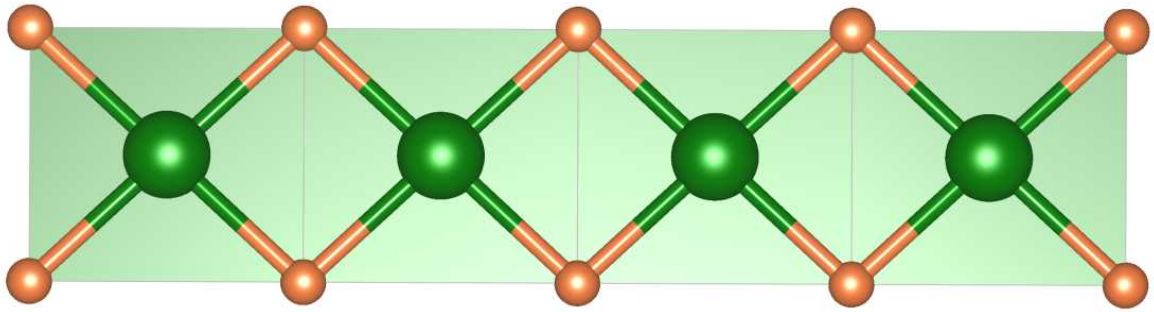
- **There are exceptions, but they confirm the rule**

Goodenough-Kanamori-Anderson: 180° vs. 90°



Sr_2CuO_3
180° superexchange
$J \simeq 2800\,\mathrm{K}$

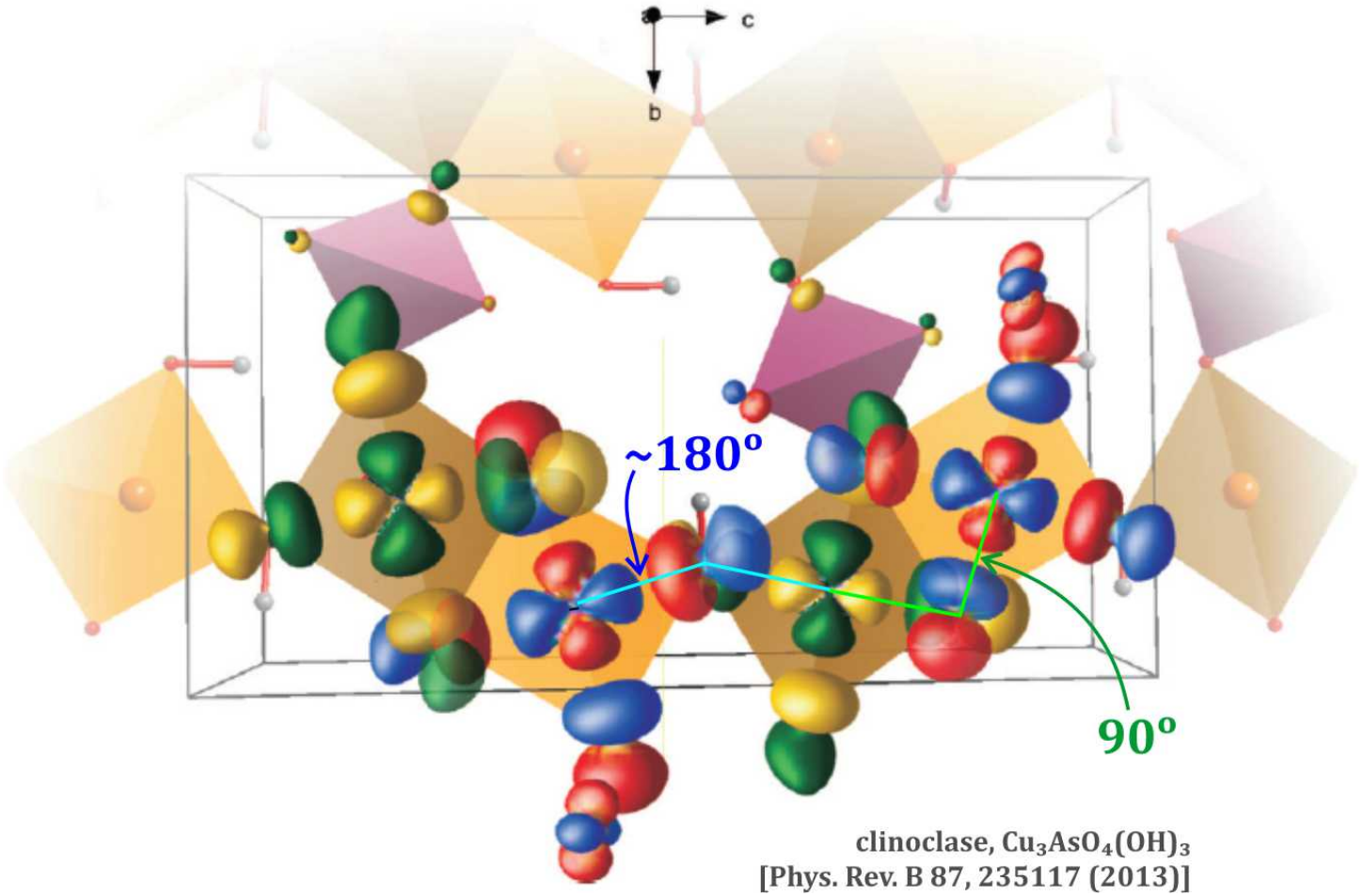


Li_2CuO_2
90° superexchange
$J \simeq -230\,\mathrm{K}$

Exchange between half-filled *d*-orbitals:

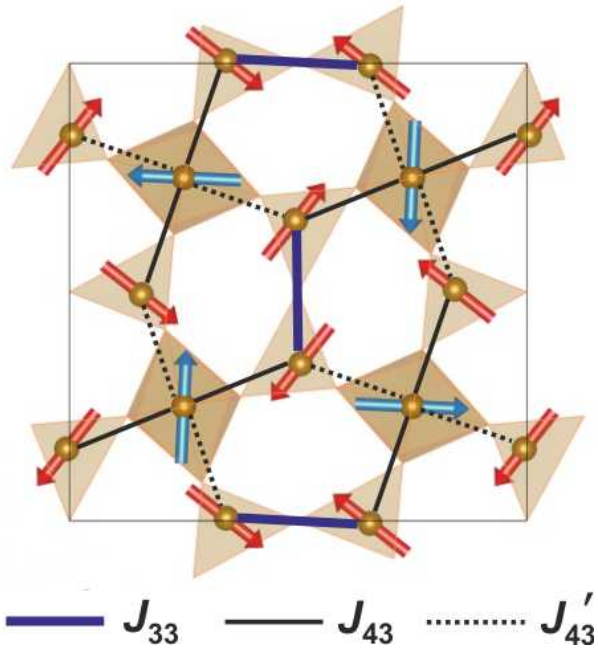
- 180° = strongly antiferromagnetic
- 90° = weakly ferromagnetic

Goodenough-Kanamori-Anderson: 180° vs. 90°

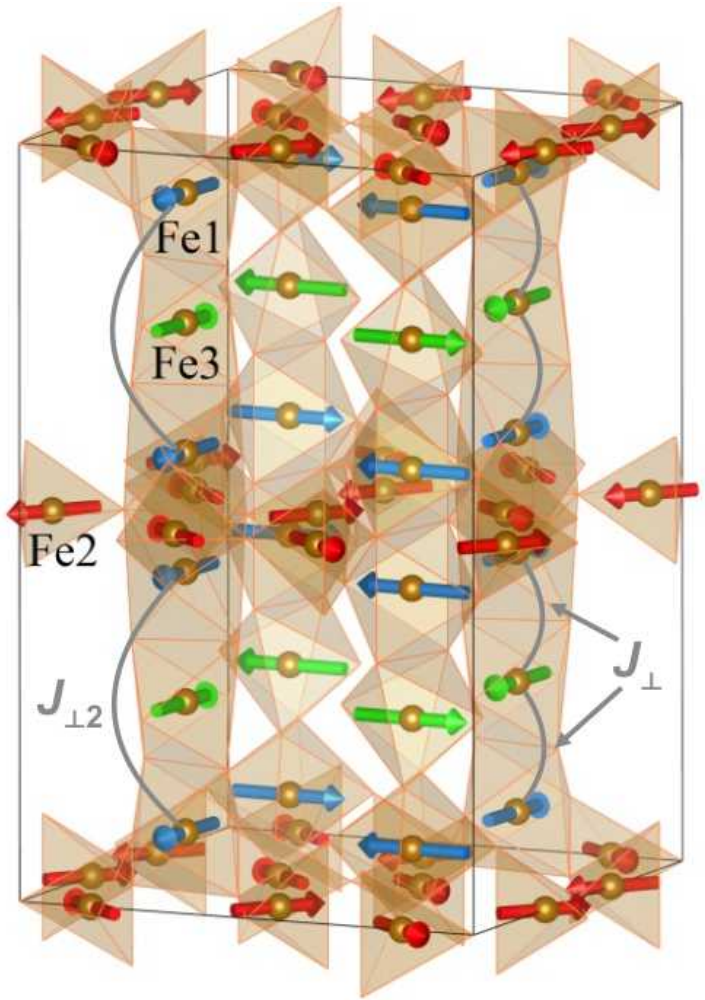


- 180° **superexchange** – magnetic *d*-orbitals overlap with the same *p*-orbital
- 90° **superexchange** – magnetic *d*-orbitals overlap with different *p*-orbitals

Goodenough-Kanamori-Anderson: example



	$d_{\mathrm{Fe-Fe}}$ (Å)	φ (deg)	J (K)
$J_\perp$	3.06	97.4	3
J_{44}	2.91	94.2	9
J_{43}	3.39	119.2	38
J_{43}'	3.53	130.9	57
J_{33}	3.64	180	116



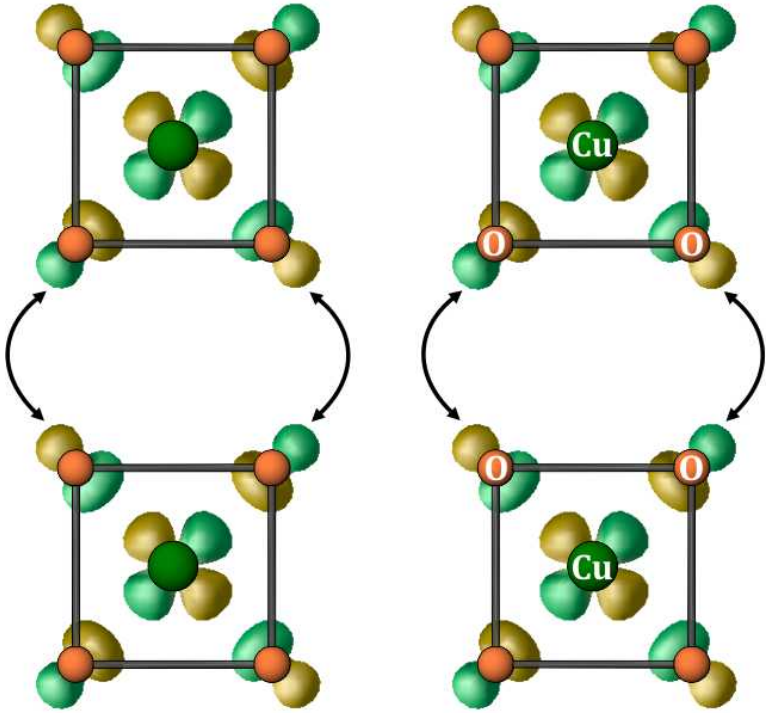
$Bi_4Fe_5O_{13}F$
[Phys. Rev. B 96, 094420 (2017)]

Super-super-...-superexchange

$Pb_2Cu(OH)_4Cl_2$

interatomic distance of 5.88 Å
$J \simeq 35\,\mathrm{K}$, $T_N = 11\,\mathrm{K}$
[Phys. Rev. B 87, 064404 (2013)]

linear Cu–O–O–Cu pathways are favorable for the superexchange



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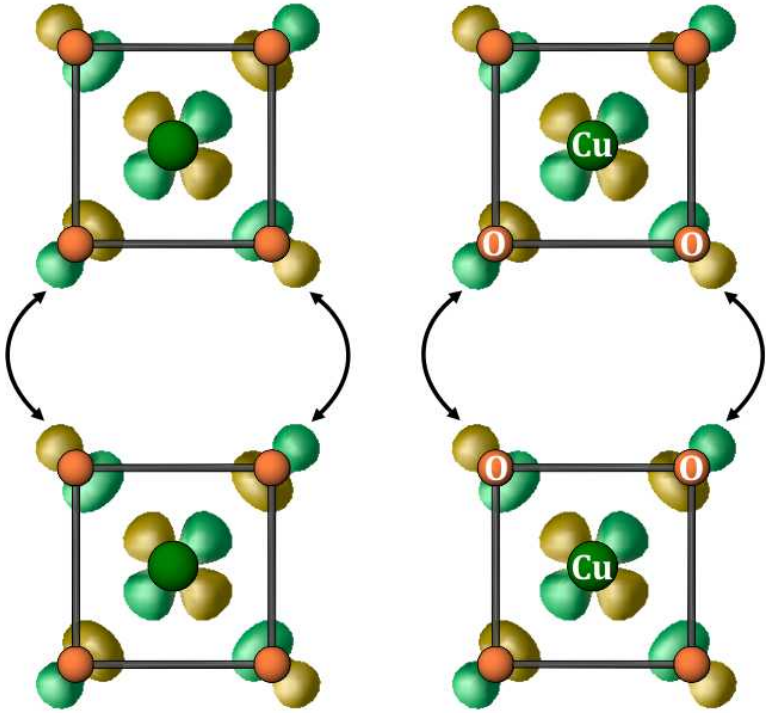
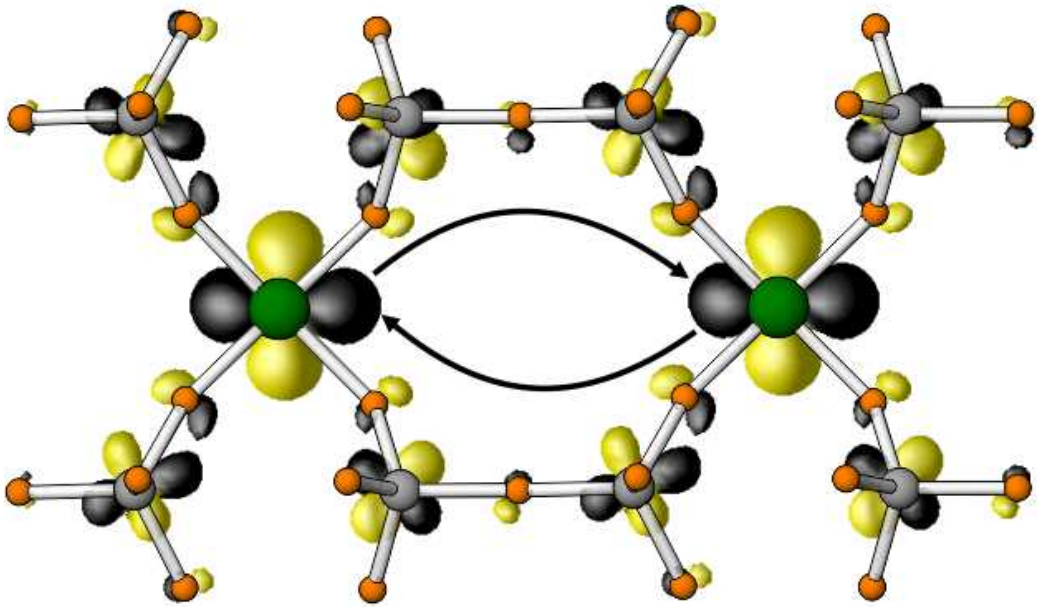




BaV_3O_8

interatomic distance of 7.43 Å
$J \simeq 38\,\mathrm{K},\ T_N = 6\,\mathrm{K}$
[Phys. Rev. B 89, 014405 (2014)]

additional low-lying orbitals
(here, d-orbitals of V^{+5})

What can we measure?

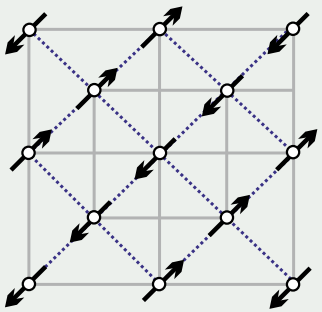
- Magnetization (+susceptibility)
- Specific heat
- Neutron diffraction

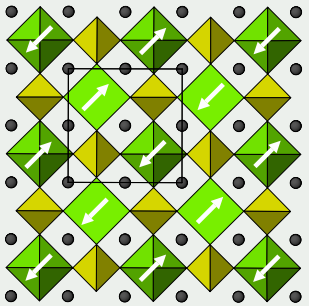
What can we calculate?

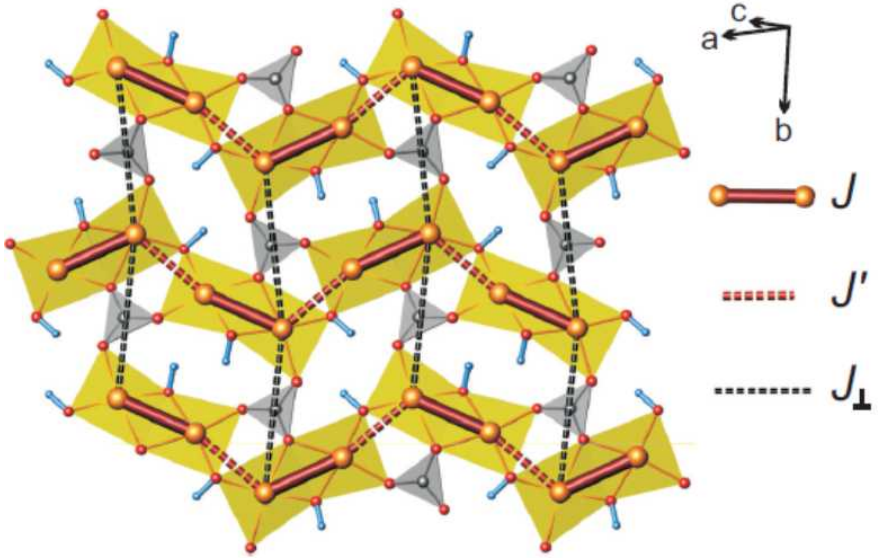
- Parameters of interest
- How to calculate?
- What to observe?

How to bring this together?

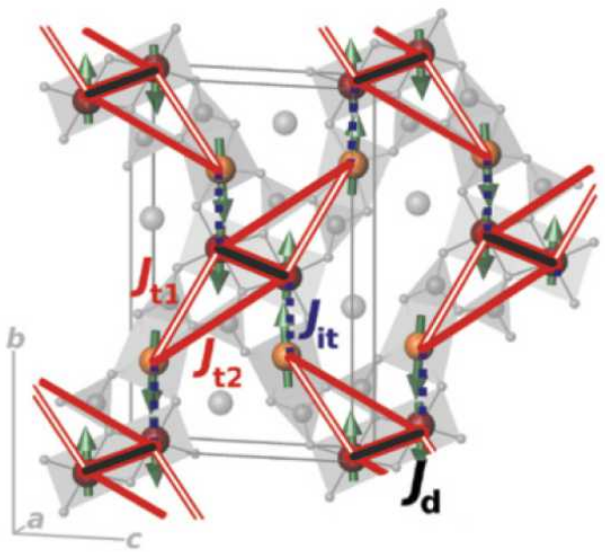
- Analytical solutions
- Numerical simulations
- Classical approximation







malachite, $Cu_2(OH)_2CO_3$ [Phys. Rev. B 88, 224406 (2013)]



$CdCu_2(BO_3)_2$ [Phys. Rev. B 85, 064404 (2012)]

$$\hat{H} = \sum_{\langle ij \rangle} J_{ij}\, \hat{\mathbf{S}}_i\, \hat{\mathbf{S}}_j$$

J_{ij} are **exchange integrals** = magnetic interaction energies denoted by bonds of a **spin lattice**

- **The model is quantum, i.e., it contains spin operators, not simply spin vectors**
- Quantum features are important when we consider the magnetic behavior

Analytical results

- In most cases, we can't solve the spin model analytically
- **but we can make approximations**

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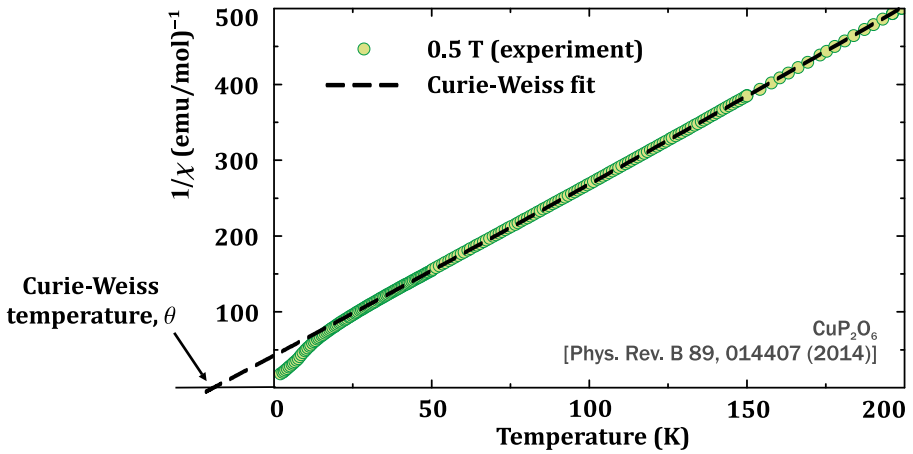
Curie-Weiss temperature:

$$\theta = \frac{S(S+1)}{3} \sum_i z_i J_i$$

sum of all couplings at a given lattice site (z_i is the number of couplings of type i)



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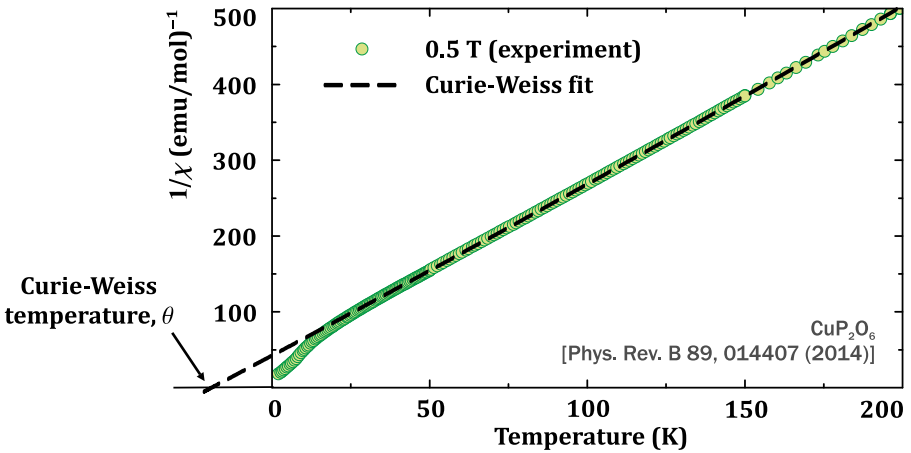
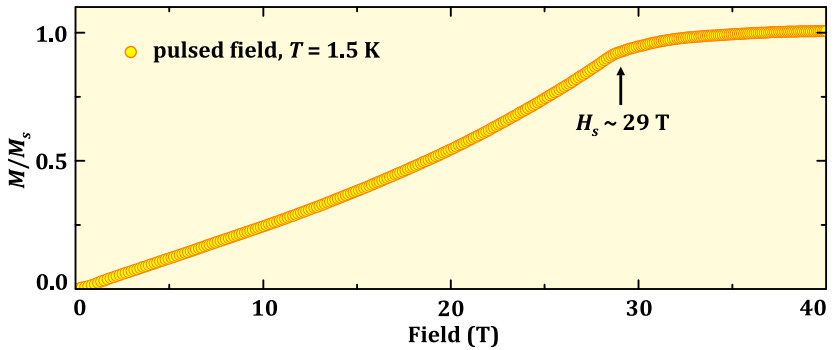


Saturation field:

$$\mu_0 H_s = \left(\frac{g\mu_B}{k_B}\right)^{-1} (E_{\mathrm{FM}} - E_{\mathrm{AFM}})$$

energy difference between the ferro- and antiferromagnetic states

example: $\mu_0 H_s = (k_B/g\mu_B) \times 8J \times S$ for a square-lattice antiferromagnet



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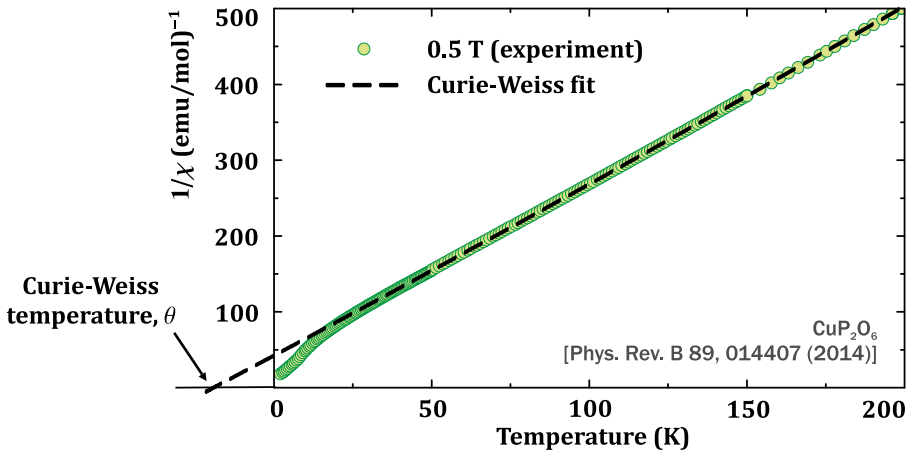

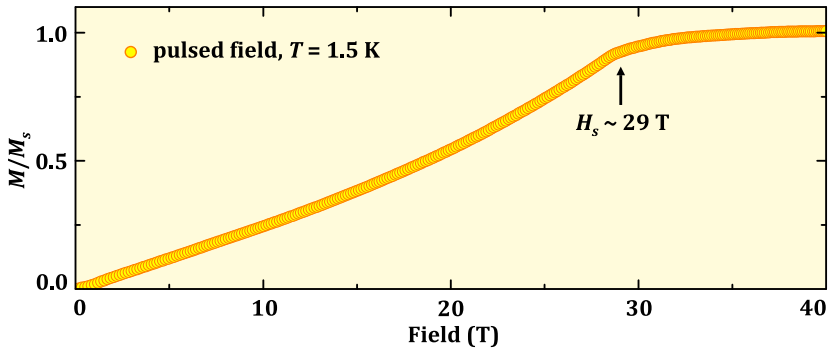

θ and H_s are a first check of your calculated J's

Numerical simulations

- In most cases, we can't solve the spin model analytically
- **but we can use numerical tools to simulate its magnetic response**

ALPS = Algorithms and Libraries for Physics Simulations

- **Diagonalization:** exact and sparse (Lanczos)
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- Computationally not very efficient

Numerical simulations: before you start

Define your lattice:

- bonds (interactions between the atoms)
- boundary conditions – open or periodic
- avoid frustration
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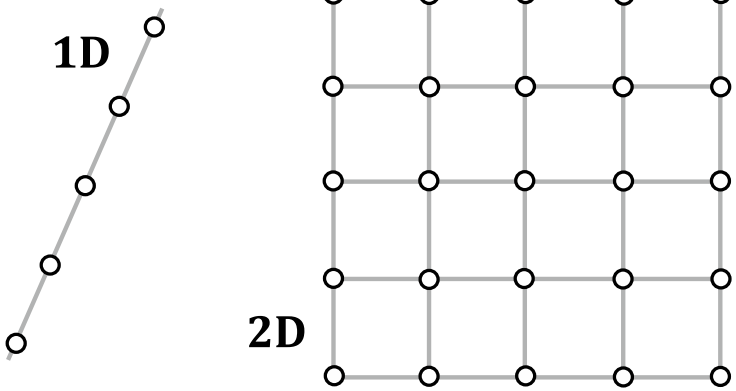

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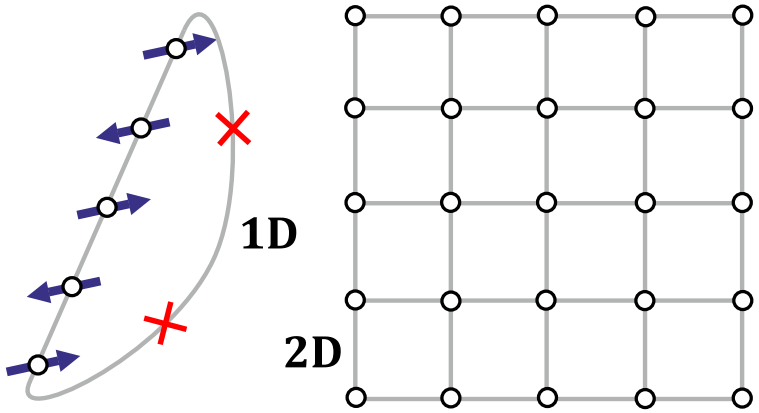

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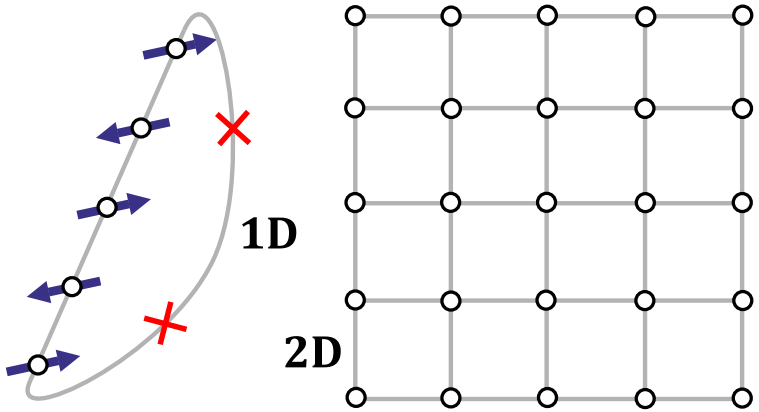
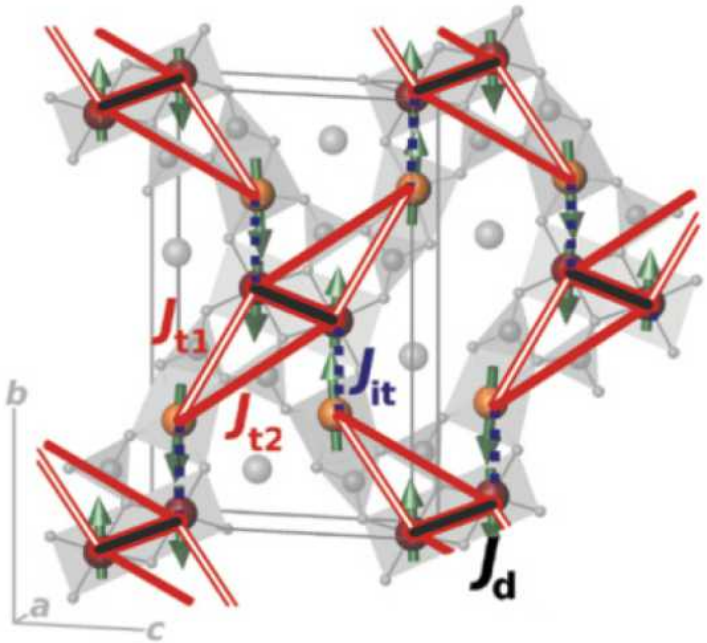


There will be mistakes. Verify your input:

- choose a *special interaction regime* and reduce your spin lattice to something simple (dimer, chain, etc.)

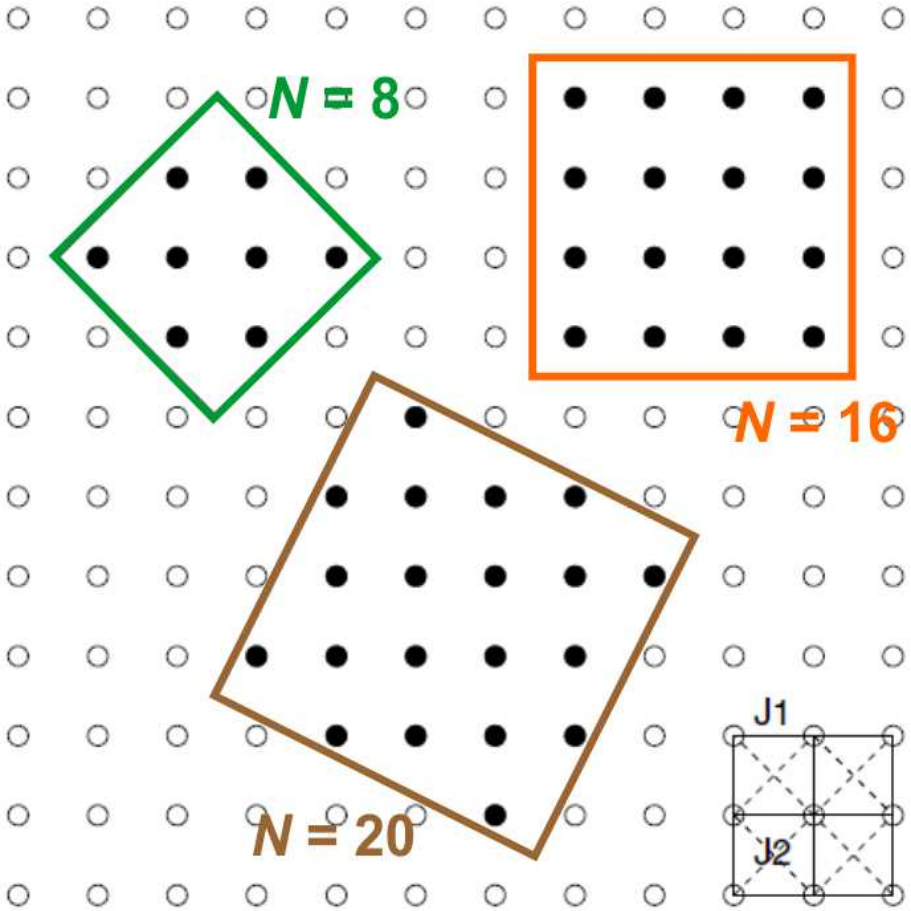
  J_{t1} only $\longrightarrow$ dimer
  J_d only $\longrightarrow$ dimer + 2 free spins

- *check* Curie-Weiss, saturation field, and overall behavior
- the program may not tell you how different quantities are normalized, but there are enough tools to check that out

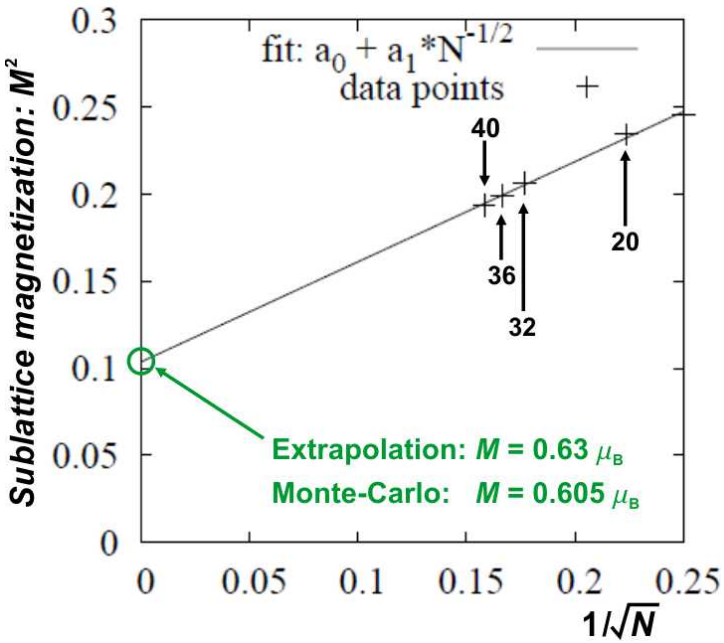


$CdCu_2(BO_3)_2$ [Phys. Rev. B 85, 064404 (2012)]

Numerical simulations: finite-size effects



Approximate infinite lattice
by a finite cluster with
periodic boundary conditions



- **Susceptibility:** it's enough to use ~ 6 unit cells along each dimension
- **Ordered moment:** you won't get the exact result, use finite-size scaling
- **Ordering temperature:** use universal scaling (Binder cumulant)

Numerical simulations: what to expect?

- **Simulation is done for a finite cluster**
  always a small spin gap
  no real long-range ordering occurs
- **Simulation is done for fixed values of J_i**
  you obtain a sequence of data points, not an analytical expression for the fitting

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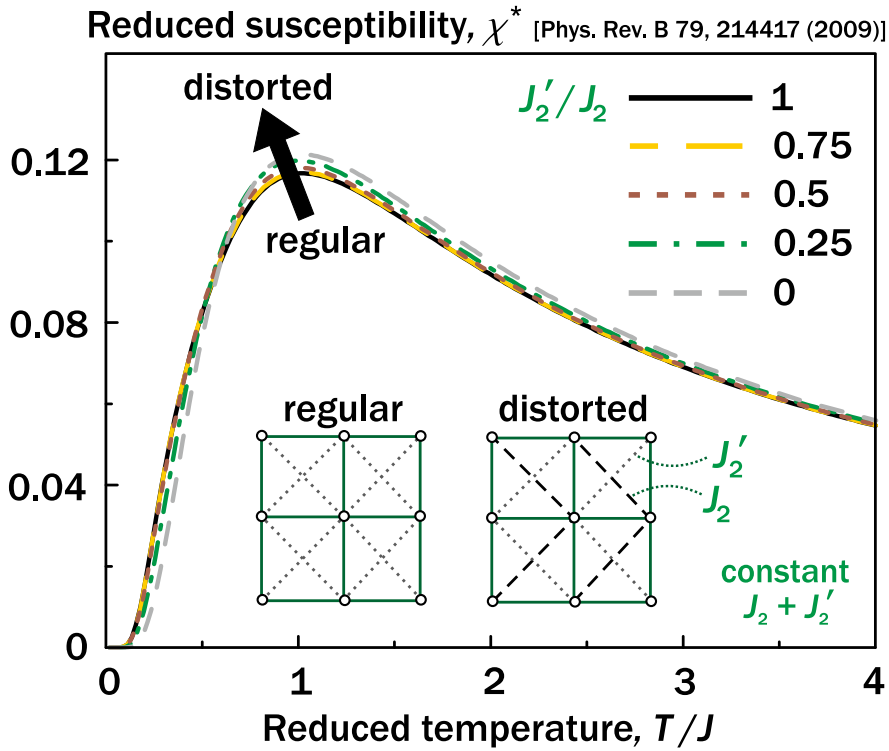
Dimensionless parameters are used

$$T^* = k_B T / J$$

$$\chi^* = \left(\frac{N_A g^2 \mu_B^2}{k_B} \right)^{-1} \times \chi J$$

- **g and J are always the adjustable (fitting) parameters**
- *Example:* $J_1 = 100\,\mathrm{K}$ and $J_2 = 150\,\mathrm{K}$
  Define $J_1 = 1$, $J_2 = 1.5$, and keep J_1 as an adjustable parameter (energy scale)
- **Each J_2/J_1 requires another simulation**

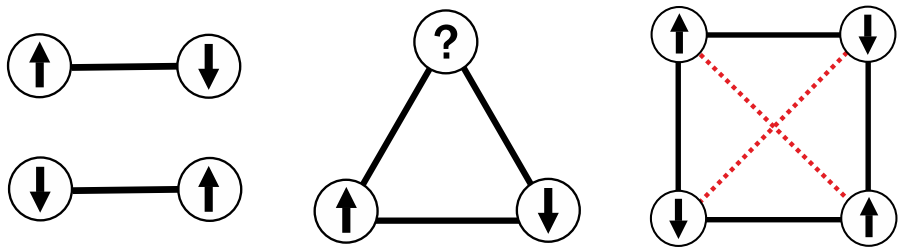


Analytical fitting expressions

Magnetic molecules – exact solution:

- dimers
- trimers / triangles
- tetramers

[Coord. Chem. Rev. 5, 313 (1970)] contains most of them



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- interpolation of simulated data, D.C. Johnston and his poor co-authors
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- *spin ladders* [arXiv:cond-mat/0001147], 63 pages **may not be accurate**

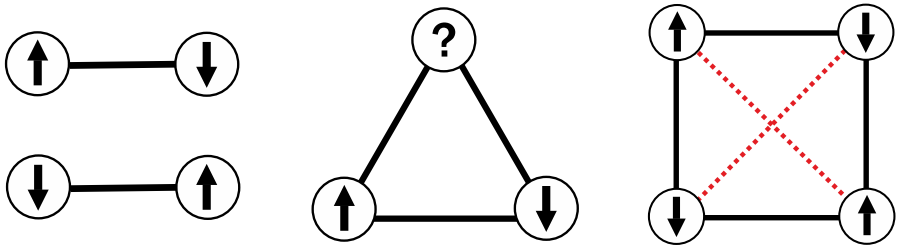

TABLE I. Fitted parameters for $\chi^*(t)$ of the $S=1/2$ antiferromagnetically coupled Heisenberg dimer ($\alpha=0$) [Eqs. (50) with $\Delta^*_{\rm fit}=1$] and $\chi^*(t)$ and $C(t)$ [Eqs. (54)] for the uniform chain ($\alpha=1$). $\chi^*(t)$ Fit 1 for the uniform chain ($0.01\leqslant t\leqslant 5$) [Eqs. (50) with $\Delta^*_{\rm fit}=0$] uses powers of $1/t$ only, whereas $\chi^*(t)$ Fit 2 ($0\leqslant t\leqslant 5$) [Eqs. (53)] also incorporates logarithmic correction terms.

parameter	$\chi^*(\alpha=0)$	$\chi^*(\alpha=1)$ Fit 1	$\chi^*(\alpha=1)$ Fit 2	$C(\alpha=1)$
N_1	0.6342798982	−0.053837836	−0.240262331211	−0.018890951426
N_2	0.1877696166	0.097401365	0.451187371598	0.024709724025
N_3	0.03360361730	0.014467437	0.0125889356883	−0.0037086264240
N_4	0.003861106893	0.0013925193	0.0357903808997	0.0030159975962
N_5	0.0002733142974	0.00011393434	0.00801840643283	−0.00037946929995
N_6			0.00182319434072	0.000042683893992
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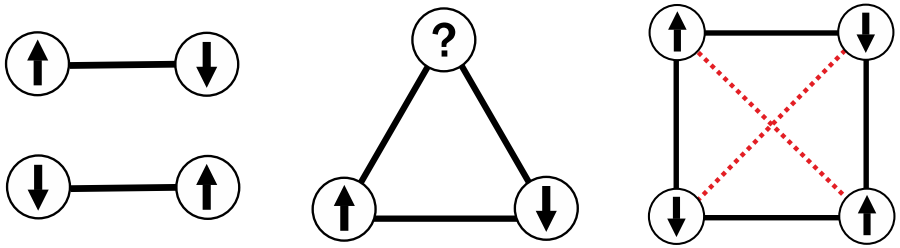

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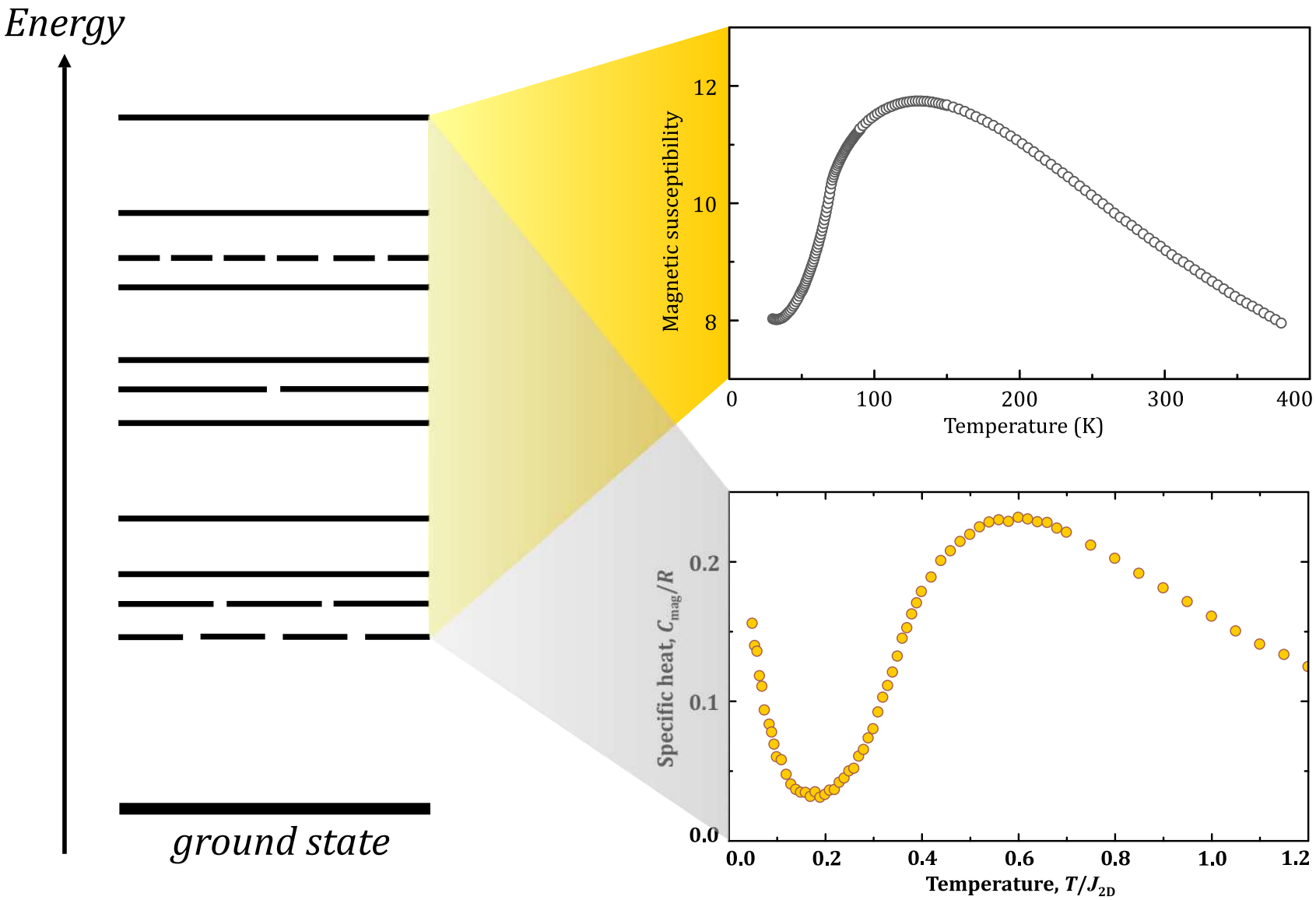
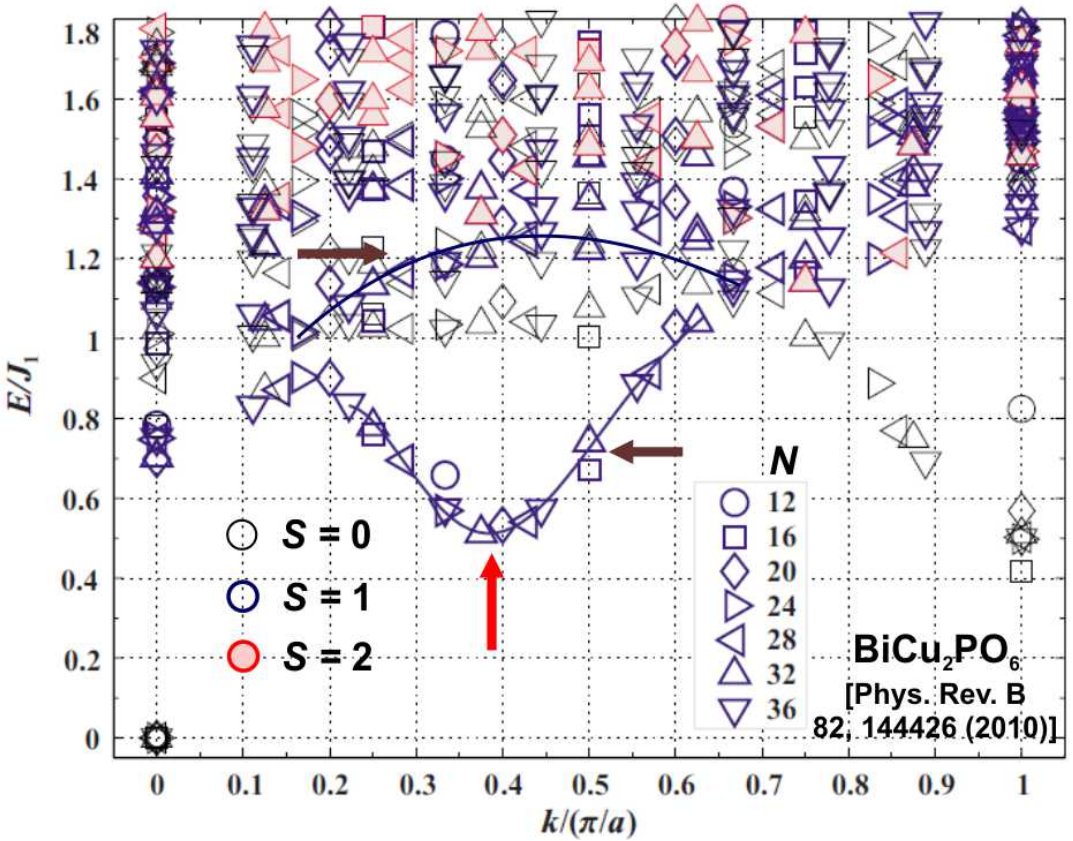
Those expressions are valid in the whole T-range
There are also expressions valid at $T \geq J$ only (HTSE, will be discussed later)

Exact diagonalization

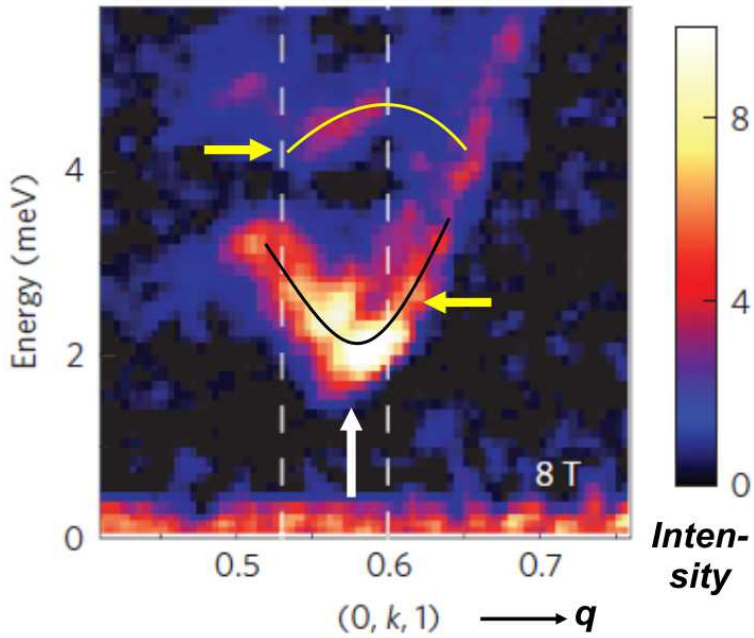


Diagonalization: example of the spectrum

Calculation by Lanczos diagonalization



Experiment



inelastic neutron scattering
[Nature Phys. 12, 224 (2016)]

- **Full (exact) diagonalization** – whole energy spectrum ($L \leq 18$ in ALPS)
- **Sparse (Lanczos) diagonalization** – low-energy states only ($L \leq 32$ in ALPS)

Monte-Carlo: quantum vs. classical

- **Quantum Monte-Carlo** (`loop`, `dirloop_sse`, `worm`) – quantum spin Hamiltonian
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- **Classical Monte-Carlo** (`spinmc`) – classical spin Hamiltonian
  any lattice you want, but **no quantum effects**

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Quantum

$$\hat{H} = \sum_{\langle ij \rangle} J_{ij}\, \hat{\mathbf{S}}_i\, \hat{\mathbf{S}}_j$$

$\hat{\mathbf{S}}_i$, $\hat{\mathbf{S}}_j$ are operators

difficult to handle,
but interesting physics

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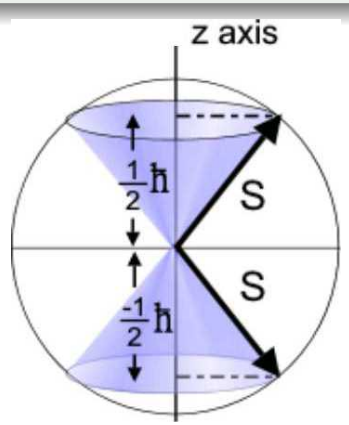
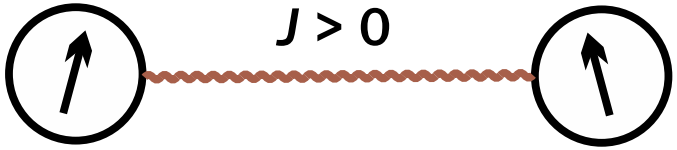
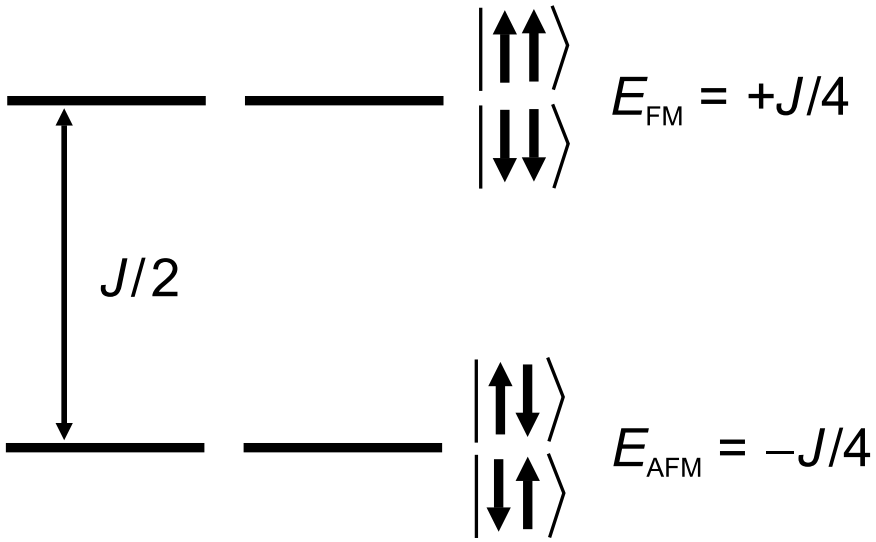
- **Classical spin is not quantized**
- Classical approximation is good for $S \to \infty$,
  and not too bad for large spins
- **Spins-$\frac{1}{2}$ are quantum**



Quantum vs. classical: dimer case

Spin dimer:
$\hat{H} = J\,\hat{\mathbf{S}}_1\,\hat{\mathbf{S}}_2$





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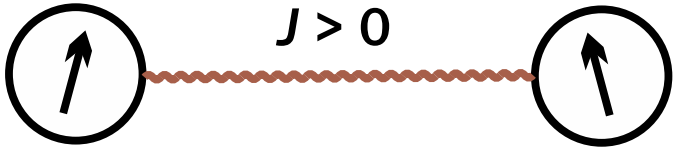

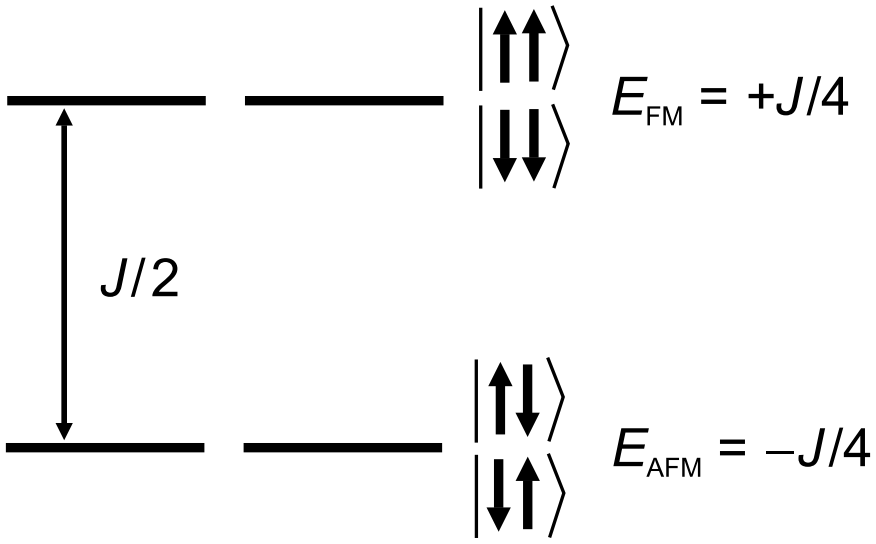

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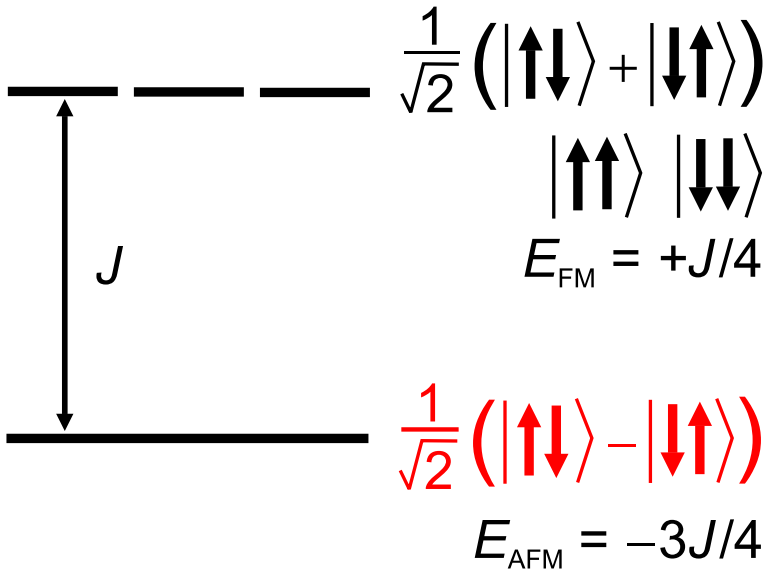
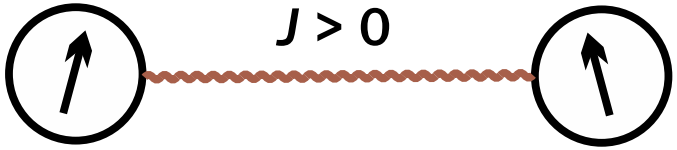


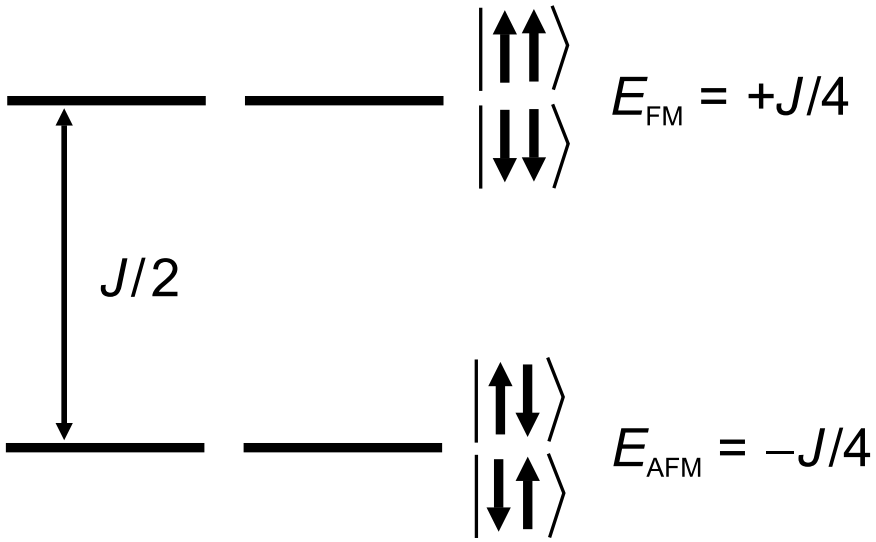
Quantum case

- **Different energy splitting**
  (magnetic interaction energy becomes *much* larger in the quantum limit)
- **Different nature of the ground state (mixing = quantum fluctuations)**

Quantum vs. classical: dimer case

Spin dimer:
$\hat{H} = J\,\hat{\mathbf{S}}_1\,\hat{\mathbf{S}}_2$





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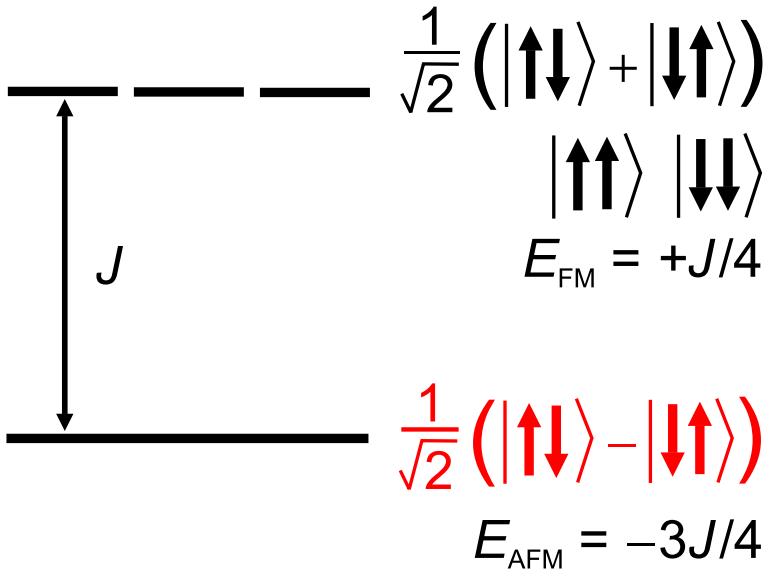
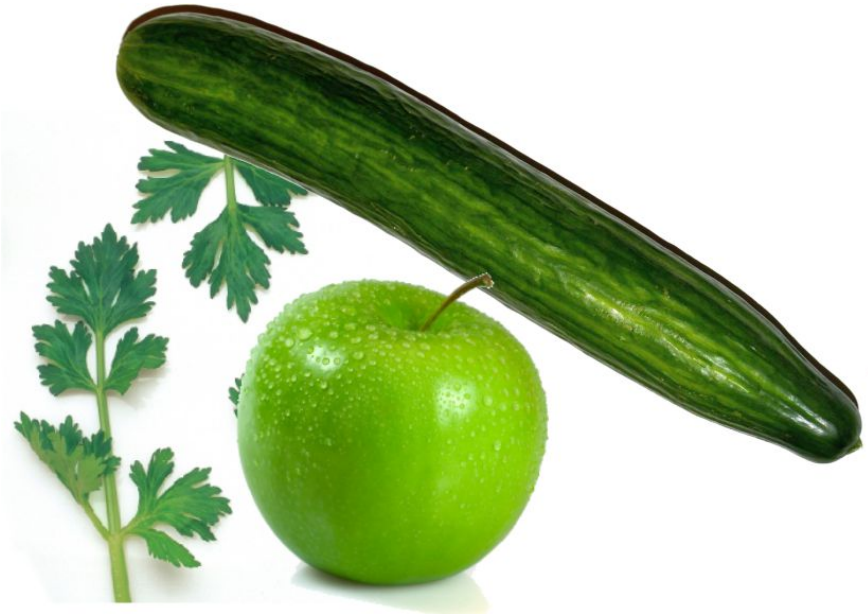


Quantum case

- Classical ground-state energy can be improved by **replacing** S^2 with $S(S+1) = \frac{3}{4}$
  ALPS does exactly this when you use `convention=quantum` in `spinmc`

Classical vs. quantum



Classical states

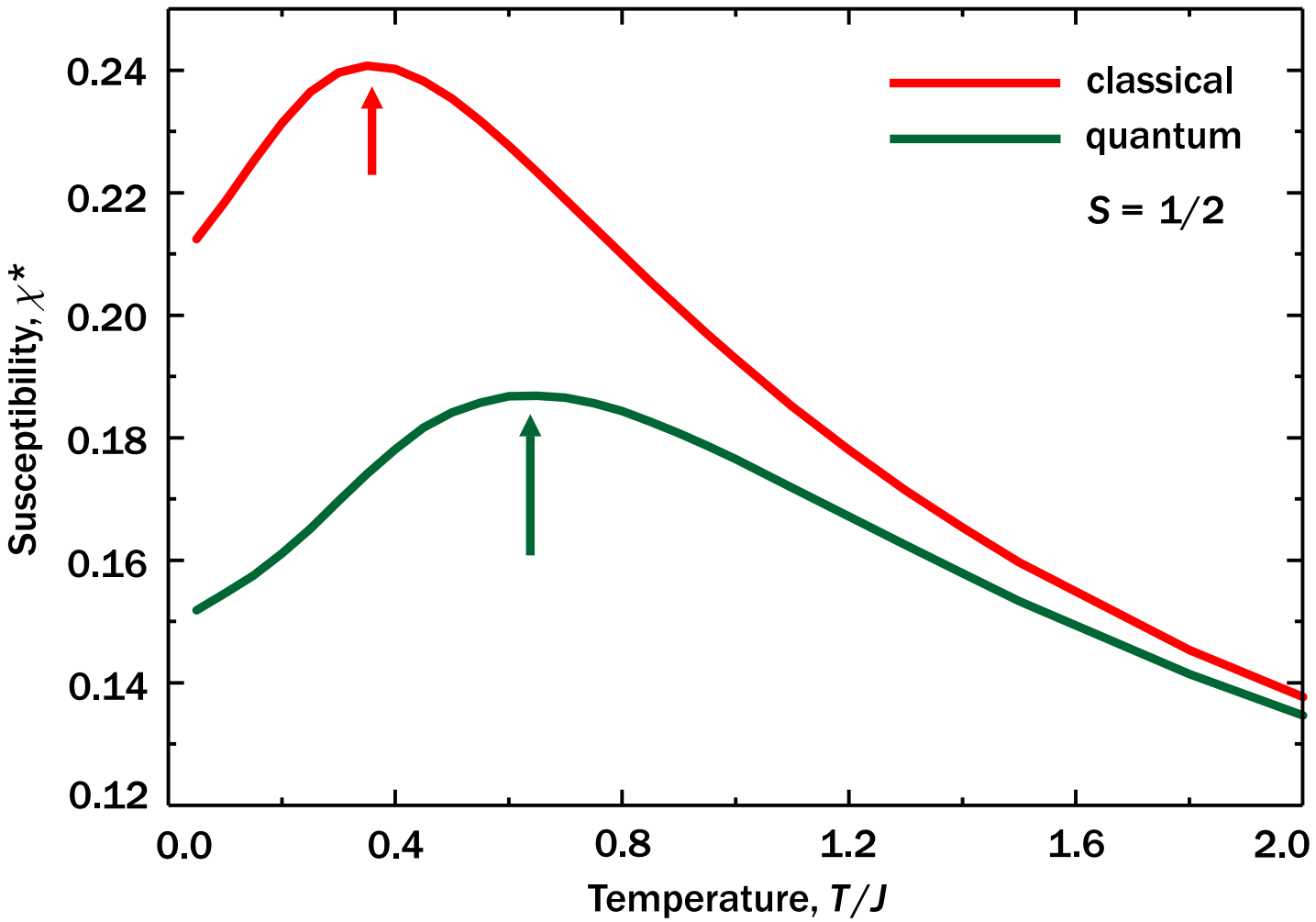
$|\uparrow\uparrow\rangle$, $|\downarrow\downarrow\rangle$, etc.

Quantum state

$\frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right)$

Image credits: WiseMan42, Kiedd 07 (Wikimedia Commons)

Quantum effects in thermodynamics



- Never use classical Monte-Carlo for spins-$\frac{1}{2}$
- Spins-$\frac{5}{2}$ may be OK, although it's better to do quantum whenever you can

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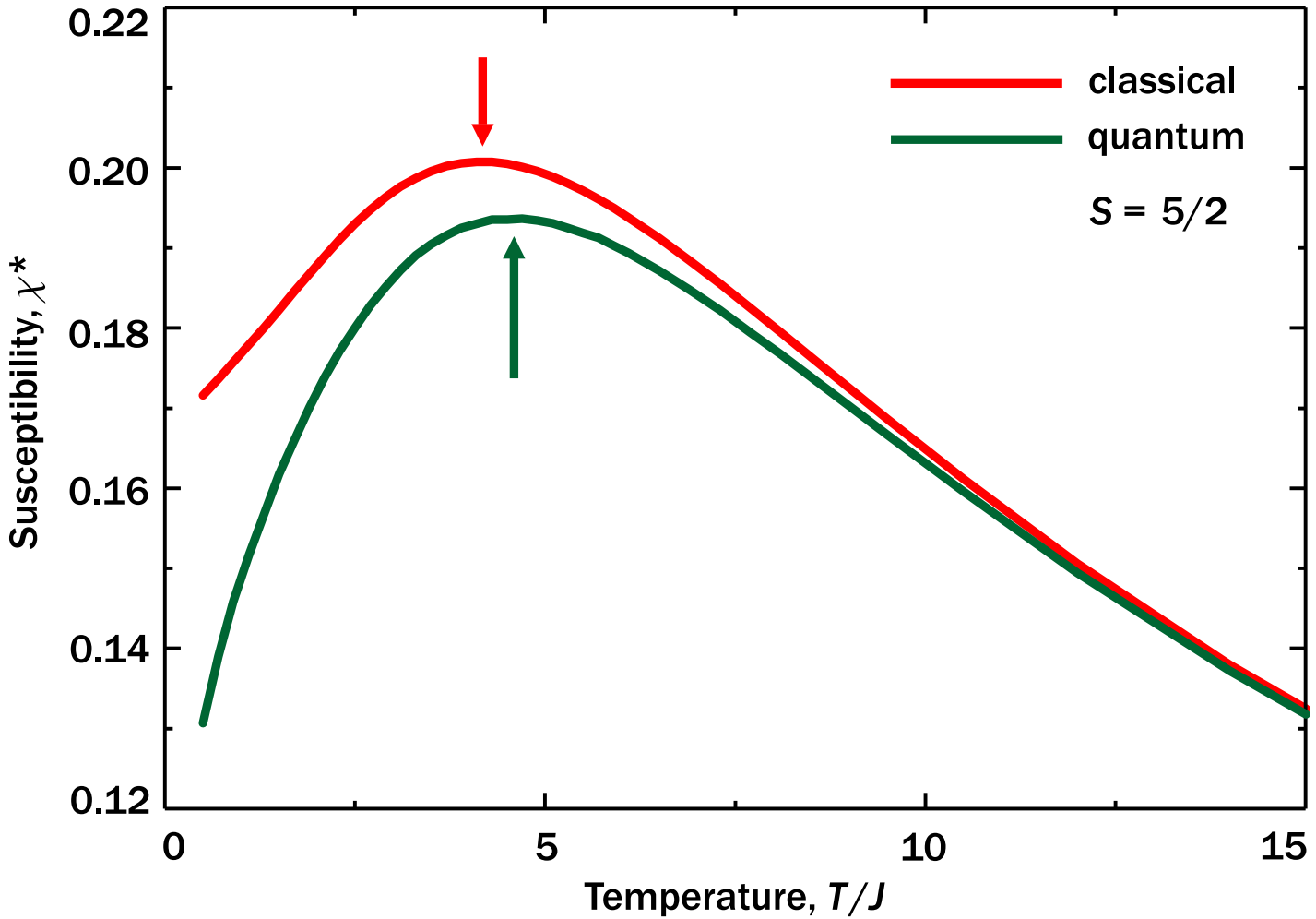

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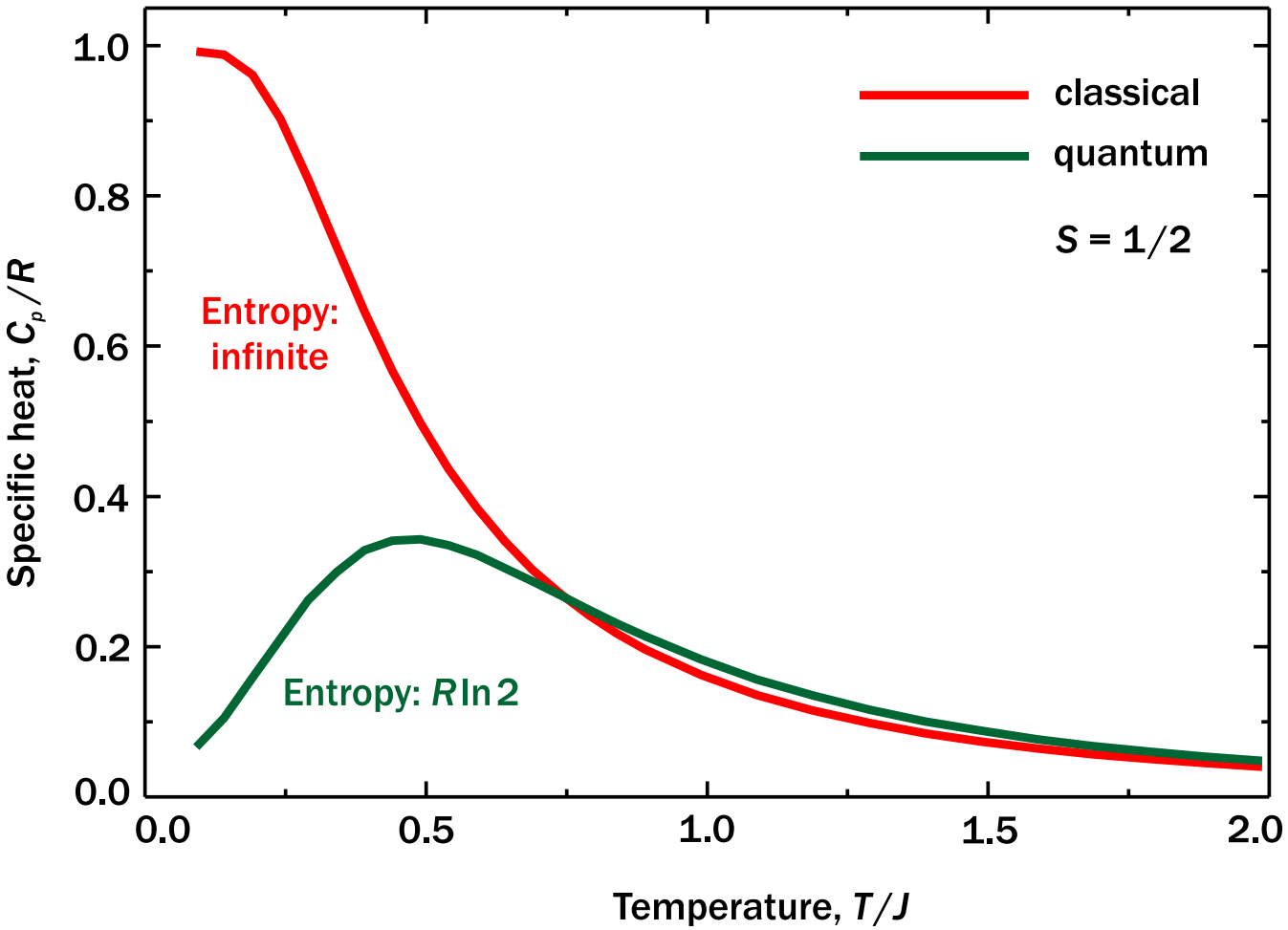


Entropy

$$S_{\mathrm{mag}}(T) = \int_0^\infty \frac{C_p}{T}\, dT$$

Quantum limit:

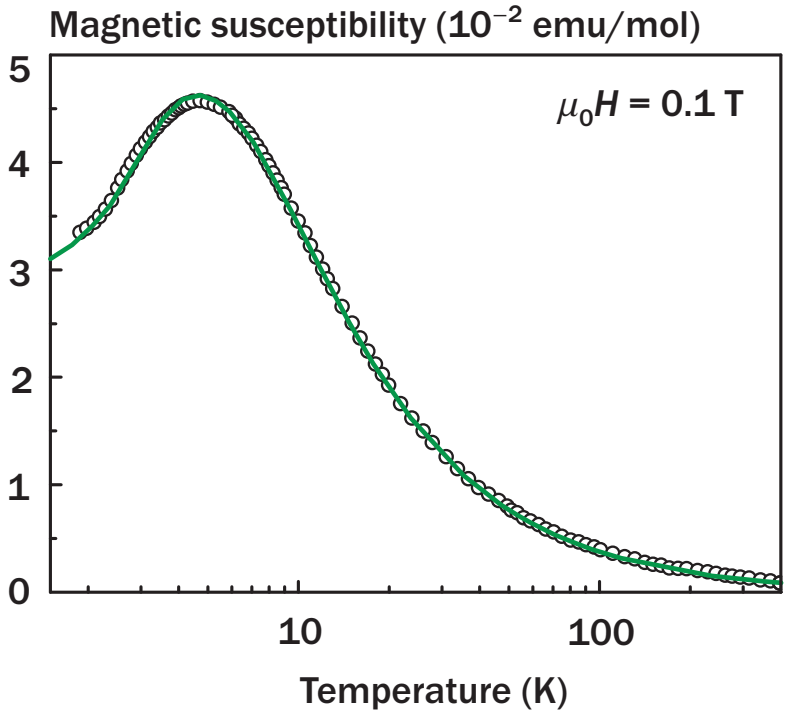
$$S_{\mathrm{mag}} = R \ln(2S+1)$$

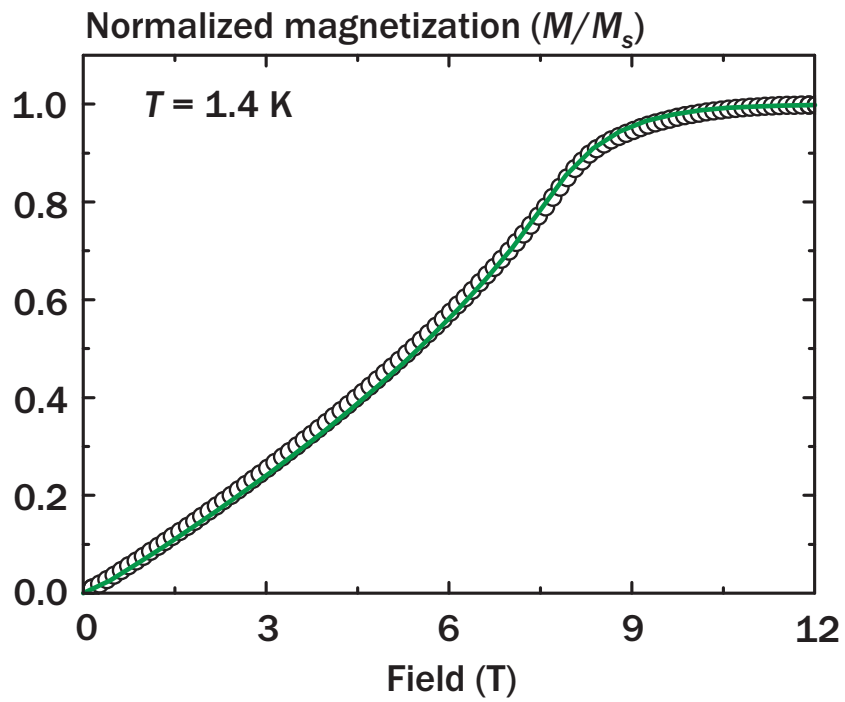
Classical limit:

$$S_{\mathrm{mag}} \to \infty$$

- **Quantum and classical heat capacities are largely different for any value of S**

Monte-Carlo: example





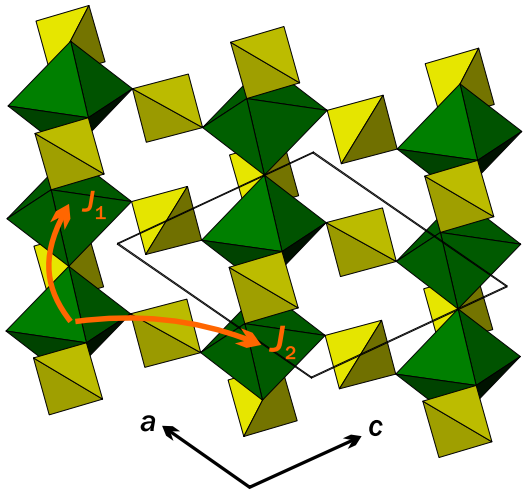
$Sr_2VO(PO_4)_2$

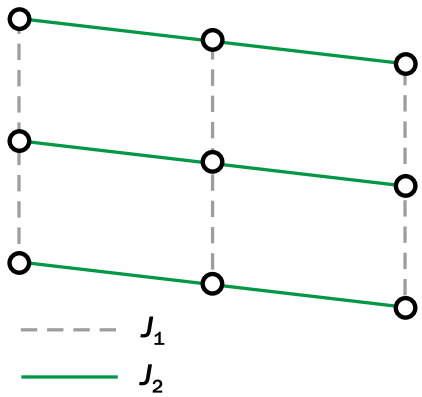
Monte-Carlo fits to $\chi(T)$ and $M(H)$

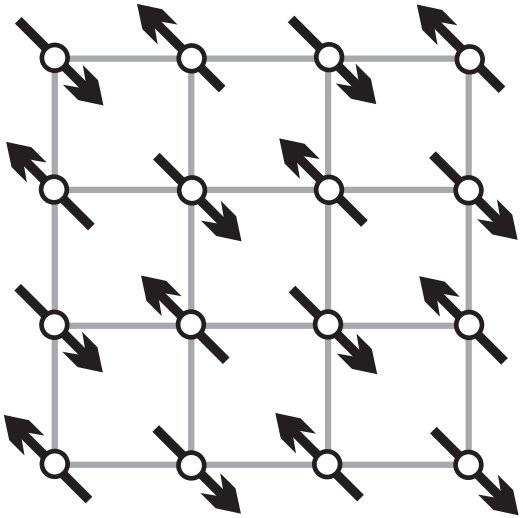
$J_1 = -8.3\,\mathrm{K}$

$J_2 = 5.9\,\mathrm{K}$

$g = 1.97$

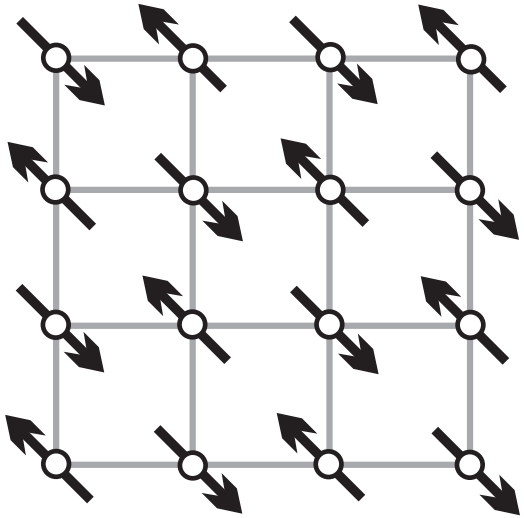






$$M = \sum_i m_i = 0$$

total magnetization



$$M_{\mathrm{st}} = \sum_i m_i \, e^{i\,\mathbf{k}\mathbf{r}} = N \times m_i,$$

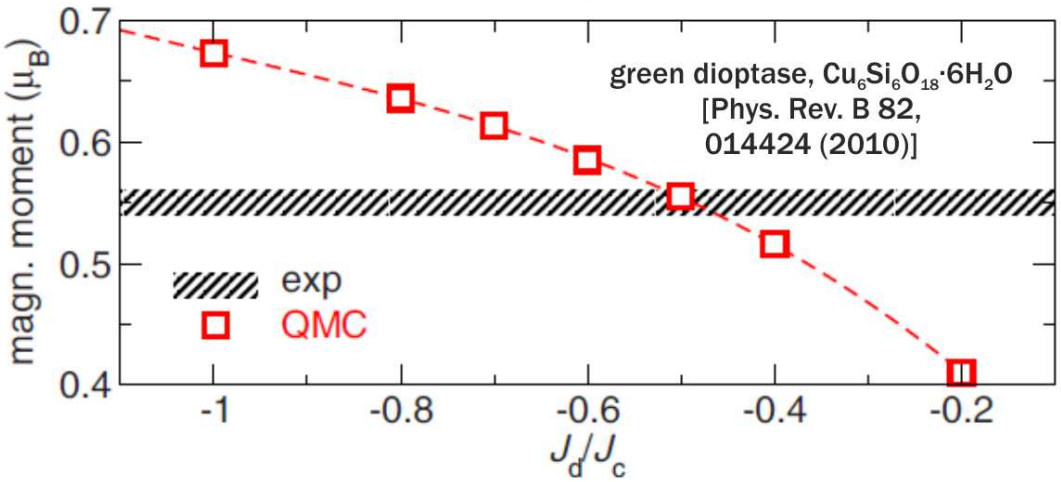
$$\mathbf{k} = \left(\tfrac{\pi}{2}, \tfrac{\pi}{2}\right)$$

staggered magnetization

Alternatively, staggered magnetization for sublattices A and B can be defined as

$$M_{\mathrm{st}} = \frac{1}{N}\left(\sum_{i\in A} \mathbf{S}_i - \sum_{j\in B} \mathbf{S}_j\right)$$

Ordered moment: example



spin-$\frac{1}{2}$, $M_{\rm st} = 1.0\,\mu_B$ (classical)

$M_{\rm st} = 0.6\,\mu_B$ (2D), $M_{\rm st} = 0.85\,\mu_B$ (3D)

even lower value in dioptase $\longrightarrow$ low connectivity

- **Staggered magnetization is equivalent to ordered magnetic moment**
  measured by neutron diffraction (up to the orbital moment and covalency effects)
- **Classical limit:** $M_{\rm st} = S$
- **Quantum limit:** $M_{\rm st} < S$
  the difference between S and $M_{\rm st}$ gauges quantum effects (quantum fluctuations)

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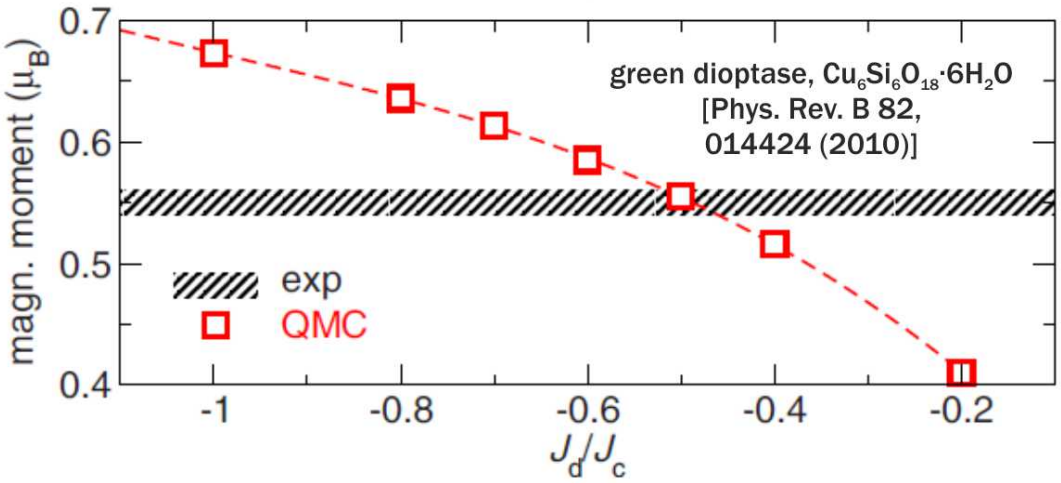

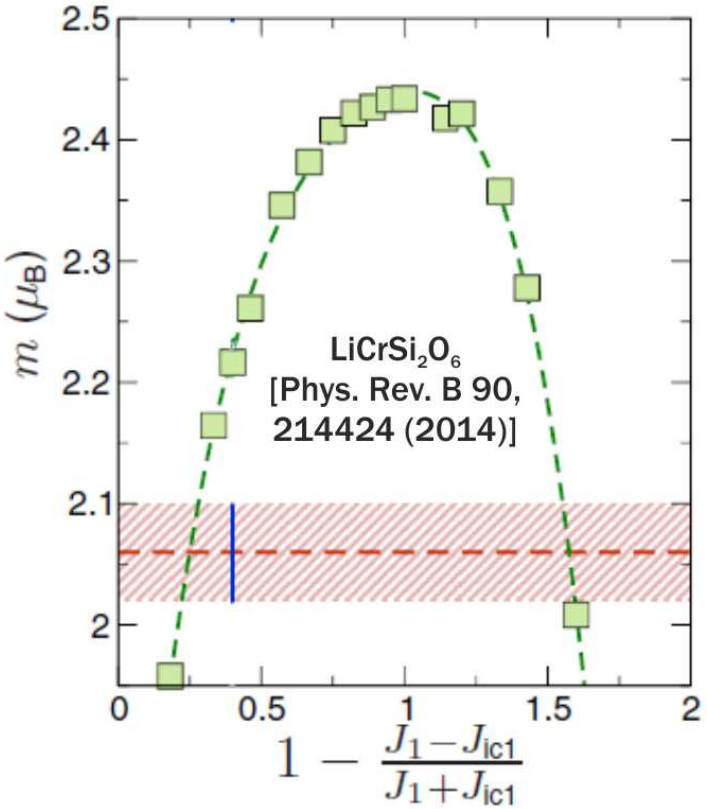

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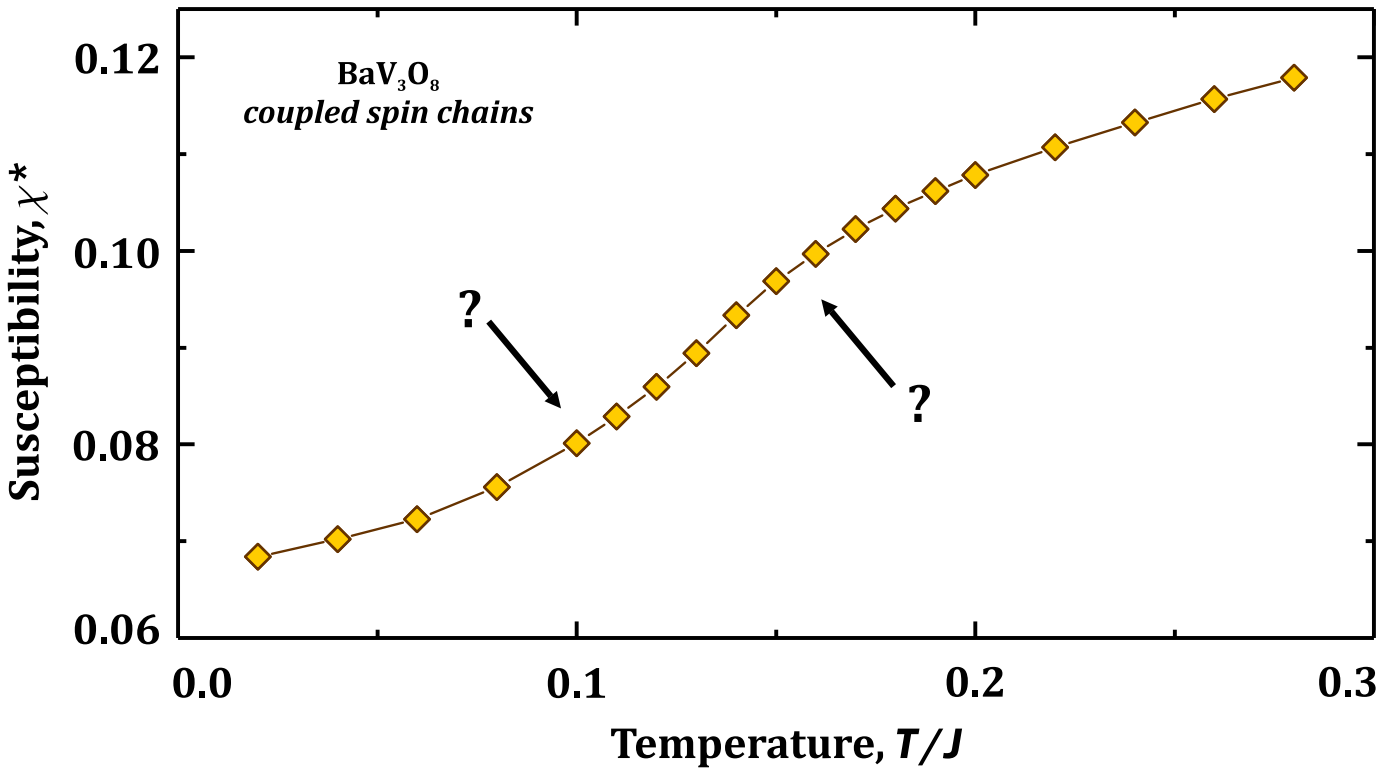
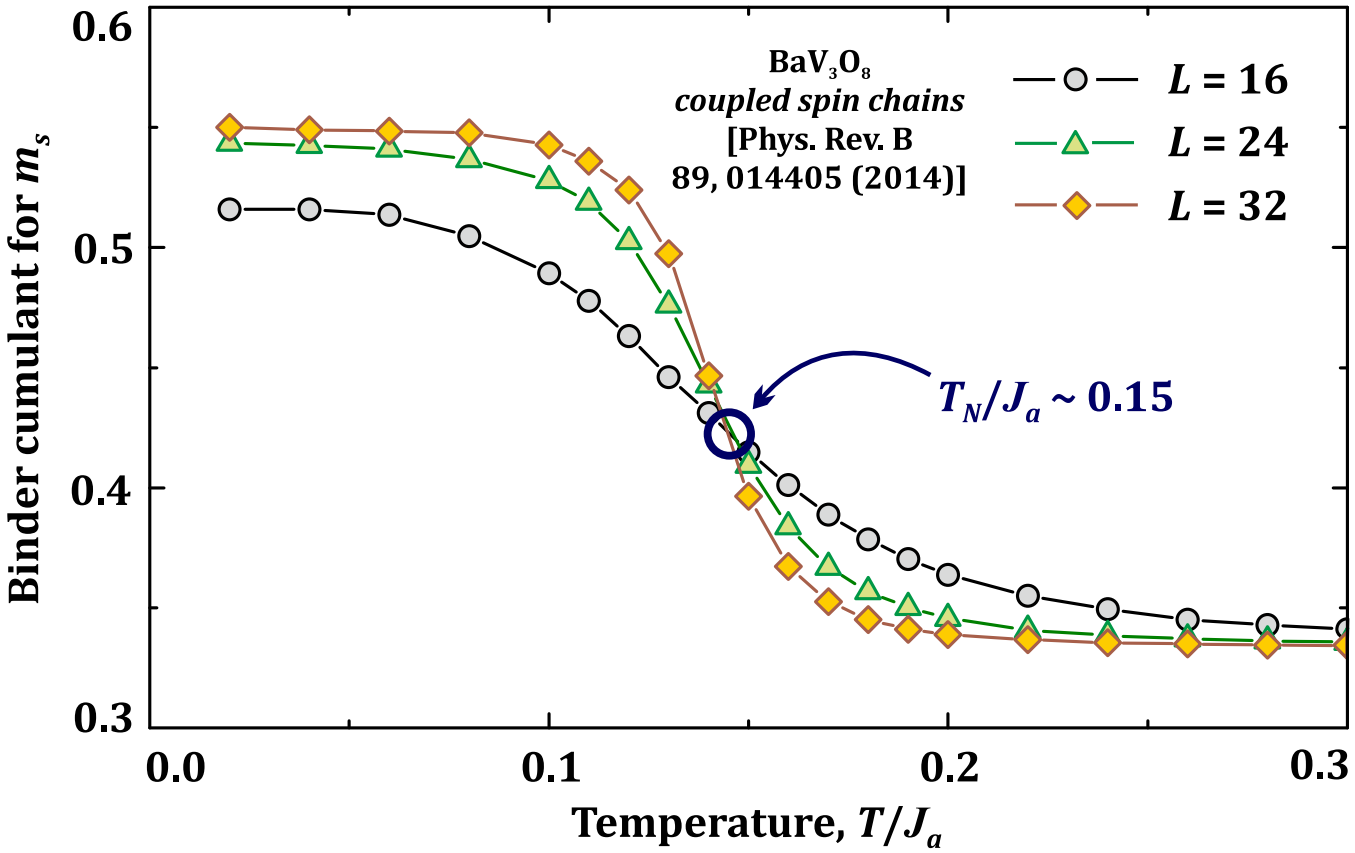


- You may not find clear signatures of a Néel temperature in simulated $\chi(T)$
- You will find it *very* difficult to get an accurate T_N from $C_p(T)$

Transition temperatures



- **Use Binder cumulant,** $B(T) = \langle M^2 \rangle / \langle M \rangle^2$ ($M_{\rm st}$ for antiferromagnets)
- $B(T)$ does not depend on the system size L at $T = T_N$,
- The crossing point of simulations performed for different system sizes yields T_N

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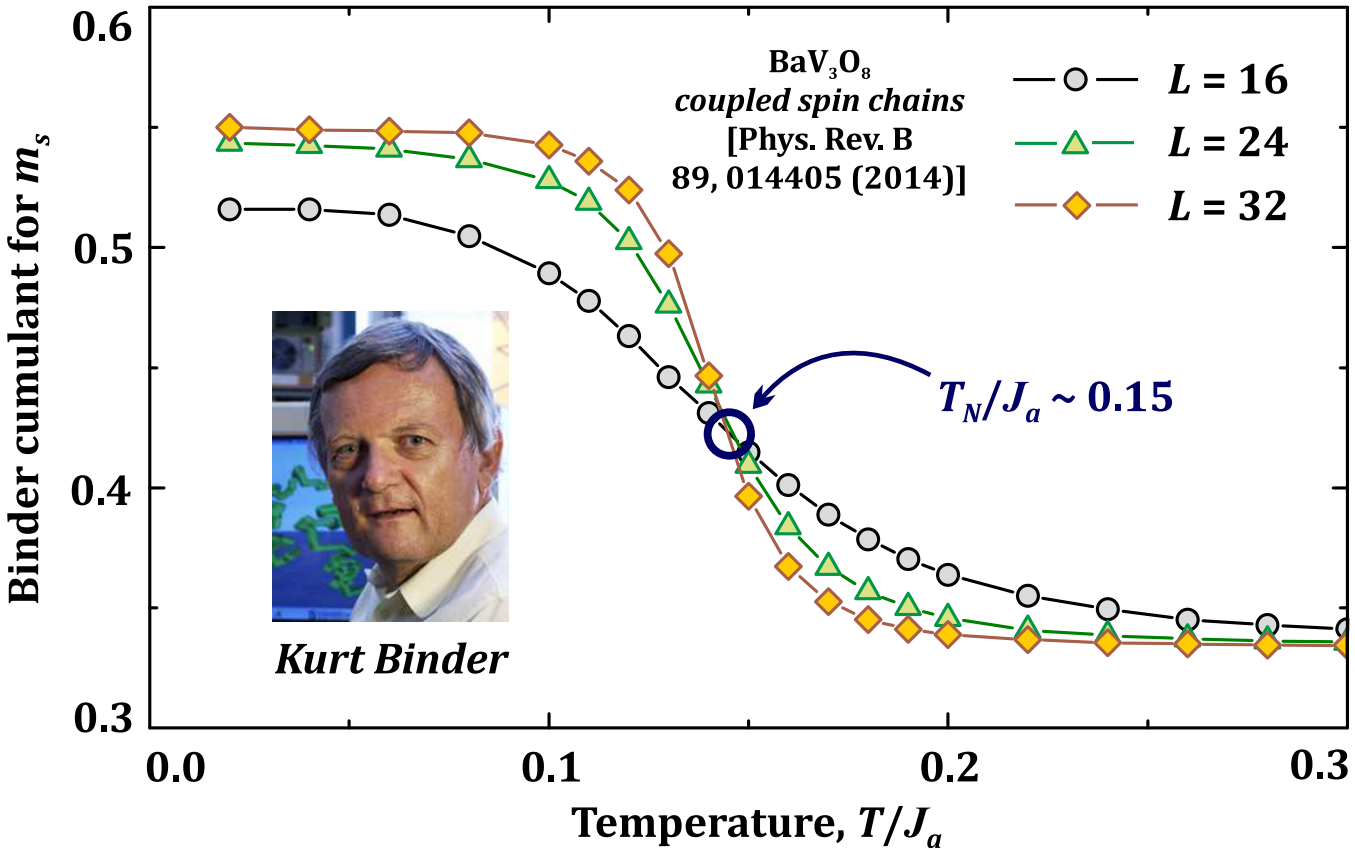

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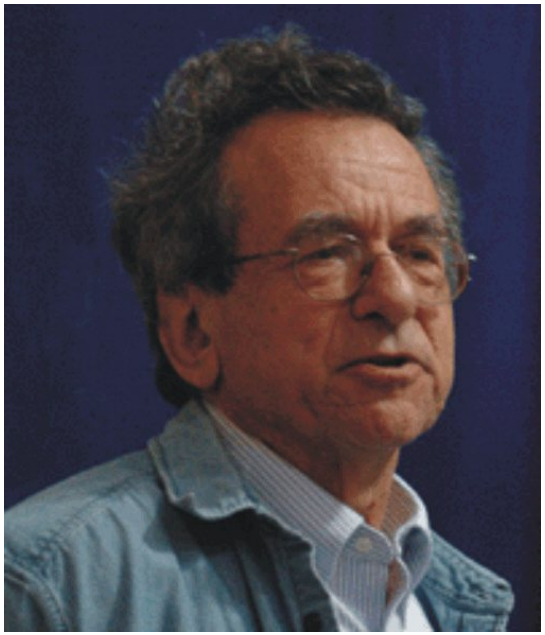
Mermin-Wagner theorem

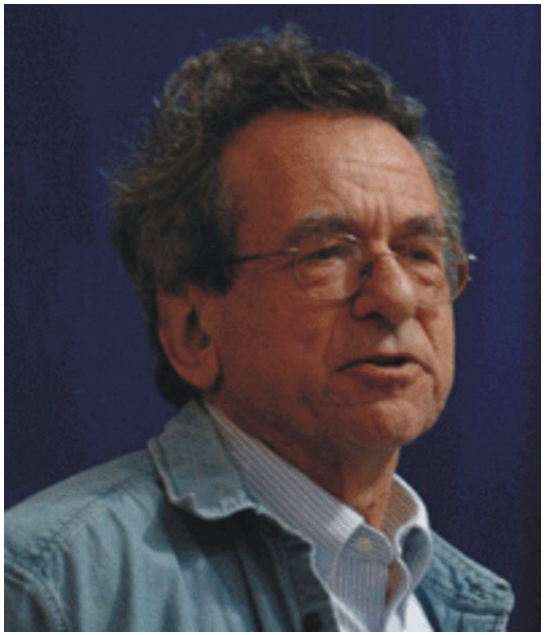


David Mermin
born 1935

Herbert Wagner
born 1935

Continuous symmetries can not be spontaneously broken at finite temperature in systems with sufficiently short-range interactions in dimensions $d \leq 2$

Mermin-Wagner theorem



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born 1935

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Human-readable version:

No long-range order in Heisenberg magnets at $T \neq 0$ in 1D and 2D

It only makes sense to calculate T_N of a 3D Heisenberg magnet

- **Non-frustrated systems:** use quantum Monte-Carlo

General strategy

- **Non-frustrated systems:** use quantum Monte-Carlo

Frustrated systems:

- Large spin $\longrightarrow$ classical Monte-Carlo
- Small spin, 0D $\longrightarrow$ exact diagonalization
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- Small spin, 3D $\longrightarrow$ you're doomed, try high-temperature series expansion (HTSE)

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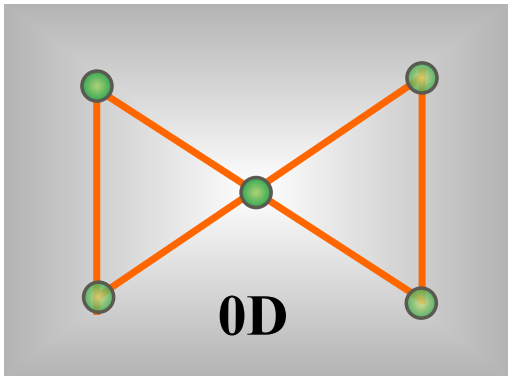

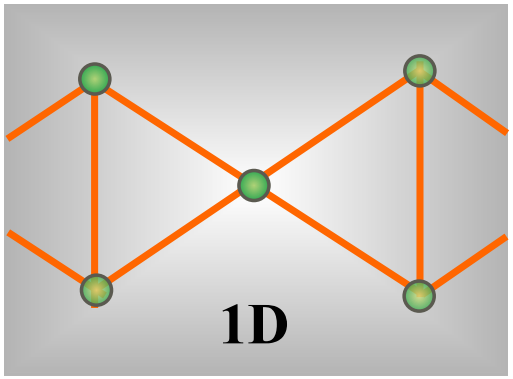

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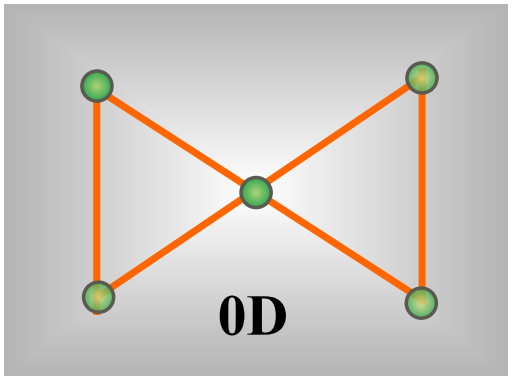

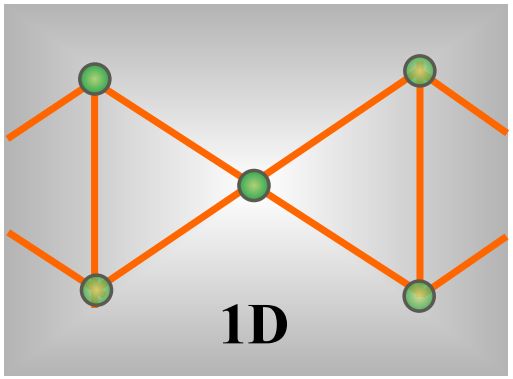

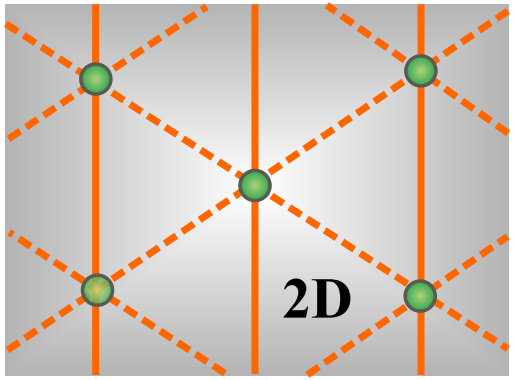

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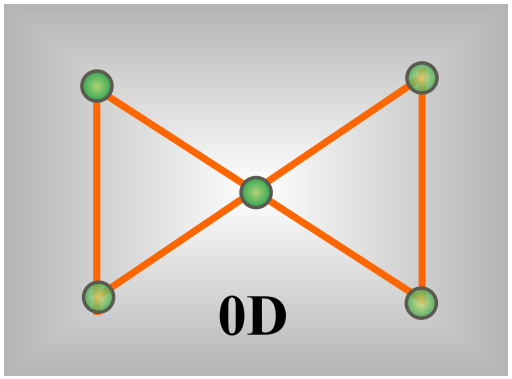

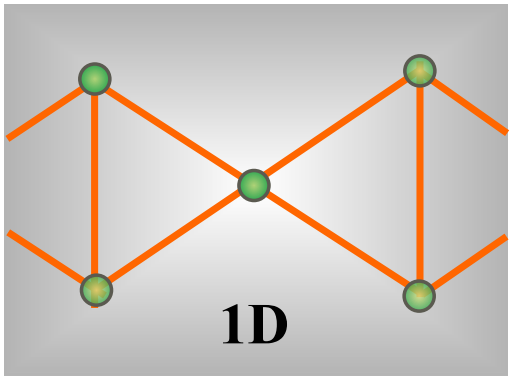

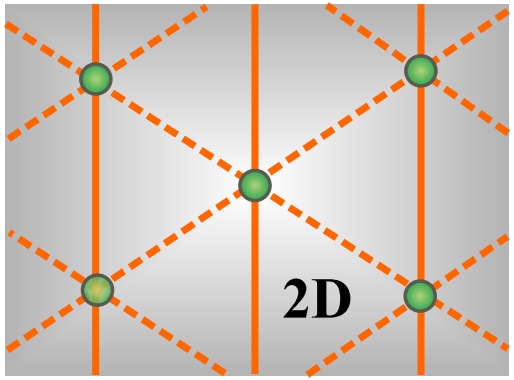

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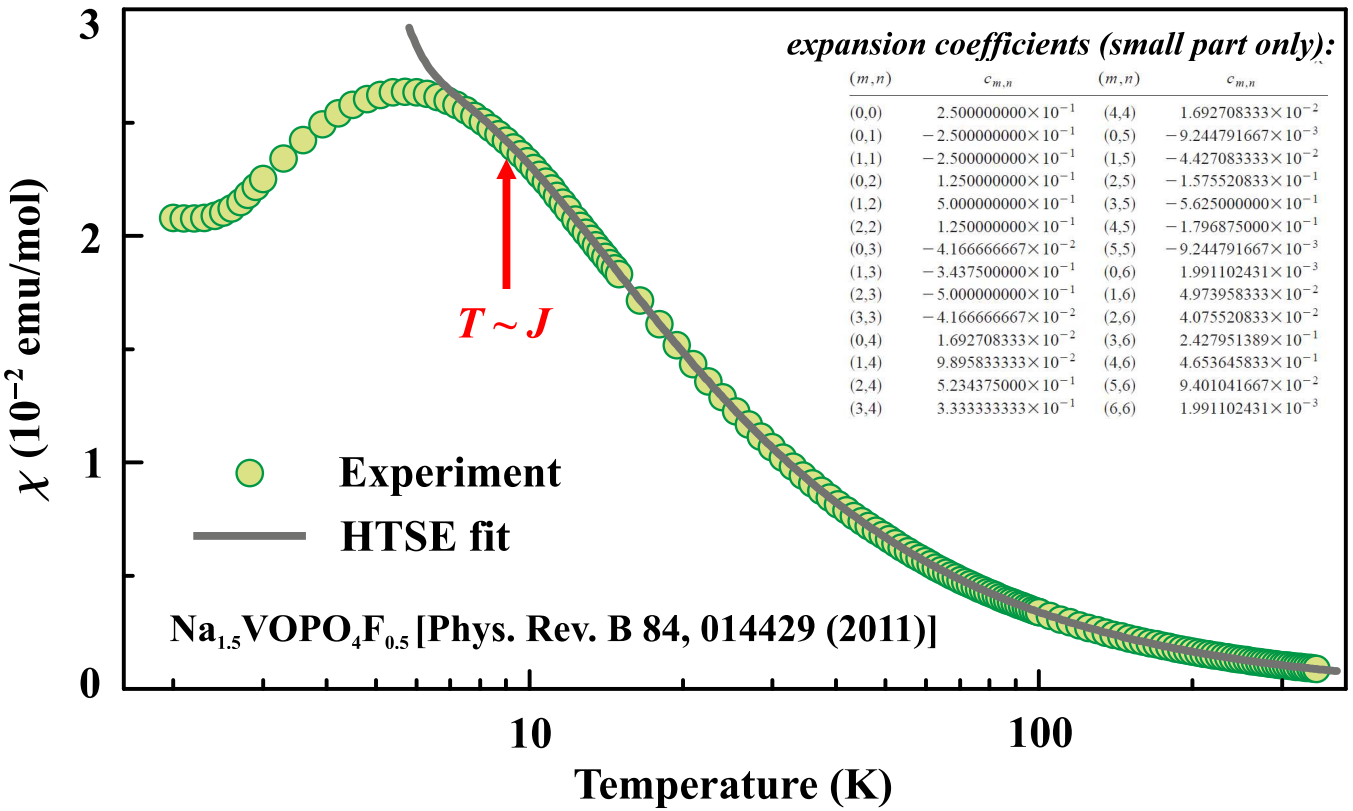
High-temperature series expansion



(m,n)	$c_{m,n}$	(m,n)	$c_{m,n}$
(0,0)	2.500000000×10^{-1}	(4,4)	1.692708333×10^{-2}
(0,1)	$-2.500000000\times10^{-1}$	(0,5)	$-9.244791667\times10^{-3}$
(1,1)	$-2.500000000\times10^{-1}$	(1,5)	$-4.427083333\times10^{-2}$
(0,2)	1.250000000×10^{-1}	(2,5)	$-1.575520833\times10^{-1}$
(1,2)	5.000000000×10^{-1}	(3,5)	$-5.625000000\times10^{-1}$
(2,2)	1.250000000×10^{-1}	(4,5)	$-1.796875000\times10^{-1}$
(0,3)	$-4.166666667\times10^{-2}$	(5,5)	$-9.244791667\times10^{-3}$
(1,3)	$-3.437500000\times10^{-1}$	(0,6)	1.991102431×10^{-3}
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- **HTSE = expansion of χ in powers of $1/T$**, reasonable at high-T only with 10-12$^{\text{th}}$ order expansion extending down to $T \sim J$ becomes possible
- **Coefficients are numerous and are to be determined numerically**
- Use the HTE code [http://wasd.urz.uni-magdeburg.de/jschulen/HTE/]
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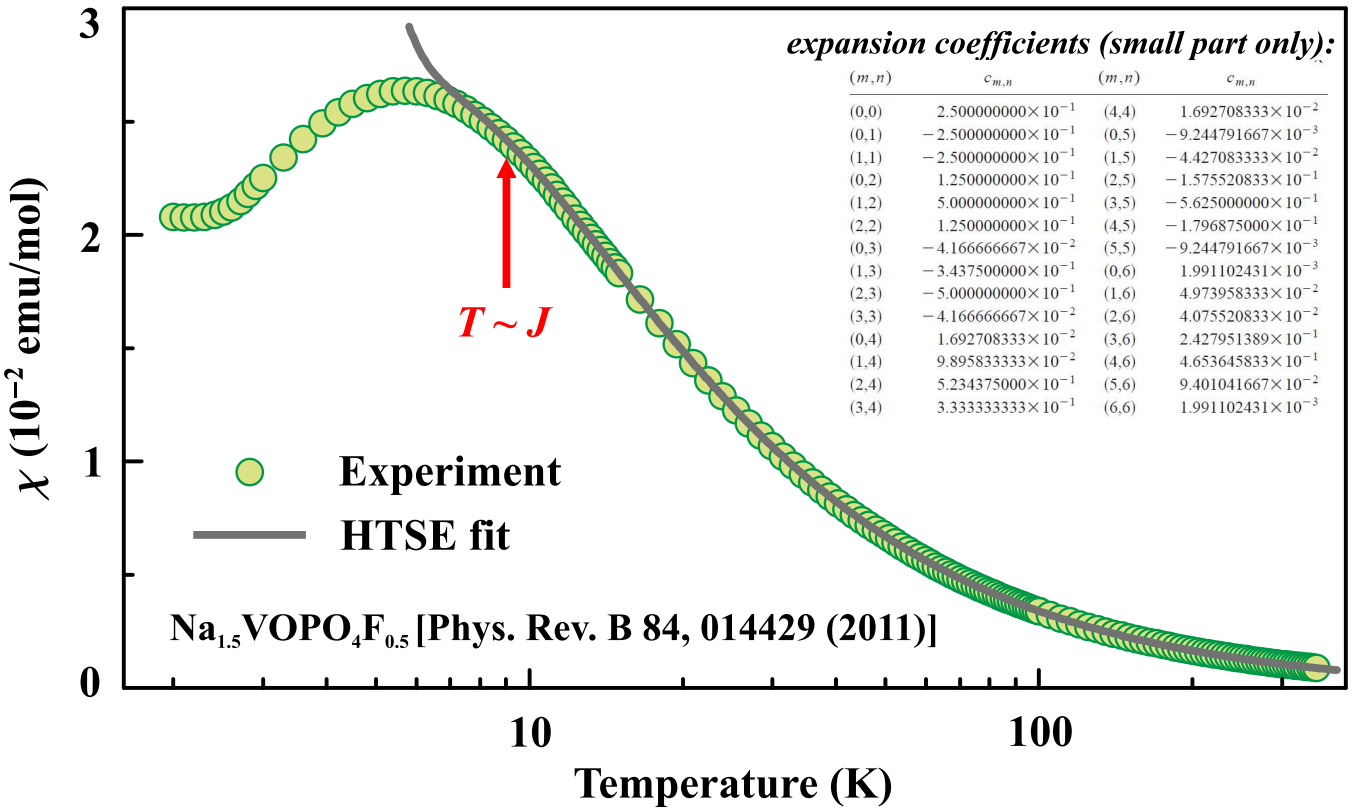
High-temperature series expansion



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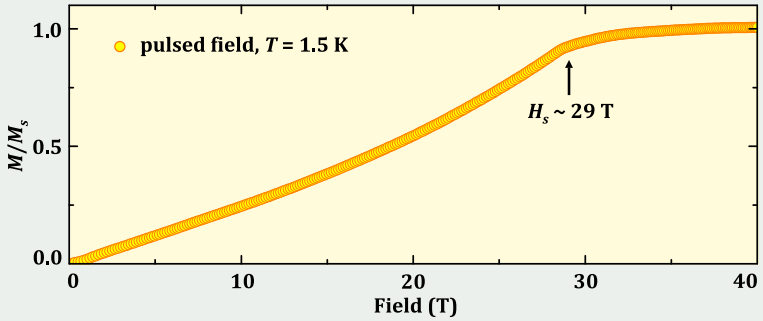
Summary

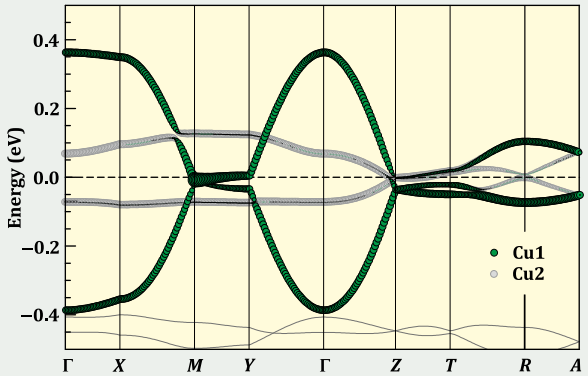
What can we measure?

- Magnetization (+susceptibility)
- Specific heat
- Neutron diffraction



What can we calculate?

- Parameters of interest
- How to calculate?
- What to observe?



How to bring this together?

- Analytical solutions
- Numerical simulations
- Classical approximation